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Editor-in-Chief: Matei Macoveanu

ECOMONDO 2013

17th International Trade Fair of Material & Energy Recovery and Sustainable Development

Extended Abstracts

"Gheorghe Asachi" Technical University of Iasi

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EDITORIAL

DEDICATED TO *ECOMONDO 2013*

17th International Trade Fair of Material & Energy Recovery and Sustainable Development

The contributions in the form of *Extended Abstracts* collected in this Special Supplement of *Environmental Engineering and Management Journal* were selected from lectures and posters of the scientific and technical conferences hosted by *Ecomondo 2013* held in Rimini, Italy, 6–9 November, 2013 (http://en.ecomondo.com).

Ecomondo is the most recognized platform for the Mediterranean basin, in terms of materials exploitation and recycling for the large industry of the future, which will be part of *Green Economy*, ensuring a weighted and rewarding balance between sales dimension and technical-scientific dimension, with extensive room dedicated to innovation.

The aim of Ecomondo 2013 was to explore recent industrial advances and opportunities in waste production reduction, waste collection, fractionation, recycling, exploitation; biomass and biowaste exploitation via integrated biorefinery scheme, bioplastics and biobased products; green and sustainable chemistry; water resources monitoring and protection; wastewater treatment and valorization with nutrients recovery and marine resources protection; sustainable remediation of contaminated sites and marine ecosystems; and indoor and outdoor air monitoring and clean up.

A special emphasis was given to European Eco Innovation in the broad field of green economy. Horizon2020 priorities and relevant innovation funding opportunities have been presented by delegates of the EU commission. Another initiative was dedicated to the promotion of industrial symbiosis and networking i.e. the creation of partnerships between industries working in the complementary sectors or different countries; in the same frame, dissemination activities associated with the most prominent international and EU RTD and industrial projects were also hosted.

The areas of particular interest addressed within *Ecomondo 2013* are:

- waste characterization, management, recycling and exploitation (*Waste)*,
- monitoring, management and treatment/ exploitation of industrial and civil wastewaters *(blue gold)*
- the sustainable and biomass-based chemical industry, with a special focus on the Join Technology Initiative Bio Based Industry (JTI BBI) (*Biobased Industry*)
- the monitoring and clean-up of contaminated sites, soils and sediments (*Reclaim Expo*)
- monitoring and treatment of air pollution (*Air*)
- smart cities and communities (*Sustainable City*)

Ecomondo 2013 hosted 100 conferences, more than 500 oral communications and over than 150 papers presented. This special issue provides some of the key information presented and discussed in the frame of some of such conferences. Over 80,000 delegates from 40 different nations were expected.

We believe that this collection of papers will be useful to people who could not able to participate directly. It is primarily towards those individuals that it is directed, but it also aspires to provide permanent records in process of turning environmental problems and challenges into new opportunities for a green economy with a bright future.

Guest editors:

Prof. Fabio Fava
Alma Mater Studiorum - Università di Bologna
(University of Bologna), Bologna, Italy
Dr. Grazia Totaro
Alma Mater Studiorum - Università di Bologna
(University of Bologna), Bologna, Italy
Prof. Maria Gavrilescu
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Fabio Fava, born in 1963, is Full Professor of "Industrial & Environmental Biotechnology" at the School of Engineering of University of Bologna since 2005.

Dr. Fava is the coordinator of the FP7 projects NAMASTE (on the integrated exploitation of citrus and cereal processing by-products with the production of ingredients and new food products) and BIOCLEAN (aiming at developing biotechnological processes and strategies for the bioremediation and the tailored depolymerization of major oil-deriving plastics). He also coordinates the Unit of the University of Bologna participating in the FP7 projects ECOBIOCAP and ROUTES (on the production of microbial polymers from different organic waste and food processing effluents), MINOTAURUS and WATER4CROPS (on the intensified bioremediation of contaminated waste- and ground-water and the integrated decontamination and valorization of wastewater of the food processing industry and of biorefineries), and ULIXES and KILL-SPILL (on the development of strategies for intensifying the in situ bioremediation of marine sediments polluted by (chlorinated)hydrocarbons and for the isolation and industrial exploitation of microbes from those matrices). He is the Past- and the current vice-chairman of the "Environmental Biotechnology" section of the European Federation of Biotechnology (EFB) . He is member of the "Task Force on Industrial Biotechnology" of the Working Party on Biotechnology of the Organisation for Economic Co-operation and Development (OECD, Paris). Further, he is joining the "High Level Group on Key Enabling Technologies" and the "Expert Group on biobased products" of the DG-Enterprise and Industry of European Commission (Brussels), as well as the "Expert Group on eco-industries" of the JRC Directorate at the European Commission. Finally, he is the Italian Representative for Bioeconomy in Horizon2020 Programme Committee.

Grazia Totaro, born in 1976, has a degree in Chemistry (University of Ferrara), a Master's Degree in Science, Technology & Management with a specialization in Environmental Chemistry (University of Ferrara) and a PhD in Materials Engineering, about modification, characterization and applications of technopolymers (University of Bologna).

She worked at the R&D Centre of Basell Polyolefins in Ferrara for 2 years in the frame of a project addressed to the development of a novel methodology for qualitative and quantitative analysis of additives in polymers. She also worked at ARPA, Regional Agency for Environment in Ferrara, division Water Analysis. Then she started working at the school of Engineering of the University of Bologna for a Ph.D. in Materials Engineering (2007-2010). After that she had a scholarship "Spinner 2013" in cooperation with Reagens spa (San Giorgio di Piano) on novel PVC nanocomposites. Now she is post doc fellow at the same school on new polymer-based nanocomposites from renewable sources and inorganic fillers. She also worked at the laboratoire de Chimie et Biochimie Pharmacologique et Toxicologique (Université Réné Descartes) in Paris in 2001 and was visiting professor at the Ecole Nationale Superieure de Chimie (Université Blaise Pascal, Clermont Ferrand, FR) in 2012.

Dr. Totaro has about 13 scientific papers and several participations at conferences and scientific schools.

Maria Gavrilescu (born in 1956) is professor at the Department of Environmental Engineering and Management–Faculty of Chemical Engineering and Environmental Protection of the „*Gheorghe Asachi*" Technical University of Iasi, Romania, where she teaches courses in Chemical and Biological Process Engineering, Process Synthesis and Analysis, Integrated Pollution Prevention and Control, Sustainable Industrial Production, Environmental Risk Assessment and Management. She supervises doctoral programs in the fields of Chemical and Environmental Engineering. Prof. Gavrilescu has authored more than 350 books and articles in the fields of chemical and environmental engineering, pharmaceutical and environmental biotechnology, pollution prevention and cleaner production, and risk assessment and management. She has also managed or participated in 18 national and 7 international research projects and 25 research projects with industrial companies. She is the Managing Editor of the *Environmental Engineering and Management Journal.*

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WATER PURIFICATION FROM HUMIC ACIDS BY CLINOPTILOLITE-RICH TUFF

Extended abstract

Vincenzo Leone, Pasquale Iovino*, Silvana Canzano, Stefano Salvestrini, Sante Capasso

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Background

Humic substances (HS) are natural polymers produced by biological decomposition of plants and other organisms (Abate and Masini, 2003) and accounting for 50–80% of natural organic matter in water, soil and sediment. HS are generally subdivided into humin, humic acids (HA) and fulvic acids (FA) based on their solubility under acidic or alkaline conditions in aqueous solution. Among numerous methods developed for HA removal from water, adsorption is the most promising approach. Adsorption by low-cost materials, either natural or by-products of industrial activity, has become the focus of intensive investigation (Leone et al., 2012). Previous work (Capasso et al., 2007a; Capasso et al., 2007b) has shown that the Neapolitan yellow tuff (NYT), a volcanic rock rich in phillipsite/chabazite zeolites, binds HA through the action of surface extra-framework exchangeable cations, whereas HA molecules are too big to enter the system of channels and cages of zeolite crystals. The binding ability is markedly enhanced when the zeolitic material is enriched with divalent cations, especially Ca^{2+}, that act as micro-bridges between negative charges on the zeolite surface framework and HA carboxylic groups. Moreover, it has been shown that HA adsorption by natural zeolites is a relatively long-lasting process with kinetic curves characteristic of a two-stage adsorption process (Ambrosone et al., 2013; Capasso et al., 2007b). Here we report a study on the HA adsorption onto a clinoptilolite-rich tuff. The influence of calcium ions and particle sizes were analyzed.

Objectives

Adsorption of humic acids in water solution onto a clinoptilolite-rich tuff from New Mexico (USA) was investigated with the batch technique, with attention to the effects of adsorbent-bound Ca2+ and adsorbent particle size. Kinetic analysis showed that the adsorption process takes several days and follows a two-step pattern. In this study, two of the most established isotherm models were used for fitting the experimental data: the Langmuir and the Freundlich equation. Interestingly, the statistical parameters show that the Langmuir equation describes the experimental data more accurately for two of the three samples analyzed. The q_m parameter did not change significantly with particle sizes and calcium concentration; the K parameter, which reflects energy interactions between the adsorbate and adsorbing sites, increased with calcium amount and decreased with particle size. The results point to the tuff investigated, a low-cost natural material, as a potentially useful adsorbent for water purification from humic acids.

Methods

1. Clinoptilolite rich tuff (CCT)

The clinoptilolite-rich tuff (CCT) used in the present investigation was extracted from a quarry in New Mexico (USA) and supplied by Coyote Cliff LLC Company. The mineralogical composition was determined by the company: clinoptilolite 89%, quartz 5% smectite <1%, feldspar <5%. The raw material was provided in two particle

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size ranges: 0.5–1.0 and 1.0–2.0 mm. Before sorption experiments, the samples were repeatedly washed with Milliq water (50 mL water for 1g tuff) until the rinse water showed no increase in the conductivity after 1 day contact with tuff. Finally the samples were dried at 40°C.

2. Enriching tuff samples by Ca^{2+}

Two hundred and fifty grams of CCT for each particle size were put in a chromatographic column and eluted with 2.0 L of 1.0 M $CaCl_2$ solution, then washed with Milliq water. The exchangeable calcium content was determined by the ammonium acetate method. 15.0 mL of 1.0 M ammonium acetate were added to 1.0 g of Ca-CCT sample. The mixture was stored at room temperature for 1 day on a shaker at one oscillation per second.

Afterwards the mixture was centrifuged and the amount of Ca^{2+} cation in the water phase determined by atomic absorption spectrophotometer (Perkin Elmer, AA analyst 100). The extraction with ammonium acetate was repeated until the metal concentration was coincident with that present as impurity in the starting solution).

3. Humic acids purification

Humic acids (HA) were obtained from Aldrich. Ten grams HA were suspended in 1 L of Milliq water containing 10.0 mL concentrated HF and 10.0 mL concentrated HCl. After vigorous stirring for 1 day, the mixture was filtered, the precipitate washed with 1.0 M HCl, followed by Milliq water and finally re-suspended in 0.8 L of water. An appropriate volume of 1.0 M NaOH was added to the suspension to bring pH to 10.

The mixture was then stirred for 1 day, filtered, brought to pH 1.5 by concentrated HCl, and stored in a refrigerator for 1 week. Afterwards, the HA precipitate was collected by centrifugation, water-washed repeatedly, and dialyzed (molar mass cutoff = 3500 Da) against Milliq water until no significant change was observed in the conductance of bath water (<100 μS cm-1 per day). Finally, the purified HA was collected by lyophilisation and dried in oven at 40°C. The elemental contents were determined using a CHN analyzer. The ash content was determined by keeping the sample in oven at 600°C for 6 h.

4. Adsorption batch experiments

All experiments were conducted using a stock HA solution of 200 mg L-1, prepared by dissolving 0.20 g of purified humic acids in 1000 mL of 0.01 mol L-1 Tris/TrisHCl buffer [Tris = 2-amino-2-(hydroxymethyl)-1,3-propandiol], 0.04 mol L-1 KCl solution, pH 7.4, and vigorously stirred for 1 day. pH was periodically tested and, when required, adjusted with a few drops of 1.0 M Tris base solution. The HA solution was then filtered through a RC 0.45 μm membrane (Chemtek). This stock solution was then diluted with 0.01 mol L-1 Tris/TrisHCl buffer [Tris = 2-amino-2-(hydroxymethyl)-1,3-propandiol], 0.04 mol L-1 KCl solution, pH 7.4 to prepare the different concentrations of HA to be used in the tests. Batch adsorption experiments were conducted using vials of 50 mL. The following particle sizes were used: 0.5-1.0 mm or 1.0 – 2.0 mm for Ca-CCT, 0.5-1.0 mm for CCT. At programmed intervals the supernatants were centrifuged at 13,000 rpm for 15 minutes and analyzed by VIS-spectrometry at 450 nm, using the extinction coefficient ε = 0.0072414 mg–1 l cm–1 determined from the concentration–absorbance linear plot. The adsorption capacity at time t was calculated using the following equation (Eq. 1):

$$q_t = (C_0 - C_t * V) / m \tag{1}$$

where: q_t is the adsorption capacity at time *t* (mg kg^{-1}), C_0 the initial HA concentration (mg L^{-1}), C_t is HA concentration (mg L^{-1}) at time *t*, *V* the volume of HA solution in the vials (L), *m* the adsorbing mass (kg).

2.4.1. Kinetics

Fifty mL aliquots of 140 mg L^{-1} HA solutions were put in vials containing 200 mg of clinoptilolite rich tuff enriched in calcium ions (Ca-CCT) or row tuff (CCT). The vials were kept at room temperature on a rotating shaker, one oscillation per second and HA concentration in solution was determined at selected times.

2.4.2. Adsorption isotherms

Fifty mL aliquots of HA solutions prepared as reported above, concentration range 28 - 200 mg L^{-1}, were added to 100 mg of adsorbing (Ca-CCT or CCT) in vials and kept at room temperature on a shaker at one oscillation per second. After 20 days, aliquots were analyzed; few experiments carried out after longer times showed no significant further changes in HA concentration.

Results and discussion

1. Kinetic study

Fig. 1a shows the sorption kinetics of HA onto row clinoptilolite rich tuff (CCT) and Ca^{2+}-enriched sample (Ca-CCT), while Fig. 1b compares the sorption kinetics of HA on Ca-CCT with different particle sizes. For all kinetic runs the adsorption process lasted several days. The data reported in Fig. 1b, obtained at a higher HA/tuff ratio than that for Fig. 1a, show a two-step adsorption kinetics, in line with results of previous studies on HA adsorption on zeolitic tuff (Ambrosone et al., 2013, Capasso et al., 2007b): after an initial phase of fast adsorption lasting a few days, the adsorption rate decreased appreciably but subsequently it raised again up to the equilibrium state.

It has been shown (Ambrosone et al., 2013) that this behaviour is described by the following equation (Eq 2):

$$q_t = q_1\,[1 - e\hat{}(-t/\tau_1)] + q_2\,[1 - e\hat{}(-\,(t/\tau_2)\hat{}m)] \qquad (2)$$

where: q_t is the amount adsorbed at time *t*.

The fist term of the second member is the pseudo-first order adsorption kinetic equation and describes the first step of the adsorption; q1 is the pseudo plateau at the beginning of the kinetic run. The second term is similar to the so-called Johnson–Mehl–Avrami function with m as exponential (Johnson and Mehl, 1939; Avrami, 1941). This relation suggests a rearrangement of HA molecules on tuff surface during adsorption, possibly through a process of nucleation. The sum $q_1 + q_2$ is the amount adsorbed at equilibrium. The parameters τ_1 and τ_2 are the times required to reach the corresponding plateau. The parameter values obtained by least square fits for the adsorption of HA (50 mL of 140 mg L^{-1} HA solution) on 100 mg Ca^{2+}-enriched clinoptilolite-rich tuff with two particle size ranges was τ_1=0.95 ± 0.26 and τ_2=15.09 ± 1.64 for particle size 0.5-1.0 mm and τ_1=0.89 ± 0.35 and τ_2=12.4 ± 1.32 for particle size 1.0-2.0 mm. Within the errors, the only difference between the two sets of values is pertained to the parameter qi found to be higher for the size range 0.5-1.0 mm. This probably reflects the increase in the adsorbing surface consequent to a reduction in the average size of adsorbing particles. The curves in Fig. 1b were drawn using eq. (2). The parameters obtained by the curves in Fig. 1a were drawn fitting the experimental data with a pseudo-first order kinetic equation (the first term of the second member of eq. 2). The parameters obtained by the fits for the adsorption of HA (50 mL of 140 mg L^{-1} HA solution) on 200 mg row (CCT) was τ_1=7.36 ± 0.50 and for Ca^{2+}-enriched clinoptilolite-rich tuff (Ca-CCT) was τ_1=3.04 ± 0.20.

2. *Isotherms study*

Mathematical descriptions of equilibrium adsorption isotherms permit a reliable prediction of adsorption parameters and afford quantitative comparison of the behaviour of different adsorption systems (Anirudhan and Ramachandran, 2007). The equation parameters of these models often provide useful insights into the adsorption mechanism, surface properties and affinity of the adsorbing. In this study, two of the most established isotherm models were used for fitting the experimental data: the Langmuir and the Freundlich equations. The Langmuir model supposes that the adsorbing sites are energetically equivalent and that at equilibrium the adsorbed molecules are arranged in monolayers. The Langmuir model is represented as follows (Eq 3):

$$q_e=(q_m\,.\,K\,.\,C_e)/(1+(K\,.\,C_e)) \qquad (3)$$

where q_e is the amount of HA adsorbed per unit weight of adsorbing material at equilibrium, C_e the equilibrium adsorbate concentration in solution, q_m the amount of solute adsorbed, and *K* the Langmuir adsorption equilibrium constant, related to the adsorption energy (Rawajfih and Nsour, 2006).

The Freundlich equation (Eq. 4) is based on the assumption that the adsorbing has a heterogeneous surface with different types of adsorption sites. Adsorption on each class of sites follows the Langmuir isotherm. The Freundlich equation has the form of:

$$q_e = K_f\,.\,C_e\hat{}(1/n) \qquad (4)$$

where: K_f and n are parameters.

Fig. 2 shows the sorption isotherms of HA onto clinoptilolite tuff. The parameters of the Freudlich and Langmuir adsorption equations are reported in Table 1.

The statistical parameters show that the Langmuir equation describes the experimental data more accurately for two of the three samples analyzed.

Moreover, we observe that there is no significant difference among the q_m values of the Langmuir equation. In contrast K_L, a parameter related to the interaction energy between the solid phase and the adsorbate, is higher for the Ca-enriched samples and increases with decreasing particle size.

The qm values reported here are higher than the values determined for a similar tuff (79% clinoptilolite) from Turkey under the same experimental conditions (Capasso et al., 2007b). Interestingly, markedly higher qm values have been reported for phillipsite and chabazite-rich tuff from Naples (Italy) (Capasso et al., 2007b), although this material had a lower zeolite amount (54%) than the clinoptilolite-rich tuff examined in the present study and that from Turkey.

Up to now the Neapolitan yellow tuff is zeolitic tuff with the higher humic-acids adsorbing capacity.

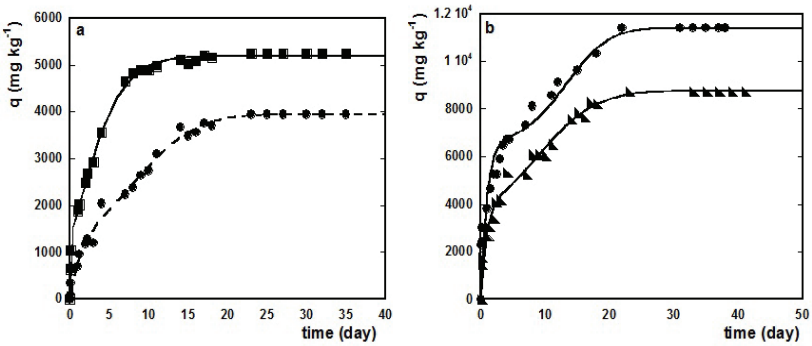

Fig. 1. Sorption kinetics of HA 140 mg L^{-1} on a) 200 mg row (●) or Ca^{2+}-enriched clinoptilolite-rich tuff (■), particle size 0.5-1.0 mm; b) 100 mg Ca^{2+}-enriched clinoptilolite-rich tuff, particle size 1.0-0.5 mm (●) or 1.0-2.0 mm (▲)

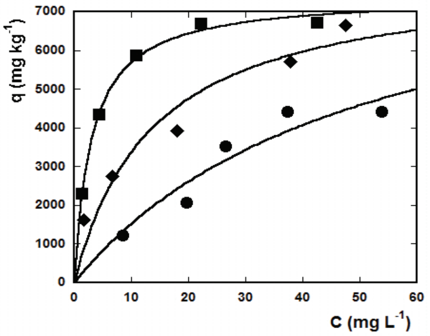

Fig. 2. Sorption isotherms of HA (50 mL of 140 mg L^{-1} HA solution) onto 100 mg row clinoptilolite-rich tuff, particle size 0.5-1.0mm (●), and Ca^{2+}-enriched clinoptilolite-rich tuff , particle size 0.5-1.0mm (■) or 1.0-2.0mm (♦)

Table 1. Isotherms parameters for HA sorption onto: row (CCT) and Ca-CCT

	CCT ***particle size 0.5-1.0 mm***	***Ca-CCT*** ***particle size 0.5-1.0 mm***	***Ca-CCT*** ***particle size 1.0-2.0 mm***
Freudlich model			
K_F	360.26±223.64	2851.7±543.26	1163.9±129.48
$1/n$	0.6529±0.1715	0.2527±0.0634	0.4434±0.0319
R^2	0.878	0.876	0.991
Langmuir model			
q_m	9246.1±3764.7	7402.5±160.21	8018.5±1286.7
K_L	0.0197±0.0136	0.3322±0.0307	0.0727±0.0339
R^2	0.908	0.994	0.930

Concluding remarks

Our results show that clinoptilolite rich tuff, a low-cost natural material, is a potentially useful adsorbing for water purification from humic acids, although it does not entirely match the Neapolitan yellow tuff. In line with previous work, samples rich in calcium are characterized by a higher energy of interaction. Moreover, under selected experimental conditions, the amount adsorbed versus time follows a two-step kinetics, suggesting a rearrangement of HA molecules on tuff surfaces during the adsorption process.

Keywords: clinoptilolite, humic acids, kinetics, sorption, zeolitic tuff

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TREATMENT AND DISPOSAL OF SEWAGE SLUDGE: COMPARATIVE LIFE CYCLE ASSESSMENT ON ITALIAN CASE STUDY

Extended abstract

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Background

The management of sludge from wastewater treatment plant (WWTP) becomes interesting due to the increasing amount and the high percentage of energy consumption (respect to the total of WWTP) for the operation as they require treatment before disposal. This means that the costs of sludge treatment, that actually are about 50% of the total management costs of WWTP, could increase. From environmental point of view, the landfill disposal of sludge has high impacts related to the leachate production and the CO_2 equivalent emissions (Houillon & Jolliet, 2005) directly in air. Estimations (EC, 2010) show that about 45 % of biogas emitted from landfill is dispersed in atmosphere. Moreover, there are some concerns for social aspects too: landfilling leads to depreciation of area and properties, dissatisfaction among people, transfer of residents to other areas.

From other hand, the sludge recovery and utilization is an option strongly promoted as it is in compliance to the European recommendations for reducing landfill disposal and, moreover, seems to be economically and environmentally convenient, as the waste valorisation leads to energy and material recovery. Also for social aspects has to be highlighted that recycling generates more jobs than landfilling (they are included in the green jobs) and promote satisfaction of citizens. Concerning the recovery options, from literature studies (AA.VV., 2011; Hong et al., 2011; Hospido et al., 2005; Odegaard et al., 2005) it could be found evaluations on use of sludge as secondary raw material in cement production and on different sludge treatments like as thermal, thermo-chemical and biological in separate or combined applications.

Actually, the sludge landfilling is the main end-of-life option used in Italy but the country has to reduce the sludge landfill disposal from 25% to 5% by 2020, in line to the European estimation (EC, 2010). So, there is the need to improve sludge treatment solutions to address the choice towards options that guarantee safety end environment protection and economic advantages and social sustainability.

In the last years the composting option was growing and, as in other European countries, Italy has also undertaken a voluntary certification programme for quality compost (both for the product and the process) promoted by the Consortium of Italian Composting plants (CIC). As often occurs, not one solution is able to solve concerns about waste management but an integration of solutions is necessary to obtain a correct management and also advantages. Concerning WWTP sludge different solutions could be:

- Improvement of Environmental Management System of WWTP;
- Reduction of sludge amount by technical improvement;
- Solution of sludge recovery and valorisation.

In this paper the environmental profiles of different treatment and disposal option for WWTP sludge are compared by using Life Cycle Assessment methodology in order to avoid shifting of burdens in a different geographical, temporal or technological context or in other phases of the same life cycle. Indeed, LCA gives the opportunity of developing qualitative and quantitative environmental evaluations to compare different options (scenarios).

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Objectives

The aim of this study is the comparison of environmental performance by using Life Cycle Assessment methodology, of five different options for WWTP sludge management: agricultural land application with and without lime stabilization, landfilling with and without lime stabilization and composting as alternative biologic treatment. The study has been developed in collaboration with an Italian firm, AQUASER, an enterprise of ACEA spa group, among the major Italian operators in the field of sewage sludge management focused on recovery and disposal of waste, produced by wastewater treatment plants.

Outline of the work

This paper reports the results of a study carried out by ENEA on behalf of AQUASER (ACEA SpA group) for the comparative evaluation of environmental impacts of various methods of treatment and disposal of sludge from waste-water treatment plants (Barberio et al., 2012). The comparative assessment has been made according to LCA methodology. The first part covers the description of the system boundaries considered in LCA studies as they are the options technically operated by and on behalf of AQUASER, to the extent permitted by law and by the sludge's characteristics, however, according to the most common treatment and disposal systems used in Italy. Of particular interest is the composting process (plant in the LT prov., Italy) that allows the sludge to have a productive use, even when it is not possible, for many reasons, use sludge directly as fertiliser.

The second part covers the Life Cycle Inventory as data collection and assumptions are important in LCA study. Finally, results of comparative LCA study are showed.

Methods

In this paper a comparative LCA study has been carried out on the basis of the same function of the systems, defined as the end-of-life of WWTP sludge throughout treatment and/or disposal, according to the Italian law. The functional unit (FU) is 1 ton of sludge from WWTP of urban water. The systems under study are agricultural land application with and without lime stabilization, landfilling with and without lime stabilization and composting. Boundaries systems are from gate (WWTP plant) to grave (end-of-life of sludge). The evaluation of environmental impacts has been performed by using IMPACT 2002+ method and SimaPro 7.3.2 software.

The steps of Life cycle analysed are: sludge production/stabilization in WWTP; sludge transport from WWTP plant to landfill (option L), agricultural land (option A, as application); chemical plant, for options with stabilization (s, as stabilization); composting plant (option C) and from chemical plant to landfill (option Ls, meaning Landfill with stabilization) or agricultural land (As meaning Application with stabilization); sludge treatment in plant, including the consumption of energy, water, raw materials and auxiliary materials, emissions and waste; Final transport of treated sludge, that becomes a new marketable product (compost). From composting system, a new marketable product is obtained and it substitutes part of fertilizers applied on soils so, the LCA study considers the avoided impact associated to the reduced production of fertilizers. The amount of avoided fertilizers is calculated on the basis of specific culture and surface on which compost or sludge is applied.

Primary data has been collected for stabilization treatment and composting concerning the consumption of raw material, energy and water, type of truck and distances. Secondary data (literature and database) are used for auxiliary materials, construction and utilization of truck, operation of spreading on soil, operation of landfill disposal and WWTP, production of electricity (Italian mix from Ecoinvent Database) and fuel. An example of Inventory is reported in Table 1 and Table 2 for composting scenario. Table 1 reports the inputs to the system while Table 2 shows the outputs.

Table 1. Composting scenario – inputs to the system

Type	*Detail*	*Quantity/Distance/Consumption*
(Sludge; organic waste, green waste)		(1 t; 3.1 t; 0.5 t)
Fuel	wheel loader, excavator bucket, mixer, plastic separation plant	2.18 litre diesel/t_{sludge}
Electric energy		32.73 kWh/t_{sludge}
Water		< 0.1 l/t_{sludge}
Sulphuric acid	5 t/week of acid pure at 98%	4.36 kg/t_{sludge}
Heather for bio-filters	2560 m^3/bio-filter*year	0.046 m^3/t_{sludge}
Transport of sludge in input	truck 16-32 t, diesel	Waste water treatment plant – composting plant: 141.5 km
Transport of sulphuric acid in input	truck 16-32 t, diesel	Sulphuric acid production plant – composting plant: 260 km
Transport of Heather	truck 3.5-7 t, diesel	Heather production (France) – composting plant: 1370 km

Table 2. Composting scenario – outputs from the system.

Type		***Amount***	***Final destination of treatment/disposal***	***Distance***	***Note***
Product	Compost [t]	0.917	user	50 km	truck 16-32 t, diesel
	Compost spreading [t]	0.917	user		“Solid manure loading spreading […]CH”
	area [ha]	0.0229	user		
Gas emissions	dust [g]	43.65	air		
	ammoniac [g]	4.75	air		
	TOC [g]	50.89	air		
Water emissions	leachate [litre]	**183**	Transport	350 km	truck 16-32 t, diesel
	leachate treatment [litre]	**183**	Waste water treatment plant DB “Treatment sewage, wastewater treatment class 2/CH U”		DataBase - litre

Results and discussion

Results of damage evaluation (Ecopoint, IMPACT 2002+ method) for comparison among the five systems analysed are presented in Fig. 1. Composting shows the lowest environmental impact, excluding the direct application of sludge on agricultural area that is very difficult option to operate because of strictly limits imposed by law. The main impacts for composting scenario are due to the distance between the WWTP and the composting plant, the leachate treatment and also for energy consumption. In composting system, the sludge is used in a mixture with other waste (Table 3) and all fluxes are referred to the FU.

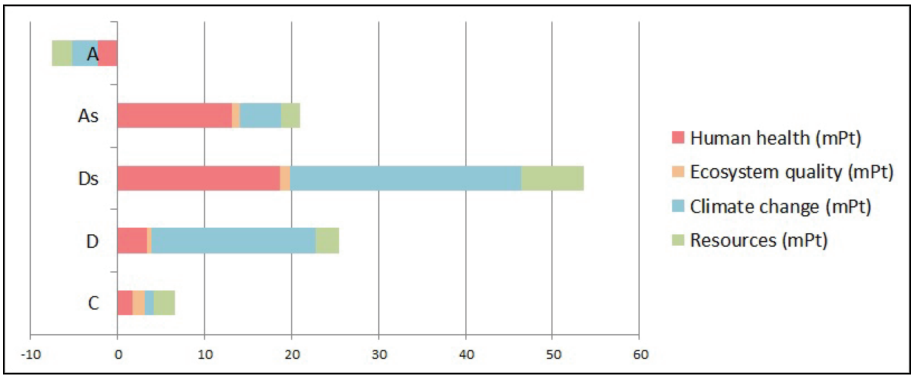

Fig. 1. Comparison between sludge recovery/treatment systems (IMPACT 2002)
L = Landfill, A = land Application, s = stabilization, C= Composting

Table 3. Amount of mixture for composting

	Sewage sludge	***Green waste***	***Lignocellulosic waste***
Amount [t/y]	12000	37000	6000
t/t sludge	1.0	3.1	0.5
%	22%	67%	11%

Concluding remarks

There is not “the best” technological solution: a strategy for sludge management that considers local issues and sustainability is needed. Landfilling must decrease as an option due to increasingly stringent standards. The impacts identified in the comparative LCA are very heterogeneous, and it is observed that the impacts generated by the composting are high in the short term, while impacts arising from disposal in landfills and direct spreading on the ground are relatively low in the short term and much higher on cumulative long-term. Moreover, in particular, social and economic impacts due to the presence of a landfill in the area that would instead be included in the comparative assessment and which are highly site-specific.

The results show that in the case of composting is necessary to reduce the impacts associated with the production and treatment of leachate (through on-site treatment and the reduction of bio-waste in the mixture). Further assessments of different options are needed including anaerobic digestion and incineration; in the composting system it is necessary to optimize the stages of transport which significantly affect overall impacts (transport heather, sludge composting at 0 km). Results of this study encourage keeping on in the reduction in landfilling and improving systems of sludge recovery. Life cycle approach tools together with exchange of knowledge and expertise can support the cooperation between research activities and companies to better understand and characterize the footprint of products and processes and to stimulate Eco-innovation.

Further investigation on other options as anaerobic digestion, incineration could lead to the optimal sludge management in terms of recovery of material and energy to obtain economic and environmental advantages.

Keywords: composting, sludge spreading, sludge valorisation, waste water sludge

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INNOVATIVE TREATMENT SOLUTIONS FOR SEWAGE SLUDGE RECOVERY ON A FP7 PROJECT ROUTES

Extended abstract

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Background

ROUTES is addressed to assess new routes in wastewater and sludge treatment focusing on three main objectives:

1. optimization of the sludge quality for agricultural use with the goal to produce a clean and full stabilized sludge through intensive stabilization processes with attention to a broad spectrum of parameters including micro-pollutants, pathogens and their indicators.
2. minimization of the sludge to be disposed by innovative technical solutions based on different approaches, either on the water or sludge treatment lines;
3. recovery of valuable resources before sludge disposal by producing a liquid fertilizer [$(NH_4)_2SO_4$], biopolymers or optimizing methane production by anaerobic treatments.

Technical and economic assessment of the investigated techniques on laboratory and pilot scale were carried out in a typical benchmarking study. The whole set of data is then provided to the partner involved in environmental assessment where different impact categories are considered (global warming potential, acidification potential, eutrophication potential and photochemical ozone creation potential).

Intensive stabilization processes

Thermophilic digestion of thermal pre-treated secondary sludge

The performance of thermophilic anaerobic digestion (55°C) of thermal pre-treated activated sludge ($T=135°C$, $\theta=20$ min) was studied carrying out semi-continuous digestion tests using lab-scale jacketed reactors ($V = 7$ L). The first test was carried out in parallel, feeding thermally pre-treated sludge to one reactor and untreated sludge to the other, with a residence time of 8 d. The anaerobic process was evaluated monitoring total and volatile solids (VS), soluble COD, soluble nitrogen and ammonia, surface charge, CST, biogas production and its composition during the test. In a second test the residence time was increased from 8 to 15 d.

In the first test higher VS destruction and biogas productions, with similar CH_4 content of about 65% by volume, were achieved with respect to the digestion of untreated sludge. The thermally hydrolysed digested sludge resulted richer in soluble COD with respect to the untreated one (1.1 g/L instead of 0.7 g/L) and showed a worse dewaterability (60% higher CST and 57% higher surface charge density). In the 2nd test a slight worsening of filterability was observed (17% higher CST and 32% higher surface charge density).

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Anaerobic + Aerobic combined process

The integration of an aerobic post-treatment for further biodegradation of residual VS sludge from the previous anaerobic stage (Kumar et al., 2006) was investigated. Experimental tests were performed in a lab scale cylindrical glass reactors (volume 7.4 L) operated in series. Sludge was fed to the anaerobic reactor once per day and an equivalent volume of digested sludge was extracted and fed to the following aerobic reactor. The first reactor operated under anaerobic conditions and was equipped with a thermostatic jacket and a control device keeping the temperature at 37 ± 0.5 °C. Sludge retention time (SRT) was controlled at 15 d. The second aerobic reactor was operated with a working volume of 4.5 L with air supply by a compressor automatically controlled to maintain a dissolved oxygen (DO) concentration around of 3 mg/L. Such an operating strategy prevented ammonia stripping. The aerobic reactor was operated at room temperature with an SRT of 12 d. Two series of tests were performed at the same operating conditions with secondary and mixed sludge respectively. Experimental results showed a satisfactory performance of the sequential digestion process with significant additional VS removal in the post aerobic digestion stage (25% for secondary sludge and 45% for mixed sludge). Nitrification efficiency ranging from 79% to 95% was observed for secondary and mixed sludge, respectively. Possibility of complete nitrogen removal by alternate aeration in the aerobic reactor was investigated with good results. Produced biogas in the two series of tests was in the range of the literature values [0.19-1.6 m^3/(kg/VS destroyed)] as reported in Speece (1988) and Bolzonella et al.(2005), demonstrating that a SRT of 15 d is suitable for a positive energy balance.

Assessment of sludge sanitation

Pathogens and pathogens indicators (*E. coli*, *Clostriudium* spores, presence/absence of Salmonella spp.) were monitored in different stages of the above intensive stabilization processes. A reduction of *E.coli* number, after thermal treatment, was observed during the all monitoring period in all the analyzed treated sludges independently on the treatments and operating conditions applied. As expected, thermal pre-treatment always reduced *E. coli* concentration below to the reference limit (500 CFU/g dry weight) of the European Draft Working document on sludge [1]. Similar performances were obtained by thermophilic anaerobic digestion, which reduced *E.coli* below detectable limits in 100% and 75% of the analyzed samples during respectively test #1 and #2. *Clostridium* spores were removed only by the thermal pre-treatment. No reduction of this bacterial indicator was in fact observed by thermophilic anaerobic digestion of raw sludge. Absence of *Salmonella* spp in 50 g wet weight was ascertained during all the sampling campaigns. As far as the sequential anaerobic/aerobic processes are concerned, data showed that the aerobic phase contribute greatly to the removal of microbial indicators. Removal of *E. coli* increased from 1.25 ± 0.39 log of the anaerobic treatment to 2.28±0.87 log of the complete process. All the samples showed a reduction of at least 2 Log10 of *E. coli* (CEE 2000). The absence of *Salmonella* spp. was achieved in all but one sampling campaigns. In this sludge digestion process, *Clostridium* spore concentration did not change from the sludge influent to the process effluent (both anaerobic and aerobic effluent).

Processes for biopolymer production

Polyhydroxyalkanoates (PHA) are biodegradable polyesters with comparable properties to some petroleum-based polyolefins. The production of these biopolymers can be achieved in mixed microbial cultures, which growth and selection is coupled to wastewater and solid residual treatment. In fact, PHA production involving microbial cultures treating wastewater is an effective strategy to decrease their production costs of conventional pure-culture PHA processes. In addition, PHA production further valorizes wastewater treatment by recycling carbon towards products and reducing sludge production. The most common approach for PHA production with wastewater treatment process is based on selectively growing/enriching PHA-storing bacteria in activated sludge through dynamic process configuration with respect to substrate feeding, i.e., alternating conditions of carbon source availability and unavailability (Dionisi et al., 2004) or electron acceptor availability, i.e. aerobic vs. anaerobic (Bengtsson et al., 2008). Substrate aerobic dynamic feeding (ADF) or feast-famine has been widely reported as appropriate enrichment approach (Dias et al., 2006). The main substrates used for the selective growth of PHA-storing bacteria and PHA production have been volatile fatty acids (VFAs), since VFAs are directly converted into PHA. Until now, a three-stage anaerobic-aerobic process configuration for PHA production and wastewater treatment has been investigated (Dionisi et al., 2004): (i) wastewater acidogenic fermentation for the VFA production, (ii) ADF enrichment of PHA-storing organisms by feeding with the VFA-rich stream and (iii) PHA accumulation by feeding with the same VFA-rich stream. PHA production from different industrial and solids streams has been demonstrated under such conditions (Coats et al., 2007).

In this project, the PHA production integrated to municipal waste management has been evaluated; as a novel approach, the selective growth of PHA-storing organisms is based on the readily biodegradable carbon sources (RBCOD) that is directly available in the municipal wastewater, in spite it is usually VFA-poor. In this way, the VFA-rich stream from the acidogenic fermentation of primary sludge was saved for the following PHA production. The feasibility of conducting wastewater treatment while also producing a functional biomass with PHA-storing ability was demonstrated at lab- and pilot-scale, by a sequence of four units: (i) wastewater treatment combined with enrichment and production of a functional biomass sustaining PHA-storage capacity, (ii) acidogenic fermentation of sludge for VFA production, (iii) PHA accumulation from VFA-rich streams, and (iv) PHA recovery and characterization. It was confirmed that the ADF regime allows the biomass selection/enrichment even with VFA-poor wastewater as well as the PHA accumulation was obtained from the VFA-rich stream from sludge fermentation, in spite of the latter feed was different from the one used for biomass selection. In these conditions, the PHA accumulation potential of the WW-acclimated biomass was around 30% (g PHA $gVSS^{-1}$), quite higher than by using un-acclimated biomass, even though lower than by using VFA-acclimated biomass. These results suggest that a) municipal wastewater treatment can be coupled to PHA production and b) VFAs for PHA accumulation can be produced via acidogenic fermentation of primary sludge: Both features makes it possible to substantially reduce the amount of the excess sludge to be disposed of.

Processes for obtaining a liquid fertilizer $(NH_4)_2SO_4$

In 2010/2011 the first air stripping plant of Switzerland was built at the WWTP Kloten/Opfikon. Besides a conventional air stripping plant with NH_3 stripper and sorber it consist of an additional column by CO_2 stripping for pre-treatment of the liquid sludge side-stream coming from sludge dewatering, in order to increase the pH of the sludge liquid thus reducing the soda dosage needed for NH_3 stripping. In the first year of operation, the conventional free ammonia stripping as well as the CO_2-pre-stripping were optimized by Eawag in terms of: optimal temperature, optimal pH and optimal air demand (air/sludge liquid flow). With increasing temperature of the sludge liquid, the free ammonia removal efficiency was clearly increased. At a pH of 9.3 and temperature of 60°C, removal efficiency in the range of 90% was reached. The ratio of air to sludge liquid has significant impact on the overall energy consumption of the plant; a higher air flow combined with higher pH resulted in higher removal efficiency. With a liquid flow of 5.25 m^3/h and an air flow of about 3.600 Nm^3/h (i.e. 685 Nm^3/m^3 of NH_3 reach liquid phase)at 60°C and a pH of 9.3 a removal efficiency of about 90% is reached With the scope of energy efficient and cost effective nutrient removal at WWTP's a removal efficiency of 90% for the air stripping plant is sufficient. A disproportionate effort would be necessary for the elimination of the remaining 10%. This residual load could be more efficiently removed by biological treatment in the WWTP. Further experiences in the second year of operation of the plant showed, that higher liquid flows in the range of 7 m^3/h result in a better distribution of the sludge liquid in the column. The air/liquid ratio of 685 was kept (corresponding to an air flow of 4.800 Nm^3/h). The N removal efficiency of the plant was kept at 90%.

In a second step the CO_2 stripper was put in operation. Different trials with different air flows were conducted. The air flow was in the range of 50 to 200 Nm^3/h. Operational results showed decrease demand of soda dosage in the range of 40% to reach a pH value of 9.3**.** Air flow rates higher than 40-50 Nm^3/h, corresponding to 8-10 Nm^3/m^3 liquid for the CO_2 stripper, did not take to a more efficient CO_2 stripping and decrease of base demands. Free ammonia losses by the off gas of the CO_2 stripper is in the range of 2 - 3% of the ammonia load to the plant.

Co-digestion of waste activated sludge with organic wastes

The main objective of this activity was the assessment of biogas production of biowaste mixtures with activated sludge in pilot-scale anaerobic co-digestion trials in mesophilic and thermophilic conditions. Preliminary tests were carried out on different organic-residues or biowaste, especially from the agro-sector, substrates such as onion, radicchio, potato, triticale silage, crops silage, and winery wastes (see Figure 1).

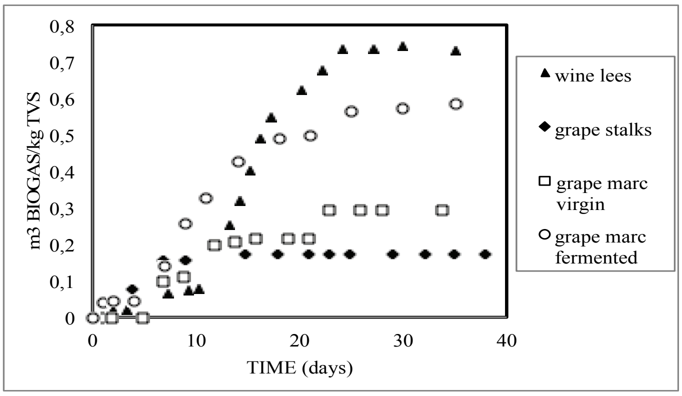

Fig. 1. Bio-methanation potential (BMP) tests with winery wastes in thermophilic conditions

These tests gave the maximum specific contribution in biogas production of each waste, considered as an indicator of the bio-methane potential when approaching to an anaerobic co-digestion process.

The anaerobic co-digestion of winery waste, i.e. wine lees (WL), and waste activated sludge was carried out in four parallel pilot scale continuous stirred reactors (CSTRs) of 230 L of working volume each, employed to study the combined influence of temperature, organic loadings (OLR) and hydraulic retention time (HRT) in co-digestion regime. The reactors were heated by a hot water recirculation system and two reactors were maintained at 37°C while others two at 55°C. The experimental protocol was designed to examine the influence of temperature on biogas production in co-digestion of WL and WAS. It was demonstrated that the co-digestion of WAS with WL cannot be sustained at an organic loading rates of 4.7 kg COD/(m^3 × d), both at mesophilic and thermophilic temperatures. The process, on the other hand, was very stable at lower loading conditions, 2.8 kg COD/(m^3 × d), especially at mesophilic temperature. The Specific Gas Productions (SGPs) were quite similar, 0.43 and 0.46 Nm^3 × kg COD fed^{-1} in mesophilic conditions and thermophilic conditions, respectively, for low loaded reactor, while considering for high loaded reactors the SGP increased from 0.37 to 0.49 Nm^3 kg COD fed^{-1}. The COD removal was 69% and 77%, respectively. From kinetic studies it was then observed that the system can produce about 70% of the biogas after 9 h, and 80% after in the first 12 hours after feeding, so the contribution of the easily biodegradable compounds directly used by the methanogens, such as acetate and ethanol, were predominant. The concentration of the polyphenolic compounds were 214 mg L^{-1} in thermophilic condition and 49 mg L^{-1} in mesophilic one. Comparison of degradation at different conditions revealed a strong influence of temperature, with more efficient phenol degradation in mesophilic conditions, according to the literature (Leven and Schnurer, 2005).

The digestate dewatering was quite poor in both mesophilic and thermophilic conditions. Values of the specific resistance to filtration (SRF) greater than 5×10^{12} m kg^{-1} were observed. With polymer dosages of at least 20 g/kg TS (Hidrofloc C 675-Hydrodepur) the SRF values still remained at high values around 10^{12} m kg^{-1}.

Concluding remarks

Sewage sludge management is often a critical issue in the wastewater treatment plants due to the unsuitable treatment for producing the right stuff to be finally used or disposed. The typical sludge outlet was the agricultural use but nowadays farmers seem not to be in favour with this approach. Presence of organic micropollutants and pathogens and undesiderable effects on soil are good arguments for stopping its further use. The project ROUTES has studied innovative techniques for an intensive stabilization of sludge with gain in methane production able to control the undesirable effects when sewage sludge is used on land. It was ascertained that pathogens can be controlled in thermophlic conditions and with thermal pre-treatments. Also a dual digestion system (mesophilic anaerobic + an aerobic stage) provided very good results of biodegradable solid removal. Good options for sewage sludge processing are also biopolymers production starting from the volatile fatty acids produced in an acidogenic phase. Recycling of liquid side-streams from the sludge dewatering is also critical in many WWTPs due to the very high ammonia load recycling. Its recovery as ammonium sulphate is an innovative way to recover a good fertilizer thus reducing this problem. Co-digestion of sewage sludge and organic solid wastes is a good opportunity to gain in biogas production when spare volume of digesters is available. In this cases attention should be paid to the final digestate dewaterability.

Keywords: ammonia recovery, biopolymers, pathogens, sewage sludge, stabilization

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CHARACTERIZATION AND AGRICULTURAL UTILIZATION OF A BIOSOLID FROM CHEMICAL STABILIZATION OF MUNICIPAL SEWAGE SLUDGE

Extended abstract

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Background

The disposal of municipal sewage sludge (MSS) is a topic of great interest as this waste is produced in large amounts in the European Community (EC) ($9 \cdot 10^6$ tons in the EC and about $8 \cdot 10^5$ tons in Italy, in 2006) and its production is rapidly increasing because of the great number of commissioned wastewater treatment plants and more stringent effluents treatment and discharge standards. On the other side, sewage sludge is rich in organic carbon (C, 50-60% of dry matter) nitrogen (N, about 1.5%), phosphorous (P, 3%) and other nutrients for plant growth (Laturnus et al., 2007). That's why the agricultural utilization of MSS is an interesting way to achieve both the disposal of this material and the closure of nutrient cycle from renewable resources. However, for a more effective agronomical valorisation, MSS should be subjected, before agricultural utilization, to one ore more treatments such as drying, biological maturation, composting, anaerobic digestion or chemical stabilization in order to remove undesired compounds, such as human pathogens and xenobiotic molecules (Fernandez et al., 2009). In this way their quality should improve, in the perspective of a rational and sustainable agriculture.

The result of these processes is no longer a sludge but a biosolid, that is the product of a transformation possessing all the features (maturity, stability, chemical and physical characteristics within the legislation limits) to be employed in agriculture as an amendment (NRC, 2002). As a matter of fact, the effect of organic amendments on soil quality should also be assessed, as their soil application can stimulate or inhibit microbial activity. For example the use of immature of unstable or immature product could led to N immobilization, moreover C mineralization could be affected not only by soil features but also by the source of the added product (Huang and Chen, 2009). Therefore the aim of the this work was to characterize, from chemical and physical point of view, a new biosolid (bio-sulphate product) obtained from the chemical stabilization of MSS with H_2SO_4 (sulphuric acid/sludge ratio 1/5 w/w) and CaO, classify it according to the current Italian legislation (D.Lgs. 75/2010) and study its behaviour as fertilizer, determining the mineralization of organic C and N, when it is applied to soil.

Materials and methods

The products (biosulphate, BS; cow manure, CM; poultry manure, PM) were chemically and physically characterized according to the Italian Official Analytical Methods for Fertilizers. The first product (BS) was a dark sludge with white-yellow particles, obtained from the chemical stabilization of MSS through hydrolysis with H_2SO_4 (sulphuric acid/sludge ratio 1/5 w/w) and following neutralization with CaO and dolomite and final drying. The other biosolids (CM and PM) were chosen among the most common commercial fertilizers as they could be replaced in their application by the new product. All biosolids were milled and sieved at 0.5 mm for analysis. The employed soil was a sandy-loam one (79% sand, 10% silt, 11% clay) collected in a horticultural farm near Rimini (Emilia-Romagna Region, Northern Italy), near the production plant of the bio-sulphate product. The soil was milled and sieved at 2 mm and then physically and chemically analyzed through the Official Methods for Soil Analysis. Particularly, the main soil characteristics were: pH 7.3, water holding capacity (WHC) 269 g/kg, total carbonates 440

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g/kg, cation exchange capacity (CEC) 18.0 cmol+/kg, total organic carbon (TOC) 14 g/kg, total nitrogen (TN) 1.38 g/kg, thus C/N ratio resulted about 10. Potential N mineralization was determined according to Stanford and Smith (1972). The soil, milled and sieved at 2 mm, was pre-incubated with quartz sand in the ratio 1:1 w/w at two different temperatures, 4 °C and 25 °C, at 60% of the WHC. At the end of the incubation period, the biosolids were added to soils in order to reach a N concentration of 100 mg kg^{-1}. Unamended soil as control was also incubated. An amount of 50 g of soil was weighted in a filtering funnel (diameter 55 mm) together with 25 g of quartz sand, to avoid the compaction of the soil, between two paper filters, at the basis and at the top of the system. The soils amended with different fertilizers were put in static incubation at 4 °C and 25 °C in order to investigate both the effect of the incubation temperature and of the type of biosolid. The soils were weekly sampled through lisciviation. Briefly, a solution of 10 mM $CaCl_2$ was slowly added (5 mL aliquots) to the soils in the filtering funnels and collected into 100 mL flasks to extract N mineral forms; an aliquot of this solution was stored at -20 °C for N analysis.

Then the samples were wet by using 25 mL of a nutrient solution without N (2 mM $CaSO_4$, 2 mM $MgSO_4$, 5 mM $Ca(H_2PO_4)_2$, 2.5 mM K_2SO_4) to restore the nutrients washed out with lisciviation. At the end of the extraction, water was eliminated from the samples through a vacuum pump (-0.33 bar) in order to restore their moisture content. The mineral N forms (ammonia and nitrate) were determined through a flow instrument analyzer (AA3, Bran-Lubbe, Germany). Cumulative net N mineralization was calculated with the following (Eq.1):

$$Nm(x)_t=Ni(x)_t-Ni(c)_t-Ni(x)_0 \qquad (1)$$

where: $Nm(x)_t$ is net inorganic N mineralized (released) at time *t* from the soil amended with product *x*; $Ni(x)_t$ is Inorganic N mineralized at time *t* from the soil amended with product *x*; $Ni(c)_t$ is inorganic N mineralized at time *t* from the unamended soil (control); $Ni(x)_0$ is inorganic N mineralized at time 0 from the soil amended with product *x*.

The curves of net N mineralization were interpolated through a first order kinetic described by Eq.2:

$$Nm=N_0\,(1-e^{-kt}) \qquad (2)$$

where: *Nm* is the net inorganic N mineralized by the amended soil at time *t*, N_0 represents the potentially mineralizable *N*, *k* the first order parameter (or mineralization constant rate), *t* the incubation time.

C mineralization was investigated through the method proposed by (Pell et al., 2006). The soil was pre-incubated at 25 °C and 60% of the WHC in 500 mL plastic pots for two weeks. At the end of this period, the three biosolids were added to the soils in order to obtain a N concentration of 100 mg kg^{-1}; also pots with unamended soil (control) were incubated. Then 50 g of soil were weighted in a plastic pot and put in a gastight closure container together with 5 mL of 1M KOH, for the capture of the CO_2 produced by microbial respiration. The system was put in static incubation at 25 °C. At scheduled times, the KOH solution was titrated with 0.1 M HCl after the addition of 5 mL of 0.5 M $BaCl_2$, employing a solution of phenolphthalein (1 g/L in 60% ethanol) as indicator. The incubation lasted until the respiration rate became constant. Cumulated net C mineralization was calculated as the difference between the mineralized C for the treatment *x* at the time *t* and the mineralized C in the unamended soil *c* at the same time *t*, with the following (Eq.3):

$$Ct(x)_t=Cr(x)_t-Cr(c)_t \qquad (3)$$

where $Ct(x)_t$ *is* net mineralized C at time *t* from the soil amended with product *x*, $Cr(x)_t$ is mineralized C at time *t* from the soil amended with product *x*; $Cr(c)_t$ is mineralized C at time *t* from the unamended soil. The calculated amounts were then normalized according to the organic C content of the products. The obtained data were interpolated with the following logistic function (Eq. 4):

$$Ct=C_0/(1+e^{-k(t-i)}) \qquad (4)$$

where *Ct* is the net mineralized *C* at time *t*, *k* represents the intrinsic respiration rate, C_0 the potentially mineralizable *C*, *i* the inflection point of the curve, *t* the incubation time. The respiration rate R_t was then calculated as the ratio between the net mineralized *C* for gram of soil and the incubation time; R_t data were interpolated through a first order kinetic described by the following (Eq. 5):

$$R_t= R_{bas} + (R_i\, e^{-k/t}) \qquad (5)$$

where: R_t is the respiration rate at time *t*, R_{bas} represents the basal respiration rate, *k* the kinetic decay constant, R_i the initial respiration rate, *t* the incubation time.

Poultry manure (PM), a NP organic fertilizer (D.Lgs. 75/2010), shows a high TN content whose about 50% is in inorganic N form, mainly NH_4^+ N. Its C/N ratio is quite low (5.85), as well as the C/P ratio (2.64). Cow manure (CM), a N organic fertilizer (D.Lgs. 75/2010), is characterized by high TOC content and consequently the higher C/N ratio (10.5) among the employed products. Bio-sulphate (BS) can be classified as a Ca-Mg based liming material (D.Lgs. 75/2010, *defecation lime*) that is “a product obtained by hydrolysis (and possible enzymatic attack) of biological materials by the use of lime and/or sulphuric acid and following precipitation of calcium sulphate". The D.Lgs. 75/2010 requires the following minimum concentrations (on dry matter basis): CaO 20% and SO_3 15%. Moreover the declaration of the hydrolyzed biological material is compulsory, while the declaration of TOC and TN content is optional. From the obtained results, the biosolid contains about 30% of total solids, respectively, 2/3 of ashes and 1/3 of volatile solids. The pH is slightly alkaline, EC and salinity show suitable values for the agricultural use of BS. Given the values of TOC and TN, the C/N ratio (8.88) under 10 is able to stimulate N mineralization when the product is applied to the soil. Regarding other parameters, SO_3 content was slightly lower than the minimum legislation limit, while CaO perfectly respected its limit. The heavy metal content was under the limits fixed by the D.Lgs. 75/2010.

Inorganic N was calculated, both at 4 °C and 25 °C, as the sum of ammonium-N (NH_4^+-N) and nitrate-N (NO_3^--N) extracted from the soils. Ammonium release (data here not shown) had a typical exponential decay trend at 4 °C, while it was constant throughout the experiment at 25 °C. At low temperatures, NH_4^+-N was released in the first 3 weeks of incubation, then it stabilized around 5 mg N kg^{-1} in all experiments. Among the tested products, such release was higher for PM (up to 30 mg N kg^{-1} after 14 days) which, however, contained itself a huge amount of NH_4^+-N. Moreover its organic N fraction was mainly constituted by urea, which was rapidly mineralized to ammonia.

Results and discussion

The main chemical and physical features of the employed products are reported in the following table (Table 1). At high temperatures NH_4^+-N was under 5 mg N kg^{-1} during the incubation, due to the rapid nitrification. Nitrate release (data here not shown) was particularly high at the first sampling time (7 days), then it rapidly decreased under 5 mg N kg^{-1} at both temperatures.

Table 1. Main chemical and physical characteristics of the employed biosolids (DL=Detection Limit)

Parameter		***Poultry Manure (PM)***	***Cow Manure (CM)***	***Bio-sulphate (BS)***
Moisture	%, fm	18.0	7.92	70.6
Volatile Solids	%, dm	37.6	71.2	28.9
pH- H_2O		8.05	7.12	7.51
Electrical Conductivity (EC)	dS/m	9.1	9.1	3.1
Total Organic Carbon (TOC)	C, % dm	14.8	31.2	13.5
Total Nitrogen (TN)	N, % dm	2.53	2.96	1.57
Ammonium-N (NH_4^+-N)	N, % dm	1.18	0.42	0.49
Nitrate-N (NO_3^--N)	N, % dm	0.002	0.013	0.002
Organic Nitrogen (TON)	N, % dm	1.33	2.53	1.52
Total Phosphorous	P_2O_5, % dm	12.8	2.61	2.11
Total Sulphur	SO_3, % dm	0.41	1.69	14.0
Calcium	CaO, % dm	5.59	4.59	27.1
Iron	Fe, %	1.5	0.42	1.1
Copper	Cu, mg/kg	120	84	120
Zinc	Zn, mg/kg	210	300	120
Manganese	Mn, mg/kg	520	370	270
Nickel	Ni, mg/kg	15	12	15
Chromium	Cr, mg/kg	110	31	<0.1 (DL)
Lead	Pb, mg/kg	30	4.6	10

However, at 4 °C, the released NO_3^--N amount was about 10 mg N kg^{-1}, while at 25 °C it was significantly higher, being in the range 30-80 mg N kg^{-1}. Regarding the products, there were no significant differences between them at 4 °C, while at 25 °C, at the first sampling time, PM reached higher nitrate concentrations (70 mg N kg^{-1}), followed by BS (60 mg N kg^{-1}) and CM (50 mg N kg^{-1}). From these data, we were able to build the curve of net N mineralization both at 4 °C and at 25 °C (Fig. 1a-1b). In this case, the data were reported against Growing Degree Days (GDD, expressed in °D), that is the product of time and temperature.

The experimental points were interpolated using a first order kinetic model (2), which resulted suitable for all data sets. At 4 °C, PM had the highest N mineralization value (from the interpolation N_0 was 28 mg N kg^{-1}), followed by BS (N_0 = 20 mg N kg^{-1}) and CM (N_0 = 12 mg N kg^{-1}). The same trend was found at 25 °C, even if at this temperature there were no significant differences between PM (N_0 = 35 mg N kg^{-1}) and BS (N_0 = 40 mg N kg^{-1}), while CM showed again the lowest value (N_0 = 25 mg N kg^{-1}). The interpolation also provided the first order parameter (k) values, that were used to calculated the half-life time ($t_{½}$), that is the time needed to reach the 50% of the total potential N release; $t_{½}$ value was very low for PM (13 °D at 25 °C), while it was quite high for BS (131 °D at 25 °C), which had a behaviour similar to that of CM (144 °D at 25°C). Clearly the incubation temperature affected form, amount and rate of N mineralization: at 4 °C N release was slow and predominantly as NH_4^+-N rather than NO_3^- -N; the N mineralized as ammonia accumulated and slowly transformed into nitrate, as at this temperature microbial processes were quite low. On the contrary, at 25 °C it is likely that microbial biomass rapidly produced ammonia that is rapidly oxidized into nitrate, so ammonia concentration in soil remained low. Among the products, PM was the one significantly mineralizing N in the first days of incubation, confirming its behaviour as a rapid effect fertilizer. Instead BS had N release slower with respect to PM, but faster if compared to CM. The different products showed also a different behaviour with the increase of temperature. In fact PM had a quite low N_0 increase moving from 4 °C to 25 °C, while for BS and CM the N_0 values at 25 °C were almost double with respect to the ones at 4 °C.

In conclusion, BS showed a potentially mineralizable N fraction similar to that of PM with a release time similar to the one of CM, thus it could be comparable to a slow release organic fertilizer.

The trend of net C mineralization is reported in Fig. 2. All the amended soils mineralized to CO_2 the organic C added with biosolids, with BS reaching mineralization values intermediate between the ones of CM and PM. Interpolation with the logistic function (4) was suitable for all data sets and provided C_0 (potentially mineralizable C) values of 31%, 21% and 13% of the added C for CM, BS and PM, respectively.

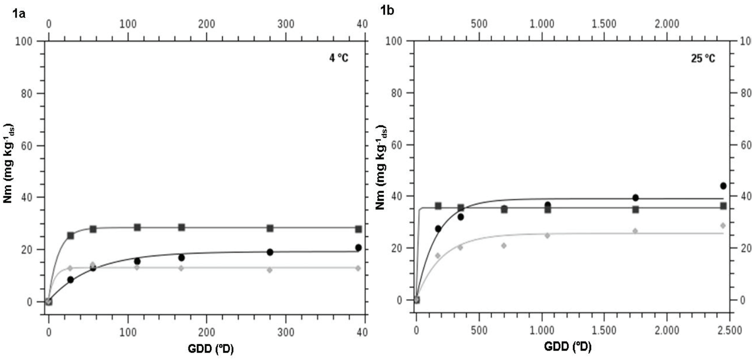

Fig. 1. Net N Mineralization: Mineralized N at 4°C (1a) and 25°C (1b) for soils amended with BS (●), PM (■) and CM (♦).

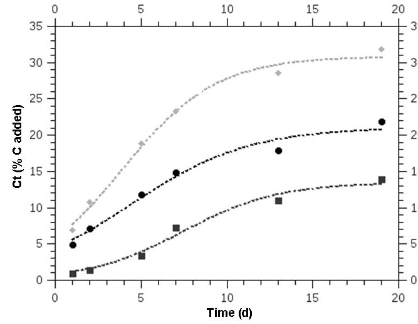

Fig. 2. Net C Mineralization: Mineralized C at 25°C for soils amended with BS (●), PM (■) and CM (♦)

From these data, we can observe that the different values of C_0 for the different products are completely different from those of N_0, as CM had the highest C_0 but the lowest N_0, while PM had the lowest C_0 and the highest N_0. Probably PM behaved as an inorganic fertilizer, with its organic fraction less involved in N mineralization, while CM was probably used as a substrate by soil microbial biomass, thus N mineralization occurred only after organic matter respiration. BS showed an intermediate behaviour between the ones of PM and CM.

C mineralization was higher in the first days of incubation, then after 20 days it reached a plateau value, thus the respiration rate (R_t) became almost constant for all products. R_t followed the trend of the exponential decay (5), with basal respiration (R_{bas}) values lower then initial respiration rate values (R_i) for all products. However R_i was significantly higher for the soil amended with CM, followed by BS, with PM having the lowest values; indeed CM and BS not only provided organic substrates for soil microorganisms, but also induced an increase of respiration.

Concluding remarks

The results of this work indicated that chemical stabilization of MSS could be an interesting method to dispose this waste and obtain a quality product (bio-sulphate) for agricultural uses. Indeed BS showed chemical and physical characteristics within the limits fixed by the current Italian legislation for amendments (D.Lgs. 75/2010).

When applied to soil, BS slowly mineralized its organic N into NH_4^+ and NO_3^- up to 40% of the added N and mineralized C to CO_2 up to 20% of added C, showing an intermediate behaviour between those of CM and PM, products that it could probably replace in the future.

Keywords: carbon mineralization, chemical stabilization, liming material, nitrogen mineralization, sewage sludge,

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THE THIRD TECHNICAL REPORT FOR END-OF-WASTE CRITERIA ON BIODEGRADABLE WASTE SUBJECTED TO BIOLOGICAL TREATMENT

Extended abstract

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Background

The Waste Framework Directive (EC Directive, 2008) introduces a new procedure for defining *end-of-waste* criteria (EoW), which are criteria that a given waste stream has to fulfill in order to cease to be waste (De Baere and Mattheeuws, 2013; IPTS and JRC, 2012). The Directive establishes several conditions and recovery operations for waste streams. In particular, article 6 of Waste Directive requires: "'certain specified waste shall cease to be waste when it has undergone a recovery, including recycling, operation and complies with specific criteria to be developed in accordance with the following conditions (EC Directive, 2008):

- the substance or object is commonly used for a specific purpose;
- a market or demand exist for such substance or object;
- the substance or object fulfills the technical requirements for the specific purpose referred to in (a) and meets the existing legislation and standards applicable to products;
- the use of substance or object will not lead to overall adverse environmental or human health impacts".

The European Commission prepares proposals for *end-of-waste* criteria for a number of specific waste streams, including biodegradable waste (IPTS and JRC, 2012). Two other important definitions are: "bio-waste" and "biodegradable waste". The second one, in particular, is a broader concept defined by Landfill Directive (Council Directive, 1999) that include "any waste that is capable of undergoing anaerobic or aerobic decomposition, such as food and garden waste, and paper an paperboard" (article 2). This concept allows us to understand the definition of compost and digestate.

In the third technical report (IPTS and JRC, 2012) compost and digestate are defined as follow:

- "**Compost** is the solid particulate material that is the result of composting and which has been sanitized and stabilized. Composting is a process of controlled decomposition of biodegradable materials under managed conditions, which are predominantly aerobic and which allow the development of temperatures suitable for thermophilic bacteria as a result of biologically produced heat";
- "**Digestate** is the semisolid or liquid product of anaerobic digestion of biodegradable materials. It can be presented as whole digestate or separated in a liquor phase and fibrous semisolid phase. Anaerobic digestion is a process of controlled decomposition of biodegradable materials under managed conditions, predominantly anaerobic and at temperatures suitable for mesophilic or thermophilic bacteria".

In Europe it remains difficult to identify clear rules, because the territories, the environmental sensibilities and diets are different. Not only every country produces different biodegradable waste and collects them in different ways, but every city produces different waste (Hall, 2011).

The characteristics of the organic fraction of waste depend on its substrate and the system with which the waste is collected. Separate collection offers high level quality of biodegradable waste. There are three types of organic fraction from municipal solid waste (Lens et al., 2004; Mata-Alvarez, 2003): the organic fraction collected in restaurant, canteens etc; the organic fraction collected door to door; the organic fraction from industrial production obtained through mechanical separation of waste (in this case it is likely to find undesirable elements).

There are three approaches for determining the status of compost in Europe (IPTS and JRC, 2012):

1. the national environmental or waste legislation establishes the end-of-waste of compost. In this case, the legislation clearly defines the conditions under which compost ceases to be waste (for example, the German Bio-waste Ordinance);

2. the Regulatory Authority establishes the end-of-waste based on protocols and standards when possible. In this case, there aren't explicit quality criteria, but the compost cease to be waste after the Authority receives the registration form and the results from testing the waste along with the justifications for agricultural benefit and ecological improvement (for example, United Kingdom);

3. the end-of-waste occurs when the compost is registered as fertilizer. In this case, the compost can be used as soil improver or fertilizer in agriculture, but only after being registered under fertilizer legislations (for example, Italy, Greece, Spain).

Many States use similar or identical legislation for determining the status of digestate.

Objectives

The objective of this work is to highlight how difficult it is to "build" a common legal way for all European States to deal with waste that could be used as a resource. Proof of these difficulties is also the number (three) of technical reports drawn up by the Fertilizers Work Group.

Compost and digestate interest different markets, so some States can be interested in importing them, others in exporting them. It is also important to take into account the many economic, legal and cultural variables.

This work would like to illustrate problems and possible solutions.

Outline of the work

This work is divided in two main parts:

- The first part covers a legal framework regarding the biological treatment (compost and digestate) in the third technical report; the legal meaning of "End-of-Waste" criteria in the Directive 2008/98/CE; the main differences between the environmental legislations;
- The second part covers in particular the topic of end-of-waste criteria in the "Third technical report for end of waste criteria on biodegradable waste subject to biological treatment" drawn up by the Fertilizers Work Group.

Methods

The third technical report does not consider by-products. The main treatment operations are the following: landfill, incineration and other thermal treatments, mechanical biological treatment, composting, anaerobic digestion.

- *Landfill*: the Landfill Directive introduces strict requirements to prevent and reduce negative impact to the environment. The Directive classifies the waste into different categories and requires the treatment of waste before it is sent to landfill. Moreover, the Directive requires the reduction of biodegradable waste in landfill: 75% by 2006; 50% by 2009; 35% by 2016.
- *Incineration and other thermal treatments*: the combustion of waste is common use, especially to produce energy. Before combusting the waste, many countries collect the biodegradable waste. In many cases there's a pre-treatment, especially if the waste is wet or if it is particularly heterogeneous.
  The Waste Incineration Directive (Council Directive, 2000) aims to reduce the air pollution caused by the incineration and co-incineration of waste. This Directive has been merged into the Industrial Emissions Directive and it will be repealed in 2014.
- *Mechanical biological treatment*: with this treatment the waste is separated through mechanical operations, which separate the biodegradable waste from the mixed waste and the remainder is sent to a landfill site or incinerated. The biodegradable fraction can be stabilized through another treatment called "Mixed Waste Composting".
- *Composting*: this treatment consists in the aerobic degradation of waste in order to produce compost (especially from kitchen waste, garden and park waste). The compost is mainly used as soil improvers.
  The problems with "MSW compost" consist in the possibility of contamination by the presence of heavy metals, organic pollutants, glass or plastic. Compost can also be produced from bark, manure and sewage sludge. In general, composting is a widespread practice in many parts of Europe.
- *Anaerobic digestion*: this type of treatment is used to produce mainly biogas. The anaerobic digestion process occurs is in absence of oxygen.
  Carbohydrates, lipids, proteins are essential to obtain a methane-rich biogas. The process of anaerobic digestion produces digestate, which may be used as a fertilizer.
  Digestate can be separated in solid and liquid parts. The solid fraction can be used as compost. Anaerobic digestion is applied to the biodegradable fraction of MSW, agricultural waste, food industry waste and sewage sludge.

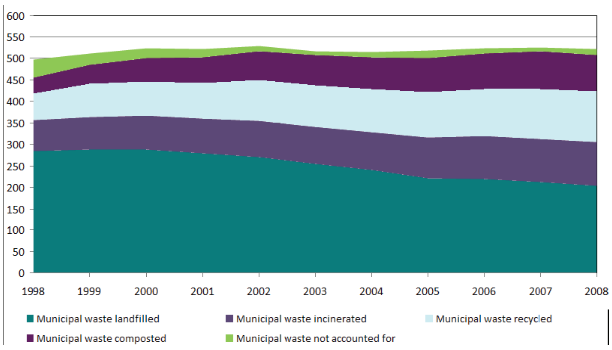

Fig. 1. Amounts of waste produced according to treatment options (in kg/capita) in the EU-27

Results and discussion

The Third Technical Report establishes the end-of-waste criteria for compost and digestate. The study follows the JRC methodology guidelines. The end-of-waste criteria are the following:

1. Product quality requirements: minimum organic matter content, no content of pathogens to an extent that poses health risks, limited content of viable weeds and plant propagules, limited content of macroscopic impurities, limited content of heavy metals and persistent organic compounds.

This criterion aspires to obtain high quality compost/digestate. Also, the content of minimum organic matter of the final product allows us to avoid the dilution of compost/digestate with mineral components;

2. Requirements on product testing for compost and digestate: a minimum sampling frequency guarantees the quality of the products across Europe and the control of the end-product. The cost for the test is necessary to avoid environmental pollution.

The testing methods are supported by EU-wide harmonized standards CEN (European Committee for Standardization). The report takes into consideration the possibility of external independent sampling;

3. Requirements on input materials: this very important criterion was established after choosing a “positive list” approach over a “negative list” approach. The latter would have put limits only on materials dangerous for the environment, health or quality of the product. The “positive list” approach is more detailed and is preferred because of fewer risks, it ensures origin and it defines “positive list” of input materials for compost and digestate. The annex 9 of this technical report provides a positive list of biodegradable waste for compost and digestate.

4. Requirements on treatment processes and techniques: it is necessary shared standards are necessary to treat waste in order to guarantee the quality of the product. The treatment operations and techniques for compost and digestate include three time-temperature profiles for the input materials of “positive list”.

By-products must be separated in order to avoid cross-contamination. Finally, physical contact must be excluded between input materials and final products.

5. Requirements on the prevision of information: it is a complementary element in respect to end-of-waste criteria and it aims to demonstrate that compost and digestate are an adequate alternative to primary raw-materials. These requirements are different for compost and digestate.

When compost is placed in the market a declaration of specific parameters is necessary: the soil improving or fertilizing function, the biological and general material properties. In the case of digestate there are similar specific parameters, with some differences: usefulness concerning fertilizing function, general material properties.

6. Requirements on quality assurance procedures (quality management): quality management system for compost and digestate include the acceptance control of input materials based on the “positive list”, the monitoring of processes and the product quality, the periodic surveillance of the analyses including the inspection of records and plants documentation, the declaration of characteristics and requirement by the competent authority and the conformity to national regulations, training of staff.

Compost and digestate cease to be a waste when all the end-of-waste criteria are fulfilled. If only one of these criteria is not fulfilled, compost and digestate remain under waste regulations. The product that respects all the criteria can be stored and traded freely in the market.

“The European Compost Network objects strongly to the recent proposal by the JRC-IPTS to allow at first instance mixed MSW to be permitted feedstock for manufacturing EoW compost and digestate that will “enable their circulation on the internal market and to allow using them without further monitoring and control on the soils on which they are used”.

ECN objects that mixed MSW, by definition, do not rely upon separate collection schemes (ECN, 2012).

“The Italian Composting Association agrees to exclude mixed MSW from the positive list as input material.

In general, both Associations are hesitant about using sewage sludge in composting and anaerobic digestion: they believe that sewage sludge should be allowed in composting as input materials only under specific limitations and restrictions” (CIC, 2012; WRAP, 2002).

Concluding remarks

Inclosing, the study of end-of-waste criteria in the third report leads us to conclude that what seems to be missing is true coherence among the criteria themselves on one hand, and between the criteria and the aim of article 6 on the other hand. This would guarantee a homogenization of national legislations which would ensure more efficiency.

Keywords: compost, digestate, sewage sludge

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POLYMERS MODIFIED CLAYS FOR SEPARATING RARE EARTHS FROM WEEE

Extended abstract

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Background

Today there is an increasing need for Rare Earths (REs) due to their usage in numerous high-technology applications. Each of these applications requires specific RE elements and they are not all interchangeable. Increasing demand for the different products containing REs has resulted in a restriction of supply from producing Countries, particularly China, which currently produces 97% of the world's REs. This constriction of supply is being met by the development of many new REs mining projects which are characterized, however, by technical, economic and environmental problems (Binnemans et al., 2013).

Currently each EU citizen produces about 17 kg of Waste Electric and Electronic Equipment (WEEE) per year. According to European Union estimates, this value is expected to rise to 24 kg by 2020. These wastes are rich in precious and strategic metals and, in many cases, are characterized by higher REs contents than those of natural minerals. Accordingly, recycling can be considered a valuable opportunity. This perspective, known as "urban mining," bases on the development of "Best Practices" for collection, transportation, recycling and recovery of precious metals and REs from WEEE, so as to transform the waste into an economic value product and, at the same time, so as to minimize the environmental impact. This approach can reduce the supply risk of such raw materials, strategic for a lot of important manufacturing industries and it can provide to small and medium enterprises the possibility of low time and relatively low cost of reconversion. For these reasons, the study of a targeted and efficient REs recovery from WEEE can only lead to undeniable both socio-economic and environmental benefits (Iannicelli Zubiani et al., 2012).

Recycling of WEEE and recovering of metals can be divided into three steps: disassembly, upgrading and refining. In this last step, recovered metals are melted or dissolved by using pyrometallurgical, hydrometallurgical or biometallurgical processing.

In the field of hydrometallurgy, several separation technologies have been extensively adapted for the recovery of metal ions from aqueous solution. Among them, Solid-Phase Extraction (SPE) presents some advantages: high recovery, short extraction time, high enrichment factor, low cost and low consumption of organic solvents (Li et al., 2011). In particular, clays as solid-phase are characterized by some outstanding advantages, such as low cost, high mechanical intensity, good acid tolerance, convenient solid-liquid separation and excellent reusability.

Objectives

The aim of this work was to study the possibility of REs recovery from WEEE by using selective chelating agents immobilized on clays. During the research activity two natural smectite clays (STx-1 and SWy-2) were modified by intercalating two different polymers: a poly-carboxylic poly-ether polymer and a phosphonate poly-carboxylic poly-ether polymer both having chelating properties. Then the modified clays were contacted with

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aqueous solutions of Lanthanum (chosen as representing element of REs family). Analyzing the Lanthanum content in the liquid phase it was possible to deduce the Lanthanum adsorbed and/or chelated by the modified clays. Time was varied to get the effects on the system.

Outline of the work

This work is divided in three main parts:

- The first part covers the experimental intercalations of two different polymers in two different clays (Iannicelli Zubiani et al., 2013). The quantification of the amount of intercalated polymers was evaluated by Chemical Oxygen Demand (COD) analyses and by Thermogravimetric Analyses (TGA).
- The second part covers the contact experiments of the synthesized organo-clays with a Lanthanum solution at different contact times. Analyzing by ICP-OES the Lanthanum content in the liquid phase (C_w) it was possible to deduce the Lanthanum extracted by the modified clays (C_s).
- The third part covers the release tests in order to verify not only the capture but also the possibility to return the Lanthanum ions.

Methods

The clays used were standard STx-1b and SWy-2 supplied by the Clay Mineral Society. They are respectively a Ca-montmorillonite and a Na-rich montmorillonite

The polymers, supplied by Bozzetto Group, were a poly-carboxylic poly-ether polymer (POL1 in the following) and a phosphonate poly-carboxylic poly-ether polymer (POL2 in the following), whose general formulas are reported in Fig. 1.

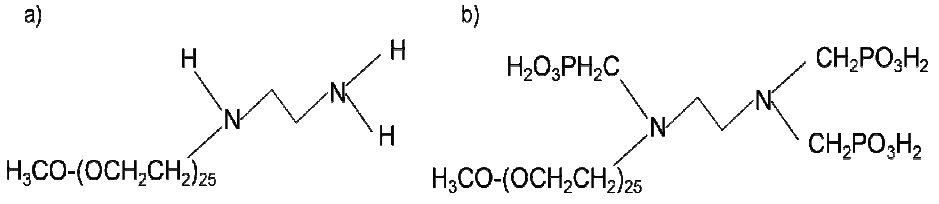

Fig. 1. Poly-carboxylic poly-ether polymer (a) and phosphonate poly-carboxylic poly-ether polymer (b) chemical formulas

Other reactants were Lanthanum(III) nitrate hexahydrate, nitric acid ACS reagent and sodium hydroxide ACS reagent by Sigma-Aldrich.

Deionised water was used throughout the whole study.

X-ray diffraction (XRD) measurements were carried out on powder samples with a Bruker D8 Advance diffractometer (graphite monochromator, using Cu-Kα radiation, step scan of 0.02°, 1 s per step). The XRD line profile analysis was performed with TOPAS P software (Bruker AXS, Karlsruhe, Germany) using a split PseudoVoigt profile function, XRD intensities were corrected for background, geometrical and Lorentz polarization factors. The refined profiles were used for the determination of reflection positions.

Thermal analyses measurements were performed with a DTA-TG SEIKO 6300 thermal analyzer for all the samples. The experiments were carried out under two different conditions: flowing of nitrogen and flowing of air. The maximum heating rate of 10 °C/min was in the temperature range of 25–1000 °C.

FT-IR spectra were recorded with a Jasco mod. 615 spectrometer at 8 cm^{-1} resolution. Organo-clay spectra were recorded employing KBr pressed disc technique.

The COD analyses were carried out using a Spectrodirect Lovibond instrument. In a standard instrumental procedure the unknown sample was oxidized by heating for 120 min at 150 °C [ASTM D1252-06].

The metal-ion concentrations were measured by an Optima 2000DV inductively plasma optical emission spectrometer (Perkin Elmer).

The intercalation experiments followed a standard procedure (Zampori et al., 2010a, 2010b). They were carried out at 30 °C. Temperature was set and controlled with a thermostat and a cooling coil was used to prevent evaporation.

Samples prepared with POL1 had an initial polymer concentration in aqueous solution (C_{P0}) of 35 mmol/L, corresponding to a polymer (g)/clay (g) ratio of 4.3; samples modified with POL2 had a C_{P0} of 30 mmol/L and a polymer/clay ratio of 5.3.

In a typical experiment a weighed amount of clay (STx or SWy) was contacted, in a jacketed reactor under vigorous stirring, with a known volume of polymer solution for a fixed time of 90 min. The pH of the solutions was measured before and after dispersing the montmorillonite and it was constant throughout the preparation at about pH 11 for POL1 and about pH 1 for POL2, respectively.

After the contact experiment, the solid phase was separated by the liquid one using a HETTICH 32 RotoFix Centrifuge.

The solid, upon drying for one day at room temperature, was analyzed by XRD, TG and FT-IR, while COD analysis was performed on the liquid in order to calculate the amount of polymer intercalated (C_{Ps}) by difference.

The synthesized modified clays (STx+POL1, STx+POL2, SWy+POL1, SWy+POL2) were contacted with an aqueous solution of Lanthanum at known concentration (C_0 = 3440 mg/L), vigorously stirred at room temperature and separated from liquid using a HETTICH 32 RotoFix Centrifuge. The contact experiments were carried out at five different contact times, 10 min, 30 min, 1.30 h, 6 h and 24 h. Analyzing by ICP-OES the Lanthanum content in the liquid phase (C_w) it was possible to deduce the Lanthanum extracted by the modified clays (C_s).

Results and discussion

XRD and FT-IR analyses, here not reported, confirmed the polymers intercalation in both the clays (Iannicelli Zubiani et al., 2013).

The quantification of the amount of POL1 and POL2 intercalated was performed by analyzing the residual solutions by COD. Two reactions (Eq. 1 refers to POL1 and Eq. 2 to POL2) have to be considered for the quantification of intercalated polymers (C_{Ps}), starting from COD expressed in g/L of O_2:

$$53C + 80.5\ O_2 \rightarrow 53\ CO_2 + 55\ H_2O \qquad (1)$$

$$56C + 85.75\ O_2 \rightarrow 56\ CO_2 + 59.5\ H_2O \qquad (2)$$

The percentage of intercalated polymer is in the range of 22-29% of the initial C_{P0} for all the organo-clays synthesized. The two polymers are in fact characterized by the same organic chain and these data confirm that the mechanism of intercalation was likely to be the same.

A quantification of the amount of polymer intercalated was performed also on the solid phase by TG.

The weight losses between 300 and 400 °C can be attributed to the intercalated polymer and resulted to be in the range of 17-25 wt.% of the total mass, slightly underestimating the COD values probably due to the not complete combustion of the polymers in the clay interlayers (Zampori et al., 2010a).

The extraction experiments were carried out at five different contact times (10 min, 30 min, 1.30 h, 6 h and 24 h) and Fig. 2 shows the levels of Lanthanum uptake, reported in mg/g and calculated according to Eq. 3, where V is the volume of the Lanthanum solution and W the weight of the solid organo-clay.

$$\text{Lanthanum uptake} = ((C_0 - C_w)*V)/W \qquad (3)$$

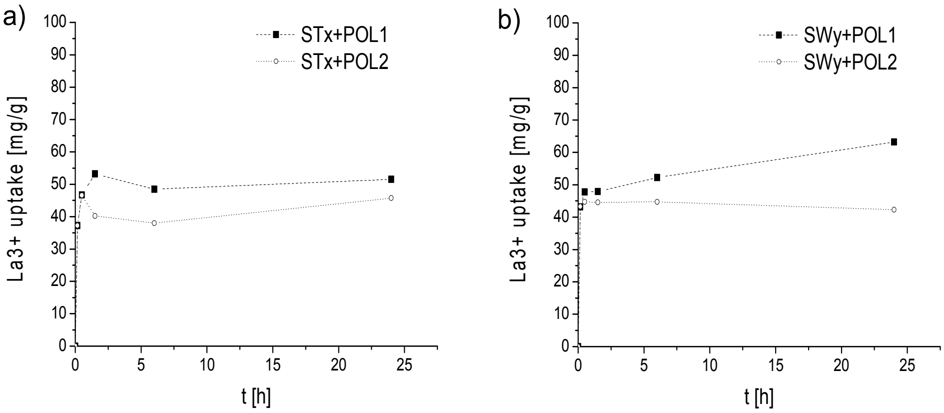

Fig. 2. Lanthanum extraction of the different organo-clays at different time

Fig. 2 shows that the La adsorption is not quantitatively affected by contact time, thus very fast.

Accordingly, the adsorption contact time was fixed at 1.30 h, slow enough to be sure of the equilibration between solid and solution and fast enough to avoid La extraction at this step.

Finally release tests were performed on the different samples in order to verify the organo-clay capability not only to capture, but also to return metal ions.

The release conditions were: 1.30 h of contact time with solutions at pH 1, room temperature and agitation at 500 rpm.

In Table 1 the main results are summarized. $C_{w'}$ and $C_{s'}$ refer to the Lanthanum concentrations respectively released and restrained by the different organo-clays.

Table 1. Lanthanum concentrations at the different phases of the process for the different organo-clays synthesized (C_0 is the initial concentration; C_w and C_s are the concentrations after contacting with the organo-clays, respectively in the liquid and in the solid phase; $C_{w'}$ and $C_{s'}$ are the concentrations after release, respectively in the liquid and in the solid phase)

Organo-clay	***C_0 [mg/L]***	***C_w[mg/L]***	***C_s[%]***	***$C_{w'}$[%]***	***$C_{s'}$[%]***
STx+POL1	3440	1312	61.9	52.1	47.9
STx+POL2	3440	1830	48.8	52.6	47.4
SWy+POL1	3440	1525	55.7	49.4	50.6
SWy+POL2	3440	1658	51.8	47.5	52.5

It is evident that all the organo-clays can adsorb about 50-60% of La^{3+} ions present in the contacting solution (see C_s [%]). About the 50% of C_s is then released after the contact with the solution at pH 1 ($C_{w'}$ [%]) while the other 50% is in the solid phase ($C_{s'}$ [%]), suggesting the possibility to operate additional release tests. Anyway, further studies are needed for the comprehension and the optimization of the process

Concluding remarks

The main following conclusions can be drawn:

- The experimental procedure is appropriate to intercalate both polymers in both clays.
- Contact time doesn't seem to affect La adsorption, thus very fast.
- The obtained organo-clays are effective in both adsorption and release processes.

Keywords: Polymers modified clays, Rare Earths, recovery, WEEE

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RECYCLED PLASTIC FROM AHP (Absorbent Hygiene Products)

Extended abstract

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Background

Today, the post-consumer Absorbent Hygiene Products (AHP) waste represents about 2% of Municipal Solid Waste (MSW) and about 0.15% of total waste (EDANA, 2012). Currently, AHP waste is not recycled and belongs to "non-recyclable" municipal waste collection. It is typically disposed of via either land filling or incineration, thus causing loss of valuable material resources and high economic, environmental and societal costs. As the EU sensibly moves towards its recycling targets, AHP waste has quickly risen to represent already up to 15-25% of the residual waste.

As a consequence, consumers and stakeholders alike perceive AHP waste management as a growing sustainability issue that needs to be addressed in an integrated way. Public authorities are aware of this issue but due to the lack of large scale recovery technologies for such disposables, they remain unable to take actions to support the recycling of this waste stream.

Fater S.p.a., has developed a novel technical method for the recovery of AHP waste. The first application on the market of this method is co-funded by EU by the CIP Eco Innovation Project RECALL "Recycling of **C**omplex **A**HP waste through a first time application of patented treatment process and demonstration of sustainable business model**"**.

Objectives

The aim of this study is to demonstrate the potential of the plastic recovered by RECALL process for valuable products manufacturing.

The analysis to assess such potentialities was carried out by CETMA. In particular here will be reported the properties of AHP recycled plastics, the identified methods for the improvement of such properties, the investigation of suitable plastic transformation processes.

The plastics are one of the raw material fraction coming from the novel technology developed by Fater S.p.a. to recover post-consumer AHP waste. This technology is based on autoclave process and therefore it allows to get sterilized, high quality plastics (PRF), in form of film and fibrous pieces, re-usable into valuable products.

The learning plan is outlined as follow:

- thermal properties have been analyzed directly on the plastic coming from the autoclave process, aiming at the evaluation of possible differences with the virgin plastics and with recycled plastics coming from most common waste recovery processes.
- physical properties were evaluated on plastics samples properly compounded by a double screw extruder.
- mechanical properties were measured on samples manufactured by injection molding process

Tests results showed that the recovery process developed by Fater permits to obtain a new typology of recycled plastic material consisting of polyolefin blends having a high purity level. The blend contains polypropylene and high density polyethylene and cellulose residues and has superior properties than the typical heterogeneous regenerated plastic coming from the recovery of the urban waste.

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The thermal analysis evidenced that sorting and sterilization processes do not cause chemical degradation of the plastic portion.

The Melt Flow Index values confirmed that the blend is suitable for a range of typical plastic molding processes.

A feasibility study confirmed the possibility to use the PRF for injection and rotational molding. Several prototypes were produced with different transforming processes

Additional analysis were carried out in order to evaluate the influence of cellulosic residues on PRF properties and to improve mechanical properties of the material, by the addition of suitable fillers.

Outline of the work

This study had the following main scopes:

- rheological, mechanical and calorimetric analysis of PRF
- improvement of PRF properties by specific additives
- technical feasibility by usual process polymer technology.

Methods

PRF coming from RECALL process is a blend of polypropylene (PP), polyethylene (PE), cellulose and traces of polyethylene terephthalate (PET) from different zones of the original nappy.

Calorimetric analysis was carried out on PRF using DSC - TA Instruments Test Machine Q200 according to ASTM D3418 in order to confirm the constituent materials. The sample was heated at 10°C/min from 50°C to 320°C. Results of calorimetric scanning are reported.

The melting temperatures evaluated by DSC analysis confirm the composition of PRF. In particular the melting peaks observed at 123°C, 160°C and 216°C can be referred respectively to PE, PP and PET while the endothermic signal at 360°C can be attributed to cellulose degradation (Yang et al., 2007).

A Physical, rheological and mechanical characterization was performed on PRF. A comparison with commercial recycled blends in terms of mechanical properties was carried out.

The PRF melt flow was measured according to ASTM D 1238 at 230°C and 2.16kg load by Atsfaar MELT index equipment. Steady rheological measurement on PRF was carried out using a Rheological Stresstech Rheometer. Tensile characterization was performed by MTS dynamometer equipped with a load cell of 2kN and an extensometer G.L. 25-634 according to ISO 527-1/2.

PRF properties were improved by melt blending with some specific additives using twin screw system HAAKE POLYLAB RheoDrive 7. In particular:

- a compatibilizer PP55EX maleic anhydride based provided by AuserPolimeri srl
- a stabilizer SILMASTAB AX 1854 by Silma srl
- a mineral charge, OMYALENE 102M, $CaCO_3$ based by Omya Spa

Ageing tests were carried out by using the QUV Accelerated Weathering Tester according to method A of ASTM D4329 on samples of stabilized and unstabilized PRF.

Finally PRF granules were processed by:

- injection moulding
- rotational moulding
- calendering.

Results and discussion

Melt flow index (MFI) is useful for comparing different grades and average molecular weights for the same polymer type. Suitability of a particular grade for a specific processing method can often be stated in terms of the range of proper melt index values.

The ranges of melt index values suitable in each process technologies of thermoplastic polymer matrix are compared to the melt flow of PRF (Fig.1). PRF melt flow index is equal to 7.6±0.3 (g/10') according to the value required by injection moulding, rotomoulding and film extrusion processes.

However, the MFI value of a polymer matrix can be modified through blending or chemical additives to extend the process ability range of the polymer to different technologies.

The evolution of viscosity as a function of shear rate at three different temperatures (205°C, 195°C, 185°C) was obtained. At each temperature, the PRF shows a shear thinning behavior: viscosity decreases with increasing shear rate. Moreover, viscosity decreases with increasing temperature; for these reasons, it can be concluded that the normal pseudo plastic behavior expected for a polyolefin blend is not affected by cellulose content in the PRF.

Tensile test was used to determine the average values of the maximum stress measured equal to 15.9±0.6 MPa and the average value of Young Modulus equal to 1076.3±8.6 MPa. The low standard deviation of mechanical data indicates the repeatability of the properties.

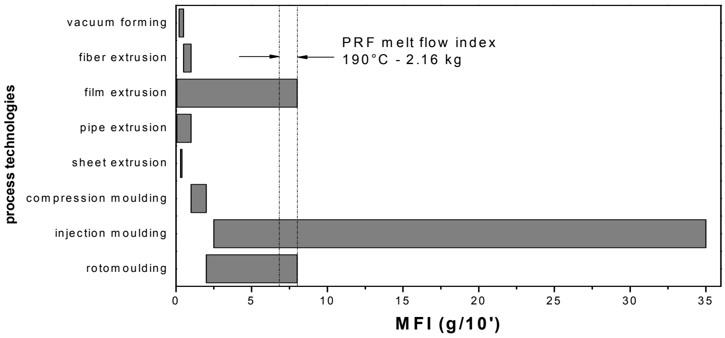

Fig.1. Comparison of PRF melt flow index with ideal range values for specific process technologies

The mechanical properties indicate the PRF can be suitable to replace the traditional polyolefin at performance no cost. Comparison of the Young Modulus between PRF and the recycled/virgin polyolefins is reported in Fig.2.

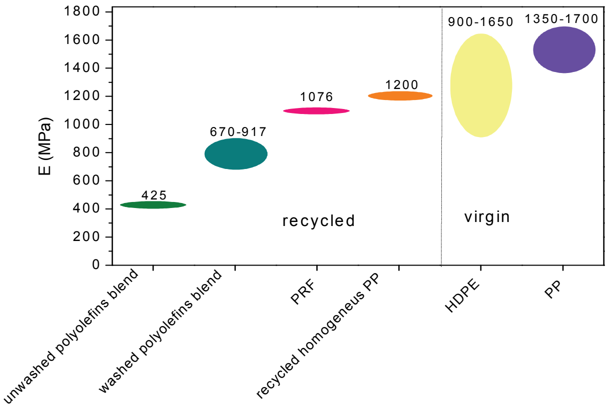

Fig.2. Comparison between the Elastic modulus of PRF and recycled/virgin polyolefins

PRF's Young modulus is comparable with that of some virgin homogenous polyolefins.

Specific additives, as reported previously in the materials description, were blended to PRF in order to improve some properties in spite of the material heterogeneity.

The elastic modulus was enhanced by 40% introducing Omyalene 25% $_w$. Addition of rigid particles to a polymer matrix improves the modulus since the rigidity of inorganic fillers is much higher than that of organic polymers (Sheles-Nezhad et al., 2013).

The UV resistance was raised by introducing Silmastab 3%. The chemical and physical changes induced by UV exposure were tracked by monitoring the changes in mechanical properties. Many studies indicate the elongation at break as direct indicator of degradation (Roy et al., 2007). The elongation at break was reduced by only 30% with respect to 50% for the unstabilized sample after 2 ageing cycles (24 h). Polymers, especially containing cellulose, are predominantly chain-scissioning polymers, and UV irradiation decreases the molecular weight. This is accompanied by the formation of oxidation products and reduction in crystallinity that explains the achieved results.

The immiscible polymer blends (PP, PE and cellulose) were melted and added with PP55EX 6% $_w$ to obtain a material having, at the same time, a stable morphology and improved performance under service conditions. The benefit of compatibilizer was detected by the toughness improvement of 60%, from 1.8 MJ/m^3 to 2.9 MJ/m^3, thanks to the improved interfacial adhesion between PP, PE and cellulose phases. As further proof, the melt flow index was reduced by 43%.The reduced fluidity is due to the increased average space occupied by polymer chains.

The possibility to transform PRF with conventional processing methods like extrusion, injection and rotational moulding and calendaring was explored via a feasibility study.

In Table 1, an evaluation of the technological feasibility of PRF is reported. The extrusion process is affected by some problems at the feeding step due to the morphology of the milled PRF. The process could be improved by two different approaches: an improved milling of PRF before the feeding stage or by designing a specific feeder to deal with the PRF morphology. During rotomoulding laboratory test, a pinholes issue was observed. There are several mechanisms that operate simultaneously to create bubbles and pinholes from the plastic melt during rotational moulding (Crawford et al., 2004).

Table 1. Feasibility evaluation of process technologies for PRF

Process	***PRF***
Extrusion	very good
Rotomoulding	good
Injection Moulding	excellent
Calendering	fairly good

It is difficult to isolate these due to the transient nature of the thermal processes that are taking place within the viscoelastic liquid. A hydrostatic pressure of 0.5bar for 60 seconds applied to the melt at the exit of the oven provided a physical mean to significantly reduce pinholes size and to accelerate the process.

The injection moulding process performed at conventional conditions used for the homogeneous polyolefins demonstrated the full suitability of PRF without any technical expedient.

Finally plastic sheets were successfully produced by calendering process reaching 300µ minimum thickness. The different rheological behavior of PP and PE part of the PRF would require a more complex calendering process to gain thickness lower than 300 µm. Indeed, the same temperature and stress applied during calendar process resulted in two different elongation deformations on the sheet, inducing tearing of the less deformable polymer.

Some prototypes were produced with the different process technologies. The following photos show some of these prototypes.

Concluding remarks

The performed characterization shows the PRF are comparable in terms of mechanical and rheological properties with some virgin homogeneous polyolefins.

The feasibility study indicates the possibility to process PRF's with conventional plastic moulding process technologies, including rotomoulding and calendering that usually are not viable for recycled plastic material.

Keywords: absorbent hygiene products, polyolefins, recovery method, recycled plastic, technical feasibility.

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NEW COMPOSITE PANELS WITH HEMP HURDS FOR SUSTAINABLE BUILDINGS

Extended abstract

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Background

The issue of developing new sustainable building materials, having a reduced impact on the environment, has become a very important task, as the building sector is responsible for huge natural resources consumption and waste production. For reducing the use of not renewable natural resources, several strategies have been investigated through the years, such as the use of recycled aggregates from construction and demolition waste to replace natural aggregates for structural concrete (Manzi et al., 2013) or the use of natural fibers from vegetable renewable resources to replace inorganic mineral fibers for thermal insulating composites (Korjenic et al., 2011; Motori et al., 2013).

In particular, the use of natural fibers (such as hemp, jute, flax, sisal, etc.) for producing thermal insulating composites offers several advantages, as natural fibers generally exhibit good thermal and acoustic insulating properties (thanks to their cellular structure), low density, good specific tensile properties, and, from the environmental point of view, they are characterized by renewability, recyclability and high carbon storage potential (Ku et al., 2011; Zach et al., 2013; Zampori et al., 2013).

The above mentioned characteristics, as well as the rapid growing and the high dry biomass production (Motori et al., 2013), have made hemp one of the most widely studied natural fibers for sustainable building materials. Indeed, hemp-based panels for building thermal insulation, produced by bonding hemp fibers and hurds with polyester, Portland cement or slaked lime, have been investigated (Balčiūnas et al., 2013; Zampori et al., 2013). So-obtained panels exhibited promising thermal-mechanical properties (Balčiūnas et al., 2013; Franzoni, 2011). Moreover, a reduced environmental impact of hemp-based panels, compared to traditional rock/glass wool panels, was assessed by Life Cycle Assessment (Zampori et al., 2013).

Objectives

In addition to the use of natural fibers and particles from plants, in place of inorganic mineral fibers, a further step towards obtaining composite materials with enhanced sustainability is using also binders with reduced environmental impact as composite matrix (La Mantia and Morreale, 2011). In the case of hemp-based composites for the building industry, hemp hurds are generally bonded with Portland cement, slaked lime or organic polymers (Balčiūnas et al., 2013; Zampori et al., 2013). In terms of environmental sustainability, these binders exhibit some limitations, as Portland cement and slaked lime require high firing temperature and petroleum-based polymers are produced from not renewable resources. To overcome such limitations, the use of alternative binders, such as starch, has been investigated (Balčiūnas et al., 2013).

In this study, the preliminary results of the physical-mechanical characterization of new hemp-based composites, obtained by using alternative binders with much reduced environmental impact, are reported. Four types of panels were produced for different applications: two panel types (P-1 and P-2), having relatively low density, were

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investigated as possible composites for building thermal insulation; for the other two types (P-3 and P-4), having relatively high density, the possible use in the building/furniture industry, as substitutes for high density formaldehyde-bonded wood particles boards, was investigated. In the latter case, in addition to the environmental benefit, a further benefit in terms of impact on human health is expected, as the new composites are free from toxic organic binders, such as formaldehyde, classified as "carcinogenic to humans", which can be emitted into the indoor environment by formaldehyde-containing building materials (Gunshera et al., 2013).

Materials

The panels were produced as described in the following and summarized in Table 1:

- panels P-1 were obtained by bonding coarse hemp hurds (about 3-6 mm in diameter and 10-30 mm in length) with an inorganic binder, consisting of a mineral oxide which reacts when a proper aqueous salt solution is added; a binder/hemp hurds ratio of 1:1 wt./wt. was used; the composites were produced by pressing the fresh mixture at room temperature for 20 minutes with a compression pressure of 5 MPa; the final panels had a nominal thickness t = 50 mm;
- panels P-2 were produced by bonding coarse hemp hurds (about 3-6 mm in diameter and 10-30 mm in length) with a new hybrid organic-inorganic binder, obtained by partly replacing the mineral oxide used for panels P-1 with a reactive organic fraction, coming from renewable vegetable resources (the new binder is currently under patent - Italian patent request MO2011A000244, filed on 26/09/2011); a binder/hemp hurds ratio of 1:1 wt./wt. was used; the composites were produced by pressing the fresh mixture at 80 °C for 3 minutes with a compression ratio of 1:3.3, after preliminary pre-heating at 80 °C in a micro-wave unit for 3 minutes; the final panels had a nominal thickness t = 50 mm;
- panels P-3 were obtained by bonding thin hemp hurds (about 3-4 mm in diameter and 10 mm in length) with an inorganic binder, consisting of a reactive hydraulic compound; a binder/hemp hurds ratio of 1:6 wt./wt. was used; the composites were produced by pressing the fresh mixture at room temperature for 20 minutes with a pressure of 5 MPa; the final panels had a nominal thickness t = 50 mm;
- panels P-4 were produced by bonding thin hemp hurds (about 1-2 mm in diameter and 2-5 mm in length) with the same hybrid organic-inorganic binder as P-4; a binder/hemp hurds ratio of 1:1.5 wt./wt. was used; the composites were produced by pressing the fresh mixture at 80 °C for 3 minutes with a compression ratio of 1:4, after preliminary pre-heating at 80 °C in a micro-wave unit for 3 minutes; the final panels had a nominal thickness t = 10 mm.

Methods

The panels were subjected to the following characterization:

- bulk density (ρ) [measured on the same panels used for mechanical tests];
- water absorption (WA), measured according to EN 13755 Standard on $5 \times 5 \times t$ cm^3 samples;
- thermal conductivity (λ), measured according to EN 12667 Standard on $50 \times 50 \times t$ cm^3 samples; λ was not determined for P-3 and P-4 panels, as their λ is expected to be relatively high because of their high density;
- compressive strength (σ_c) corresponding to a strain ε = 10%, measured according to EN 826 Standard on $5 \times 5 \times t$ cm^3 samples; σ_c was not determined for P-4 panels because, considering their thickness (t = 10 mm), the friction between the loading plates and the panel would make the test results scarcely reliable;
- flexural strength (σ_f), according to EN 12089 Standard on $26 \times 12 \times t$ cm^3 samples;
- microstructural features, by means of a stereo-optical microscope (SOM, Olympus SZX10).

Five measurements were performed for each physical and mechanical test.

Results and discussion

As reported in Table 1, P-1 and P-2 panels, designed as possible composites for building thermal insulation, have a bulk density of 620 and 640 kg/m^3, respectively. As can be observed in Fig. 1, they are characterized by a highly porous microstructure, which is responsible for a high water absorption (Table 1).

As a consequence of the low bulk density, as well as the cellular structure of hemp hurds, panels P-1 and P-2 exhibit relatively low values of thermal conductivity: λ = 0.087 W/mK for P-1 and λ = 0.138 W/mK. Such values are in good agreement with thermal conductivity values reported in the literature for composite materials from natural resources with a similar bulk density (e.g. wood wool boards and wood chip boards) (Domìnguez-Muñoz et al., 2010).

Even if thermal insulation provided by P-1 and P-2 results lower than that obtained by using traditional materials (e.g., glass and rock wool, expanded polystyrene, polyurethane foam) with lower density, P-1 and P-2 are characterized by higher mechanical properties. As shown in Fig. 2, compressive strength reached 1.9 MPa and 3.0 MPa for P-1 and P-2 panels, respectively. As a comparison, for a hemp hurds-Portland cement-based composite with a comparable bulk density (ρ = 519 kg/m^3) a compressive strength of 1.5 MPa was reported (Balčiūnas et al., 2013).

As for flexural strength, P-1 and P-2 reached 3.5 MPa and 6.8 MPa, respectively, also in this case exhibiting very promising mechanical properties.

Table 1. Mix design and physical properties of the panels

	Unit	***P-1***	***P-2***	***P-3***	***P-4***
Hemp hurds	**-**	coarse	coarse	thin	thin
Binder/hemp hurds ratio	**wt./wt.**	1:1	1:1	1:6	1:1.5
Bulk density (ρ)	**kg/m^3**	620	640	1260	1280
Water absorption (WA)	**wt.%**	69	54	39	13

If a comparison among properties of P-1 and P-2 is made, it can be observed that the partial substitution of the mineral oxide, used for bonding P-1, with the reactive vegetable fraction, used for bonding P-2, led not to a decrease in mechanical properties, but, on the contrary, an improvement was achieved (Fig. 2). In terms of environmental impact, the mineral oxide used for P-1 can be considered as an improvement with respect to Portland cement or slaked lime, as lower firing temperatures are needed for its production. Moreover, the reactive vegetable fraction used for P-2 represents a further significant improvement in terms of environmental sustainability, as this binder is obtained from renewable agricultural resources.

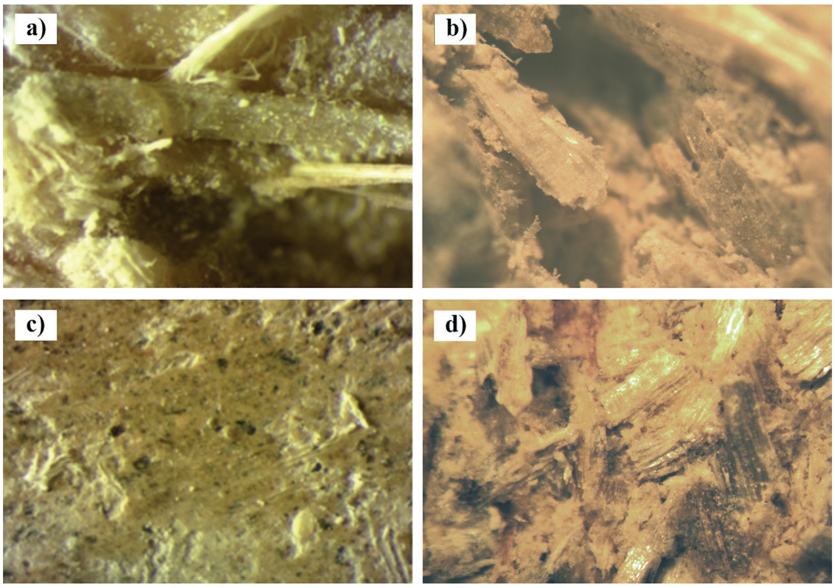

Fig. 1. Stereo-optical microscopy images of the panels (magnification 16x): (a) P-1, (b) P-2, (c) P-3 and (d) P-4

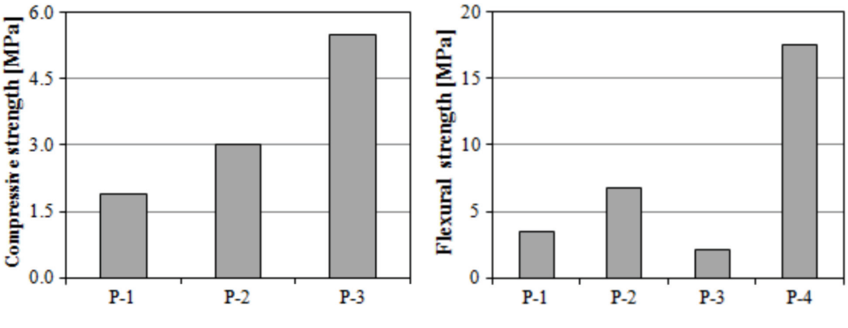

Fig. 2. Compressive and flexural strength of the panels

Also in the case of P-3 and P-4 panels, designed as possible substitutes for high density formaldehyde-bonded wood particle boards, promising results were obtained. The P-3 and P-4 panels exhibited a bulk density of 1260 kg/m^3 and 1280 kg/m^3, respectively, and a corresponding water absorption of 39 wt.% and 13 wt.% (Table 1). The densification in panel microstructure, with respect to P-1 and P-2, can be observed in Fig. 1, where a lower open porosity is present for panels P-3 and P-4. Correspondingly to the high density, very good mechanical properties were obtained, particularly in the case of P-4. The compressive strength of P-3 reached 5.5 MPa, a value sensibly higher than that of P-1 and P-2 panels (in the case of P-4, compressive strength was not measured, due to the low panel thickness). As for flexural strength, it reached 2.1 MPa for P-3 and 17.5 MPa for P-4 (Fig. 2). In the case of P-3, flexural strength results lower than that of panels P-1 and P-2, presumably because the coarse hemp hurds (used for P-1 and P-2) performed a more effective bridging action than thin hurds used for P-3, thus allowing a more effective hindering of crack propagation in the region subjected to tensile strength. Panel P-4 exhibited a definitely high flexural strength, which can be ascribed to the good adhesion between the binder and the hemp hurds, as noticed by SEM observation (not reported here).

Concluding remarks

The studied panels, obtained by bonding hemp hurds with different binders, characterized by a reduced environmental impact, exhibited very promising properties, both in the case of the low density panels, intended as composites for building thermal insulation, and high density panels, designed as possible substitutes for formaldehyde-bonded wood particle panels.

Further tests are in progress to evaluate additional physical-mechanical properties (such as tensile strength and resistance to withdrawal of screws), as well as reaction to fire and physical-mechanical durability.

Keywords: building materials, green materials, hemp, sustainability, thermal insulation

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RECYCLING WASTE FOR THE PRODUCTION OF SUSTAINABLE MORTARS FOR BRICK MASONRY

Extended abstract

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Background

For many years bedding mortars have been considered a secondary component in structural brick masonry walls and they were classified only on the base of their binder (see, e.g., the Italian law DM 20/11/1987 concerning the Regulation for designing, building, testing and strengthening masonry) rather than characterized for their actual mechanical performance. This approach has recently changed and joint mortars have gained higher and higher attention, as they substantially influence the final mechanical performance of masonry. At the same time, a growing awareness of the sustainability issue has been registered in the field of building materials (Bignozzi, 2011), given the extremely high environmental impact of the construction sector (Franzoni, 2011) and its expected increase due to the global population growth (estimated to pass from 6.5 billion in 2005 to about 9.0 billion in 2035 (Dixit and Fernandez-Solis, 2010)). In this scenario, mitigating the consumption of raw materials and energy the manufacturing of building materials is of paramount importance and recycling waste and by-products appears as a feasible route toward this goal.

Nevertheless, while recycling waste in concrete was widely investigated and has now entered the building practice, even if with some limitations and die-hard prejudices, the use of not hazardous waste and by-products for masonry (and in particular for mortar joints) is much less considered, despite the widespread presence of structural masonry and wall plug all over the word.

In this paper, different mortars with improved sustainability were prepared, partially or totally substituting the fine aggregate with recycled fractions (sand from grounding demolished concrete or end-use tyre rubber) or replacing the cement with a low-carbon binder (alkali-activated binder).

After a first characterization of the mortars in terms of strength and microstructure, some brick masonry triplets were built and characterized to assess their properties, with particular reference to their shear behaviour, in view of their possible use in masonry buildings in seismic zones of the world.

Methods

A reference mortar (*REF*) was prepared with cement CEM II/A-LL 42.5R (EN 197) and standard quartz sand (EN 196-1), according of the same proportions of the EN 196-1 standard mortar (450 g cement, 1350 g sand) and adjusting the amount of water in order to obtain a mortar diameter at the flow table test (EN 1015-3) equal to 18±1 cm (water 250 g). This flow was considered representative of the workability of a typical mortar for brick masonry construction.

Mortars with improved sustainability were prepared according to the following formulations, respect to REF:

- mortars with a partial (25%) or total substitution of the natural quartz sand with recycled sand, obtained by grinding the concrete coming from the demolition of the well known unauthorised structures in Punta Perotti, Italy

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(Manzi et al., 2013). The grain size distribution of the recycled sand was selected in order to reproduce the distribution of the natural one. These mortars were labelled as *DEM25%* and *DEM100%* respectively;

- mortars with a partial substitution (25 v/v% and 50 v/v%) of the natural sand with ground end-use tyre rubber (*RUB25%* and *RUB50%*). Exploring new routes for tyre rubber recycling is of great environmental relevance after to the European Directive 99/31/EC banned the disposal of this kind of waste (Ferretti and Bignozzi, 2012). Also in this case the grain size distribution of the recycled aggregate was selected in order to reproduce the distribution of natural sand;
- mortar where cement was totally substituted with an alkali-activated binder (*AAB*). Such binder was obtained from 300 g ladle slag from steel production, 200 g metakaolin and 300 g aqueous solution of NaOH 8M and sodium silicate (weight ratio 1:1).

In all the mortars the amount of water was adjusted in order to achieve the same workability obtained for REF. The resulting water amounts were 283 g for DEM25%, 455 g for DEM100%, 300 g for RUB25%, 330 g for RUB50% and 100 g for GEO.

For each mortar, 3 prisms 4×4×16 cm^3 were prepared in a Hobart mixer, according to the procedure in EN 196-1, demoulded after 1 day and then cured at 20±2 °C and relative humidity >90% up to 28 days.

Then masonry triplets were built using three full bricks (RDB, Italy), having size 5.5×12×25 cm^3 and mean compressive strength 36 MPa. Mortars of 1 cm thickness were placed between the bricks, previously water saturated. Curing at room conditions (T = 20±2 °C and RH = 45±5%) for 28 days followed. Before the tests, the triplets were left to further dry at room conditions for 1 more week.

Compressive strength test was carried out on the mortar prisms at 28 days according to the procedure in EN 196-1. Microstructural characterization was performed by mercury intrusion porosimetry (Porosimeter 2000 Series Carlo Erba and Fisons Macropore Unit 120). Given the presence of a low elastic modulus and compressible fraction (tyre rubber) in the mortars RUB25% and RUB50%, the porosimetry was not carried out on the relevant samples and the main physical-mechanical parameters (bulk density and open porosity) were obtained by water absorption test and hydrostatic weighing of the water saturated mortar samples.

The masonry triplets were tested for shear strength in an Amsler Wolpert Machine (100 KN), under constant strain rate 1 mm/min (Amsler Wolpert Machine, 100 KN), with no lateral constraint (Gentilini et al., 2012), according to the scheme in Fig. 1 (left). The shear strength values obtained are the average of three samples.

The compressive strength test was performed in a Metro Com machine (400 t, 4 MPa/s), after capping the samples with a cement-based grout, according to the scheme in Fig. 1 (right). The compressive strength is the average of three samples.

Fig. 1. Scheme of the shear and compressive test and a triplet during the testing

Results and discussion

The results obtained on the mortar samples are reported in Table 1.

Substituting quartz sand with recycled sand from demolished concrete can lead to a decrease in the compressive strength of the mortar respect to REF, due to an increase in the total open porosity of the material. This is due to the intrinsic porosity of the recycled aggregate, which contains not only crushed aggregates but also cement paste. The higher porosity of the recycled sand also involves a significant increase in water demand for achieving the same workability than the reference mortar (283 g and 455 g for DEM25% and DEM100% respectively, against 250 g for REF).

Conversely, the use of ground tyre rubber (RUB25% and RUB50%) involves a slight porosity decrease respect to the reference sample, as the water absorption of the rubber is essentially zero, and a drastic decrease in compressive strength. However, given the low density of tyre rubber, the bulk density of the relevant mortar is very low. In terms of water demand at the fresh state, the mortar with recycled tyre rubber requires more water than REF, probably due to the angular shape of the rubber particles which hinders the fresh mortar flowability. The mortar with alkali-activated binder exhibits a slightly higher porosity and a lower compressive strength than REF.

In Table 1 the results obtained on the masonry triplets are summarized, comparing the shear and compressive strength and the shear modulus of the recycled mortars with those of the reference one.

In terms of compressive strength (Fig. 2), the decrease experienced by the triplets with the recycled mortars is less pronounced respect to the decrease experienced by the mortars alone, due to the confinement exerted by the bricks on the mortar layers. For example, substituting a 25% of the sand with recycled sand from concrete demolition (DEM25% in Table 1) leads to a masonry compressive strength substantially identical to REF. Also in the case of AAB, the reduction of compressive strength in the masonry triplet is much more limited than in the mortar prisms.

Conversely, a 25% substitution of sand with sand from concrete demolition almost redoubles the shear strength of the triplets respect to REF and does not substantially alters the shear modulus, probably due to the angular shape of the recycled sand, which opposes the shear sliding. However, when the sand is fully substituted with recycled one, the effect of the porosity increase prevails and the shear strength slightly decreases, but in any case marginally respect than in the case of mortars alone. In any case, the partial substitution of sand with tyre rubber causes a significant loss of shear strength and modulus (Table 1), although a possible contribute to the energy dissipation during earthquake is still to be investigated. In the case of the alkali-activated binder, the decrease of shear performance is considerable.

Table 1. Samples properties (σ_c= mean compressive strength, OP=open porosity, ρ = bulk density, σ_s= mean shear strength, $\Delta\sigma_c$= variation of compressive strength compared to REF, $\Delta\sigma_s$= variation of shear strength compared to REF, ΔG= variation of shear modulus compared to REF)

Sample	***Mortars***			***Masonry triplets***				
	σ_c (MPa)	***OP (%)***	***ρ (g/cm^3)***	***σ_c (MPa)***	***$\Delta\sigma_c$ (%)***	***σ_s (MPa)***	***$\Delta\sigma_s$ (%)***	***ΔG (%)***
REF	47.5	18.0	2.04	40.7	-	0.8	-	-
DEM25%	39.8	22.0	1.92	39.2	-4	1.5	+80	+5
DEM100%	22.2	35.4	1.64	28.6	-30	0.7	-16	+3
RUB25%	14.2	17.4	1.70	25.6	-37	0.6	-30	-20
RUB50%	3.5	14.7	1.35	18.4	-55	0.3	-66	-53
AAB	32.2	21.2	2.06	35.4	-13	0.3	-66	-44

Fig. 2. A triplet after the compressive strength test

Concluding remarks

Sustainable mortars containing different recycled fractions in place of sand or binder were formulated, prepared and characterized, and their properties compared with those of a reference cement-based mortar.

Then, the compressive and shear performance of brick masonry models manufactured with these mortars was investigated.

The results obtained for the brick triplets showed that the substitution of a 25% of natural quartz sand with a recycled sand from concrete demolishing involves almost an identical compressive strength and a strong benefit in terms of shear strength (+80%), leaving substantially unaltered the shear modulus. This increase is of great relevance when masonry is subjected to seismic actions.

For a 100% substitution, however, the beneficial effect of the angular aggregate shape is counterbalanced by its higher porosity respect to the natural sand, hence a slight decrease in the shear strength (-16%) and a marked decrease in compressive strength (-30%) are found.

The use of recycled sand also involves a higher water demand for achieving a suitable fresh state workability. The use of tyre rubber as a replacement for sand has a beneficial effect in terms of mortar bulk density, but it leads to a performance downfall, although its possible contribution to energy dissipation in dynamic conditions is currently under investigation. The alkali-activated binder involves a moderate decrease in compressive strength of the triplets (-13%), but a relevant worsening of their shear behaviour.

Hence a reduction of AAG mortar porosity, by an improvement of the formulation of the precursors, seems necessary for improving the mortar properties and it is presently under investigation.

Keywords: alkali-activated materials, C&D waste, end use tyres, shear behaviour, sustainability

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INERTIZATION OF CHROMIUM LIQUID WASTE IN INORGANIC POLYMERS VIA ALKALI ACTIVATION OF METAKAOLIN

Extended abstract

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Background

Inorganic polymers are obtained by chemical reaction of an aluminosilicate source with Na-silicate as binder under highly alkaline conditions. Different alkaline solutions based on alkali metal hydroxides, carbonates and silicates have been used in the last years. Among these solutions, sodium silicate has been extensively used in the activation of many kinds of aluminosilicate precursors such as metakaolin, fly ash, incinerator bottom ash, blast furnace slag, because of its activator action which generally promotes materials with higher mechanical strength (Fernández-Jiménez et al., 2003; Wang et al., 1994).

The proposed mechanism of geopolymer setting (first step including monomers formation and beginning of hardening) and hardening, or curing, (second step corresponding to polymeric structure formation and improvement of mechanical properties) consists of dissolution, transportation or orientation, as well as a polycondensation process (Van Jaarsveld et al., 1998). An alkali metal salt and/or hydroxide is required for dissolution of silica and alumina to form $Si(OH)_4$ and $Al(OH)_4^-$ monomers or short chain polymers, as well as for the catalysis of the condensation reaction to form rigid chains.

Geopolymeric binders exhibit technological and ecological advantages in comparison with ordinary Portland cement, one for all energy saving. If the industrial use of geopolymers in the production of high performance building materials is expanding (van Deventer et al., 2010), many parameters (curing time, curing temperature, relative humidity, etc.) can be adjusted so that to use geopolymers as resistant matrix for inertization of hazardous wastes (Lancellotti et al., 2013). In this context in the last years geopolymers are used as matrix for immobilization of many kinds of hazardous wastes, in particular in solid form, such as incinerator fly ash, electric arc furnace dust, ferronickel slag, lead smelting slag, red mud, etc.

Objectives

In the present work, a hazardous waste deriving from the colouring process of ceramic tiles surfaces was immobilized in geopolymeric inorganic matrix. This waste is in liquid homogeneous form composed prevalently of aqueous solutions of metals compounds which develop colours during the firing cycle.

The colorant solution contains Fe, Mo, Mn, Co, Cr, depending on the final colour, together with mineralisers and complexes. One of the innovative aspects of this research is the exploitation of water content of the waste and the absence of the drying step, the latter being a common step in the management of liquid hazardous wastes.

Outline of the work

This work is divided in two main parts:

- the first part covers the liquid waste characterization;

- the second part is related to the alkaline activation of waste mixed with metakaolin as aluminumsilicate source and to the evaluation of the Cr immobilization efficiency by means of leaching test and conductivity measurements.[*]

Methods

Waste characterization

The liquid waste was characterized in terms of pH (measured by an Orion 555A pHmeter with pentrode probe), density, chlorides and sulphates (determined respectively by Mohr titration and a turbidimetric method).

The liquid waste was characterized determining the dry residue and then the nature of the liquid phase.

Two different procedures were followed in order to safeguard the chemical composition of the dry residue:

a) High temperature condition: the waste, previously weighted, was heated at 180° C for 2hs into an extractor fan in order to remove the liquid phase and to determine the dry residue amount.

The boiling temperature of the liquid phase was determined at near 100°C; it has suggested that the solvent could be water and it was confirmed by the second approach use to remove solvent.

b) Low temperature condition: the waste, previously weighted, was frozen at -80°C overnight and then freeze-dried.The dry residues obtained from the two different treatments were completely identical so that were characterized by chemical (X-ray fluorescence, Philips PW 2004) and elemental analysis and loss of ignition at 650°C for 2 hs. The results are reported in Table 1.

Geopolymers preparation

In order to evaluate the matrix immobilization capability an amount of liquid waste added to the aluminosilicate precursor (metakaolin) ranging from 3 to 20 wt% was tested.

This procedure is patented by the authors (Leonelli et al., 2012).Metakaolin with Si/Al = 1.3, in terms of mass ratio, produced by calcination of kaolinite at 700°C for 4 h and then ground and sieved below 75 μm, was used as the principal source of aluminosilicate.

This commercial kaolinite, which is used in the ceramic tile industry, is quite inexpensive and usually presents a good degree of purity.

The procedure for sample preparation was carried out according to the following steps, taking into account the water contained in the liquid waste which was exploited in the mixing and forming steps: mixing of liquid waste, sodium hydroxide pellets and sodium silicate solution (with a mass ratio Si/Na = 3,64) in a beaker in order to obtain a homogeneous solution; addition of aluminosilicate powders to obtain a homogeneous mixture; intensive/thorough stirring until a homogeneous and fluid paste is formed; the paste is poured into plastic moulds; setting stage maintaining the cast at room temperature, curing stage at room temperature for 15 or 28 days.

The stability of the matrix and its capability to immobilize chromium has been followed by leaching tests accordingly to EN 12457 regulation (European norm "Characterisation of waste-Leaching-Compliance test for leaching of granular waste materials and sludges").

Solid residue was separated by filtration and each eluate solution, after acidification (with HNO_3 to pH=2), was analysed by ICP/AES to determine the amount of Cr.

Leaching process was monitored after 15 and 28 days of curing. On the eluates pH and conductivity measurements were conducted to evaluate the stability of the material.

Results and discussion

Waste studied in this paper is in liquid state and the medium is water. Water contained in the liquid waste is 67 wt% being the dry residue 33 wt%. In the dry residue, the content of Cr is around 25 wt%. After calcination at 650°C the inorganic residue is 27 wt% and organic fraction is 73 wt%.

The characterization of waste liquid fraction shows that the waste is acid (pH= 3.07), with a density of 1.213 g/mL. The high content of soluble salts as reported in Table 1. The elevated content of C determined by elemental analysis demonstrates the presence of a significant organic fraction, not analyzed in this paper; also the content of N compounds could indicate the presence of ammonium ions.

The inertization process via geopolymers formation has been tested by determining the chromium content in the eluate by ICP_AES (Fig.1). For compositions containing up to 10wt% of liquid waste, Cr release falls within limit values set by Italian regulation (DM 30/08/2005) for non-dangerous waste landfill disposal, confirming the effectiveness of the matrix to fix this metal.

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The chemical efficiency in terms of heavy metals immobilisation of the geopolymerization process has been evaluated by comparing to the chromium content in the waste, calculated taking into account of the percentage of waste introduced (right part of the graph in Fig. 1).

Table 1. Chemical characterization of liquid waste (std. dev. ± 1 wt%)

Chemical species	***Level***
Cr	24.81
S	0.68
Fe	0.52
Ca	0.51
Na	0.11
Ni	0.09
Al	0.07
Si	0.05
Mn	228 ppm
P	209 ppm
Mg	171 ppm
Ti	52 ppm
LOI	73.00
C	17.23
H	1.92
N	5.01
Cl^-	700 ppm
SO_4^{2-}	12500 ppm

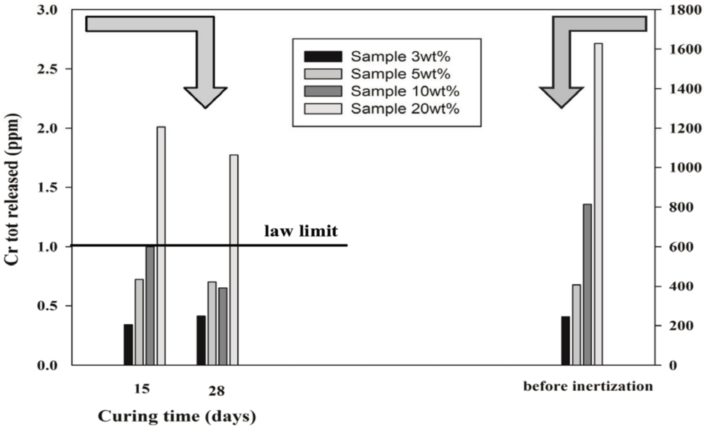

Fig. 1. Cr leaching as a function of curing time and compared to chromium in the waste

It is evident from Fig. 1 that the release of chromium from geopolymeric materials is greatly reduced with respect to the waste. In particular, by considering the effect of curing time, it is evident a decrease in the leaching of chromium for higher curing time in particular for high introduced percentages (10 and 20 wt%) demonstrating that the matrix consolidates, while for low amount (3 and 5wt%), values remain almost constant and still low.

In order to better evaluate the geopolymer stability in water for all the formulations, conductivity was monitored over leaching time from 2 min to 24 hours and reported in Fig. 2. While pH value rises quickly in the first few minutes and stabilises at pH values >10 within few minutes, conductivity values rise more slowly. The conductivity value for all samples except for the sample 20 wt% show a decrease as a function of curing time demonstrating the increasing stability of the matrix due to its consolidation. Probably the waste amount of 20 wt% is the threshold beyond which it is the matrix that is no longer able to stabilize and inertize this kind of waste.

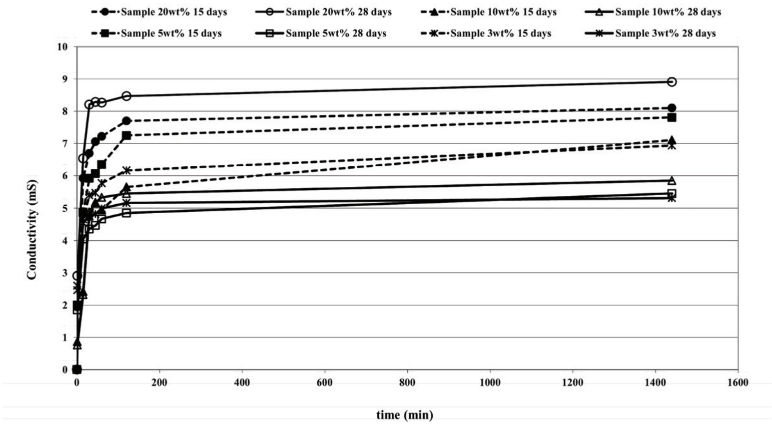

Fig. 2. Conductivity values as a function of curing time

Concluding remarks

The results obtained by the introduction of a complex liquid wastes into a geopolymer matrix highlight that, from an environmental point of view, the waste is successful incorporated into the inorganic polymeric matrix. Geopolymers, based on metakaolin and sodium silicate compositions, stabilize the Cr-bearing liquor as it comes out the industrial productive cycle with no need of any pre-treatment. Leaching studies of the consolidated material show a release of Cr which allow the disposal in a landfill suitable for not dangerous wastes. The absence of a drying pre-treatment reduces both the use of energy and handling necessary for the management of this kind of hazardous liquid waste. The abundance of literature on heavy metals immobilization by means of geopolymerisation makes this encouraging also for liquid wastes containing metals different from chromium.

Keywords: Alkaline activation, inertization, leaching test, liquid waste, geopolymers**.**

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DESIGN, CONSTRUCTION AND MONITORING OF A PASSIVE METHANE OXIDATION BARRIER PLACED IN THE CAPPING OF A LANDFILL FOR HAZARDOUS AND NON-HAZARDOUS WASTE

Extended abstract

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Background

The landfill final capping, besides ensuring the isolation of waste from the external environment and the minimization of water infiltration and erosion, can be integrated with elements aimed to the emission attenuation of biogas into the atmosphere, especially against methane. These systems, which are called Passive Methane Oxidation Barriers or biofilters, find their best application in those landfills where biogas recovery is not technically or economically feasible. An analysis of the experiences already made shows the possibility of designing passive barriers in different ways with each other resulting in the achievement of different treatment efficiencies.

Following a study on biogas management for a landfill site, located in Ravenna Via Romea Nord km 2.600 and managed by SOTRIS S.p.A., it was observed that the 3rd operational phase landfill for hazardous and non-hazardous waste is characterized by the production of low quantities of biogas mostly resulting from fermentation processes taking place in redox conditions. The results showed that the quality and quantity of biogas produced by the landfill does not allow any exploitation or justify the need for additional forms of collection. It was, however, assessed the need for a not substantial modification of the landfill final capping, in order to realize a treatment system capable of adequately handling the volume of biogas emitted by the landfill body.

This article then outlines the design choices made for the passive oxidation barrier that consists of a two-stage oxidation biofilter realized by mixing different percentages of fine rounded gravel and composted green soil. The article also explains the installation modalities (mixing of materials, methods of installation), the operations provided for maintaining the passive oxidation barrier and the arrangements for renewal of the barrier including the management of exhaust substrate. It also describes the monitoring activities and the instrumentation designed for the study of treatment efficiency of the barrier and for the analysis of gaseous species that this system is capable of treating.

Introduction

The study on biogas management, realized in July 2008, shown that the 3rd operational phase landfill for hazardous and non-hazardous waste is characterized by the production of low quantities of biogas with a specific flux emitted approximately 0.9 - 1.6 l/m^2h (values obtained with the dynamic accumulation chamber method as a result of a measurement campaign of the flow of biogas emitted from the surface).

The chemical and isotopic analyzes conducted on samples, collected from gas wells present on the landfill, highlighted the lack of relevance of fermentation processes of organic material, typical for MSW landfill. Prevail instead processes that occur in different redox conditions, generating a gas generally poor in methane (average concentration lower than 20% in volume).

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1. Passive oxidation barrier dimensioning

The passive methane oxidation barrier has the following general characteristics, as well as visible in Fig. 1:

- it is positioned on the top of the landfill, presenting a thickness varying between 1.0 m and 1.2 m;
- it has 4 "biogas supply screens", produced below the barrier directly in the HDPE geomembrane; these areas have almost rectangular shape with sides approximately 25 x 10 m for a total area of 1000 m^2;
- the oxidant section presents almost rectangular shape with sides approximately 25 x 60 m for an overall planar development equal to 1550 m^2.

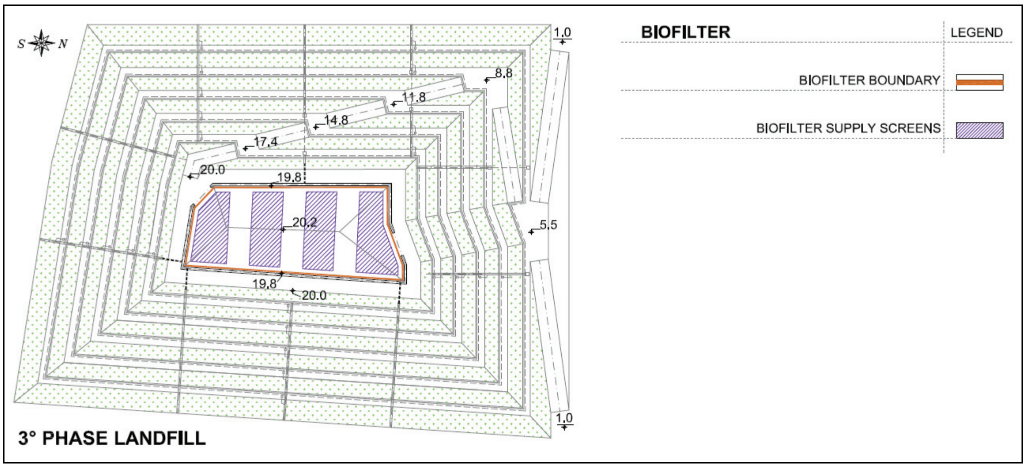

Fig. 1. Schematic plan of 3rd phase landfill with identification of biofilter boundary and supply screens

The following is a detailed description of each element that constitute the final capping of the landfill, in vertical succession from bottom to top, with particular reference to the oxidation barrier. This succession is observable in the section illustrated in Fig. 2:

- leveling layer: its function is to allow the proper installation of the overlying layers; it is realized with variable thickness soil;
- biogas drainage layer: it performs the double function of conveying leachate to the bottom and convey any biogas side emission towards the top part of the landfill in which there is the barrier of oxidation;
- low conductivity barrier: it consists of a HDPE geomembrane coupled to a bentonite geocomposite that cover the entire surface of the landfill. On the top portion of the landfill there are four "supply screens" with dimensions 25 x 10 m, covering a total area of 1000 m^2 (Fig. 1) obtained removing rectangular elements of geomembrane. These windows are the feeding areas of the passive oxidation barrier realized on the top and will then allow the upward migration of the flow of biogas originating from the waste body. It is, however, necessary to ensure that the cover system does not permit the infiltration of rainwater inside the waste body. To this end, in correspondence of the areas without geomembrane, the capping has been integrated by installing a second bentonite geocomposite that goes to entirely cover such areas (including an adequate overlap with the underlying geomembrane for about 1 meter of the overall perimeter);
- rainwater drainage layer: prevents the formation of a hydraulic head above the impermeable barrier, evacuating rainwater filtration that will affect the top part (biofilter) to the discharge system. This element is also the first homogenization horizon, uniformly distributing the diffusion of biogas below the oxidant barrier.

The final element of the landfill capping system is the passive oxidation barrier. This has been structured in vertical succession with two biofilters with different characteristics between them and separated by an intermediate drainage layer, as illustrated in Fig. 2. The elements that constitute the passive oxidation barrier are (from bottom to top):

- planar gravel drainage, thickness of 10 cm: this element, in addition of increasing the rainwater drainage efficiency is a further homogenization horizon of the biogas flow out of the waste body. It is also functional to the maintenance of the biofilter, preserving from damaging underlying elements during the regeneration phases of the barrier (consisting in the removal of the exhausted substrate and replacement with fresh material);
- first oxidation stage: 50 cm of thickness, made with a mixture consisting of 30% organic substrate and 70% inert material (percentages by weight); having a measured a density of 0.6 t/m^3 for the organic substrate and 1.6 t/m^3 for the gravel, the volume ratio is 1,2:1. This first stage is characterized by a higher percentage of solid skeleton, compared to the next stage, in order to avoid compaction phenomena once subjected to the load of the upper stage, and allow the air migration to deeper layers ensuring an adequate intake of oxygen necessary for the oxidation processes;

- intermediate drainage geocomposite: this element performs the dual function to redistribute the flow of biogas output from the first oxidation stage prior to its entry into the second stage; also facilitates the circulation of ambient air toward the first stage of oxidation;
- second oxidation stage: variable thickness 50 ÷ 70 cm: made with a mixture consisting of 40% organic substrate and 60% inert material (percentages by weight); with the same density considered previously we get a volume ratio of 1,8:1. This stage has a higher percentage of organic substrate, in order to achieve a higher efficiency of treatment and facilitating the plant vegetation.

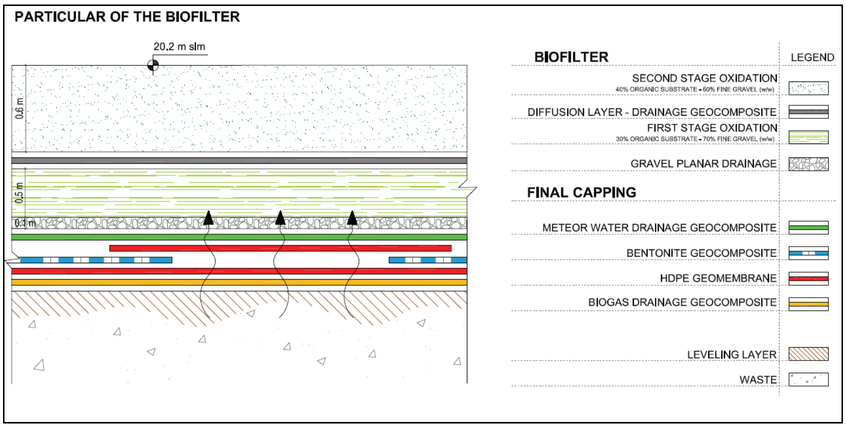

Fig. 2. Schematic section of the oxidation biofilter

2. Passive oxidation barrier construction

The constituting materials of the barrier must have the following characteristics:

- the inert material consists of rounded gravel with a grain size d 5 ÷ 10;
- the organic substrate is made of green composted soil that has the characteristics set out in Annex 2 of Legislative Decree no. 75 of 29 April 2010 (Italian legislation).

The mixing of these materials was carried out prior to its installation, using a suitable machine for mixing (like a cement mixer). Adequate quantities of the two materials were taken in such proportions to respect the weight ratio previously specified and differentiated for the two oxidants stages. The installation of the mixture occurred without any type of compaction but simply leveling the substrate to achieve the required thickness. Considering also that the construction operations for the second oxidant stage were held above the first stage and that the quantities of material to be handled are contained, the machine used for the realization of the barrier was a small size excavating, in order to ensure the minimum level of compaction on the lower layers.

In order to ensure full treatment efficiency for the passive barrier it is assumed to regenerate the biofilter with appropriate timing of intervention. These operations, consisting in the removal of the exhausted material and reconstitution of the oxidant barrier, have multiple purposes:

- ensure the regeneration of the organic substrate, partially used in the bacteria metabolic processes, which over time will tend to deteriorate;
- restore sufficient porosity of the materials that over time have undergone a natural compaction with consequent system efficiency loss.

For these reasons, it was expected a theoretical restoration of the barrier approximately every ten years. This intervention is anyway made according to the results obtained from the monitoring of the barrier oxidation efficiency.All the material generated from barrier maintenance operations may be subjected to a Soil Washing treatment, with the aim of recovering the fine fraction of the substrate constituted by the inert matrix present in the mixture. This process will ensure the dissolution of the organic substrate in the aqueous extraction that will later be sent to normal purification processes. The inert material recovered can be directly reused for the construction of new oxidation stages.

3.Passive oxidation barrier monitoring

The monitoring plan and instrumentation designed for the study of the treatment efficiency and for the analysis of gaseous species that this system is capable of processing is illustrated in Table 1.

In particular, the analysis of fugitive emissions of biogas is carried out with the dynamic accumulation chamber method on a mesh sampling of 5.0 x 5.0 m (for a total of 125 points). The oxidation efficiency monitoring were made by measurements and sampling directly inside the barrier as well as in deep biogas wells. To this end, specific probes were designed: each sampling point is constituted by a battery of five probes which allow monitoring of the biofilter at various depths from the ground level: 0.2 m, 0.4 m, 0.6 m, 0.8 m and 1.0 m. There were a total of 3 installed sampling points (North, Central and South) for a total of 15 probes.

Table 1. Methods and frequency for oxidation barrier monitoring

Object of control	***Parameters / Methods***	***Frequency***
Biogas diffused emission from landfill body	Accumulation chamber method (CH_4 and CO_2)	Annual
Biogas analysis for assessing biofilter efficiency (inside the oxidant barrier)	Moisture content, temperature, pH, O_2, CH_4, CO_2	Half-yearly (first 3 years) then annual
Biogas analysis for assessing oxidation process efficiency (inside landfill body and in surface of the landfill top)	O_2, CH_4, CO_2, CO, organic and inorganic compounds	Half-yearly (first 3 years) then annual

Results and discussion

Data of the monitoring carried out are available for about two years. In august 2011 and february 2012 were realized campaigns for diffused biogas monitoring in atmosphere with the accumulation chamber method. The target is to quantify the total flow of biogas emitted from the biofilter and, consequently, to estimate the amount of CH_4 and CO_2 emitted daily from the top of the landfill and then check the efficiency of the biofilter. The survey showed generally negligible flow of methane and medium-low values for carbon dioxide. More than 90% values of Methane detected were below the detection limit of 0.3 ppm s^{-1} (corresponding to 1.6 g m^{-2} d^{-1}), while with regard to the Carbon Dioxide about 10% values resulted below of the detection limit of 0.1 ppm s^{-1} (corresponding to 2.2 g m^{-2} d^{-1}). The outflow from the biofilter, calculated only for the carbon dioxide because of the small number of useful measurements for methane, is approximately 5.0 Nm^3 h^{-1} (corresponding to about 3.3 Nl m^{-2} h^{-1}). The data confirmed a good performance of the oxidation biofilter which tends to reduce the emission of biogas produced by the landfill.

With regard to the field measurements made using the measuring probes specially designed and implemented, the results show that the deeper horizons of the biofilter present low concentrations of oxygen (never equal to zero), which is used by the bacteria for metabolic processes. Oxygen levels recorded in the barrier are otherwise considerable over the entire vertical: this is essentially due to the adequate permeability of the barrier that allows the oxygen to spread effectively even at greater depths. Everywhere it is also present an increasing temperature profile with the depth associated with an increasing gradient of carbon dioxide, which demonstrates the presence of bacterial respiration. In all survey points and in each measurement campaign the methane content at the surface is null result.

As regards for the chemical analysis carried out on biogas collected samples, the analysis of the results show that in general the considered compounds have decreasing profiles proceeding towards the surface of the landfill. In particular, the concentration of methane diffusing from the barrier is substantially zero over the entire surface analyzed. The results show that the barrier reduces over 80% of the emission of BTEX (in particular for Toluene, Ethylbenzene and Xylene) than that for ammonia and Tetrachloroethylene. It is not recorded the presence of odour compounds (hydrogen sulphide and mercaptans). Nitrogen concentrations are high enough in relation to a significant presence of such compound in the biogas produced from 3rd operational phase landfill connected to redox processes taking place within the waste body. There is also an increase of HCl starting from the bottom of the biofilter to the outside; this situation can be attributed to the aerobic cometabolic biodegradation of compounds containing chlorine (CVM, tetrachlorethylene, trichlorethylene) based on the presence of reactions on hydrocarbons (methane in particular but also BTEX) as substrate.

Concluding remarks

The designed passive barrier is currently able to handle the volume of biogas emitted from the waste body. The flow emitted (less than 3.0 Nl m^{-2} h^{-1}) is characterized by values of methane almost zero over the entire surface of investigation. There is a more substantial emission of carbon dioxide as a product of the oxidation process.

The measurements carried out within the monitoring probes show typical profiles of oxidative processes realized by bacterial organisms. The design and construction of the barrier has allowed the achievement of significant levels of oxygen over the entire vertical even at the greatest depths.

Keywords: barrier, biofilter, capping, methane, oxidation

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END OF WASTE CRITERIA FOR THE TERMINATION OF THE STATUS OF WASTE AND THE CSS DISCIPLINE IDENTIFIED BY DM FEBRUARY 14, 2013, N. 22

Extended abstract

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Background

The Directive 2008/98/EC of 19 November 2008 "on waste and repealing certain Directives" (EC Directive, 2008), transposed into Italian law by Legislative Decree no. 152/2006, has intervened to substantially change the legal framework on waste, introducing measures to enhance the principles of precaution and prevention in the management of waste and to maximize recycling/recovery.

The most important provisions regard the identification of criteria to clarify when a waste ceases to be such, which has a significant impact on the internal market and for the promotion and realization of the "recycling society". These end-of-waste criteria should be laid down at European level, if they are not, the Member States may decide case by case whether certain waste has ceased to be such, taking into account the applicable case law (COM, 2011; Rottgen, 2013).

With the decree of the Ministry for the Environment 14 February 2013, n. 22, in accordance with the Directive, Italy has laid down the rules for the termination of waste status of certain types of Solid Fuels Secondary (CSS). As indicated in Article 184-ter of Legislative Decree 3 April 2006, n. 152 the material that ceases to be waste is defined as "CSS-Fuel".

End of waste criteria

The classification of the Solid Fuel Secondary (CSS), is based on the requirements of the harmonized technical standard UNI EN 15359 "Solid recovered fuels" (SRF), which takes into account three parameters (and related classes) of strategic importance for environmental technology and performance/economy, such as LCV (commercial parameter), Cl (process parameter) and Hg (environmental parameter). According to the Regulation are to be classified CSS-secondary solid fuel only the fuel (CSS) with LCV and Cl as defined by the classes 1, 2, 3, and their combinations and - with regard to the Hg - as defined by the classes 1 and 2 , reported in Table 1 of Annex 1 to the Regulation.

Table 1. Classification of secondary solid fuels (from EN 15359)

Characteristics of classification							
Characteristic	Statistical measure	Unit of measurement	Limit value for each class				
			1	2	3	4	5
LCV	mean	MJ/kg as fed	≥25	≥20	≥15	≥10	≥3
Cl	mean	% s.s.	≤0.2	≤0.6	≤1	≤1.5	≤3
Hg	median	mg/MJ as fed	≤0.02	≤0.03	≤0.08	≤0.15	≤0.5
	80th percentile	mg/MJ as fed	≤0.04	≤0.06	≤0.16	≤0.3	≤1

In Table 2, Appendix 1, there are identified the limit values for a number of physical and chemical parameters, which if exceeded will not affect the end-of-waste classification. For the production of CSS-Fuel are allowed municipal waste, special non-hazardous waste and also materials not classified as waste, as long as non-hazardous under the CLP Regulation. In Annex 2 of the Decree is given a negative catalog, which lists the waste (European List by code) that is not allowed for the production of CSS-Fuel.

Annex 3 of the decree indicates the techniques and treatment processes for the production of CSS, which, however, are only illustrative not prescriptive. The manufacturer, in fact, has full power to the choice of techniques to be used for the production of CSS-Fuel.

The CSS-Fuel may only be used in cement kilns with a production capacity exceeding 500 t/d clinker (subject to IPPC Directive) for the production of heat, or in power plants with a rated thermal input exceeding 50 MW combustion (subject to IPPC Directive) for the production of electricity. The plants must be in possession of integrated environmental authorization (AIA) and equipped with quality certification ISO 14001 or EMAS registration.

In order to ensure a high level of environmental protection and human health defense, the systems which use CSS - Fuel should apply, where pertinent, the provisions of Legislative Decree 133/2005 on co-incineration, as well as the values emission limit set out in Annex 2 of the decree, unless AIA provides more stringent requirements.

Additional requirements for the production and use of CSS

In accordance with the European regulations on the end of waste, the standard specifies that the manufacturer of CSS-Fuel should adopt a system of quality management in compliance with UNI EN 15358 (quality management systems - Particular requirements for their application to the production of secondary solid fuels) or should be in possession of EMAS registration.

The regulation also requires disclosure obligations and documents, which are:

- The declaration of conformity by the manufacturer, attesting that, for each sub-lot of CSS - Fuel, verification of compliance with the quality requirements set out in Table 1 and all the other requirements laid down by decree. This certification, which also contains data identifying the user, must be kept for one year and presented at the request of the competent authority;
- An annual communication that the manufacturer must provide the competent authority, which covers detailed information on the type and quantity of waste input, the amount of CSS-fuel product, the results of the performed analysis, the types and quantities of waste resulting from the process and its final destiny, the biodegradable part of the CSS-Fuel and user of the same;
- An annual communication that the user must transmit in the same manner as referred to in the preceding paragraph and which concerns, among other things, the identification data of the manufacturer of CSS-Fuel used, the results of the characterization of sub-lots, the percentage of replacement of fossil fuels.

Finally, are also provided specific requirements for the storage, handling and transportation of the CSS-fuel.

Concluding remarks

The decree is part of the measures to ensure a sustainable use of resources in line with the European guidelines expressed in the Communication to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions "Roadmap to a Resource Efficient Europe ".

The use of fuels produced from waste reduces, in fact, the consumption of fossil fuels, promotes the use of biomass and contributes to achieving the objectives laid down in Directive 2009/28/EC on renewable sources.

Additionally, through the lightening of administrative procedures is promoted the recovery of waste and its removal from the landfill with consequent benefits in terms of emissions of greenhouse gases.

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MINIMIZING THE ENVIRONMENTAL IMPACT OF METALWORKING FLUIDS BY AUTOMATIC DETECTION OF BACTERIAL CONTAMINATION

Extended abstract

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Background

Metalworking Fluids (MWFs) have been used in the metal cutting industry for 200 years to cool, remove metal fines, lubricate and prevent corrosion during metal grinding and cutting procedures. All MWFs, and in particular water based formulations, share the problem of susceptibility to microbial attack, since their constituents (mineral oil base stocks, glycols, fatty acid soaps, amines etc.) provide essential nutrients for the proliferation of bacteria, as well as molds and yeasts, (Rabenstein et al., 2009).

Microbial contamination of MWFs causes a number of problems, such as development of unpleasant odors (particularly in the case of sulphate reducing bacteria), changes in emulsion stability and coolant chemistry resulting in increased corrosion rates, loss of quality of the work pieces and tool failure (Passman, 2004). Moreover, high concentrations of microbial contamination represent a risk for the health of exposed workers, since, during machine operation, aerosols are generated and the contaminants in MWFs could be inhaled with potential respiratory problems. Prolonged direct contact with MWFs can also result in dermatitis and skin irritation (Perkins and Angenent, 2010). Furthermore, since microbial contamination causes a reduction in MWFs lifetime, it affects also fluid disposal, normally making it more frequent and subject to stringent requirements, with impact on both costs and the environment.

Microbial contamination is often counteracted by adding small concentrations of biocides to MWFs (Marchand et al., 2010), but this solution presents also problems of biocide toxicity (most biocides can release formaldehyde, a well known irritant for the respiratory tract and a carcinogenic agent) and potential generation of biocide-resistant strains. Currently, biocide is added when primary symptoms of microbial spoilage are noticed (development of odor, decrease in pH, formation of biofilms and changes in emulsion stability). At this point, however, MWFs are already deteriorated and, even if biocide addition lowers bacterial concentration to an acceptable level, fluid properties cannot be fully restored. A better solution is, of course, to add the biocide only when it is really needed, namely when microbial contamination reaches a warning level (about 106 cfu/mL). This, however, requires that bacterial concentration is monitored on a regular basis.

The official procedure for bacterial concentration measurement is the Standard Plate Count (SPC) technique, which is reliable and accurate but requires long time (from 24 to 72 hours) and is a laboratory based method that must be carried out by trained personnel. As an alternative, the Impedance Technique (ImpTech) is highly competitive with SPC since it features faster response time (from 2 to 14 hours depending on the type of Sample Under Test – SUT) and is suitable to be performed with electronic systems, to be "embedded" in industrial machineries or implemented as portable instruments for in-situ measurements (Grossi et al., 2010).

ImpTech essentially works as follows (Firstemberg-Eden and Eden, 1984): the SUT is stored at a temperature suitable for bacterial growth and its electrical characteristics are measured at regular time intervals. After a short time needed for the SUT to stabilize, the electrical characteristics remain almost constant (at a "baseline value") until a

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critical bacterial concentration (in the order of 107 cfu/mL) is reached and the electrical characteristics start exhibiting significant changes.

The time needed for the electrical parameters to deviate from their baseline values is normally referred to as Detect Time (DT) and, since the DT is linearly related to the logarithm of initial bacterial concentration of the SUT, this latter can then be easily worked out.

In this work, the ImpTech has been used to measure microbial contamination in MWFs and the results show that high contaminated samples (> 106 cfu/mL) can be reliably recognized in 4 to 10 hours (depending on the sample/nutrient media ratio). The method is also suitable to detect the effectiveness of biocide addition to MWFs, thus allowing to determine the minimum inhibition concentration of biocide suitable to stop bacteria proliferation.

The use of the ImpTech to monitor bacterial concentration in MWFs can offer many advantages, such as: minimum and optimal use of biocides, longer MWFs lifetime and lower costs for fluids replacement, minimal disposure of worn-out MWFs, with beneficial effects on the ambient.

Methods

A measurement setup, formed with benchtop instrumentation, has been used to test samples of MWFs taken from different metalworking plants in Bologna (Italy). The setup is shown in Fig. 1 (a): during the measurements, the SUT is stored in a thermal incubator at 37 °C and is electrically characterized by means of the LCR meter Agilent E4980A (in the frequency range 20 Hz – 2 MHz), at time intervals of 5 minutes. Measured data are acquired with a portable PC and saved on the hard disk for further analysis. All the software for instrumentation control has been created with LabVIEW (National Instrument, USA).

The tested MWF samples are oil-in-water emulsions obtained diluting a soluble oil (produced by Mecasystem) in water (with concentration from 2% to 10%). SUTs are created by diluting the MWF sample in the enriched medium Lauria Bertani broth (tryptone 3 g/l, yeast extract 5 g/l, glucose 5 g/l) in the ratio 1:10.

The SUT is hosted in the sensor shown in Fig. 1 (b), namely in a 10 mL container featuring a couple of cap-shaped stainless steel electrodes for electrical characterization.

Different concentrations of biocide (EBOTEC BT 80 produced by Total) have been added to some of the samples to test the effects on the measured electrical characteristics.

Total bacterial concentration for all MWF samples has also been measured by SPC (in Lauria Bertani) for reference and control.

A few samples of MWF have been initially characterized to build an electrical model of the electrodes-fluid system. Electrical parameters (|Z| and Arg(Z)) have been measured in the frequency range 20 Hz – 2 MHz with the LCR meter by applying a sinusoidal test signal of amplitude 100 mV. Fig. 1 (c) shows the Nyquist plot (i.e. imaginary vs. real component of Z) for the investigated frequency range. As can be seen, in the frequency range 20 Hz – 10 kHz an almost linear relationship exists between Im(Z) and Re(Z) while, for higher frequencies, the model deviates from this behavior, mainly due to parasitic effects. Thus, in the following, only the frequency range 20 Hz – 10 kHz will be considered.

The electrical circuit used to model the SUT – electrodes system (Fig. 1 b), is composed of a resistance R_m, accounting for the SUT electrical conductivity, and a Constant Phase Element (CPE), namely an empirical component used to model the non-ideal capacitance of the electrode-electrolyte interface.

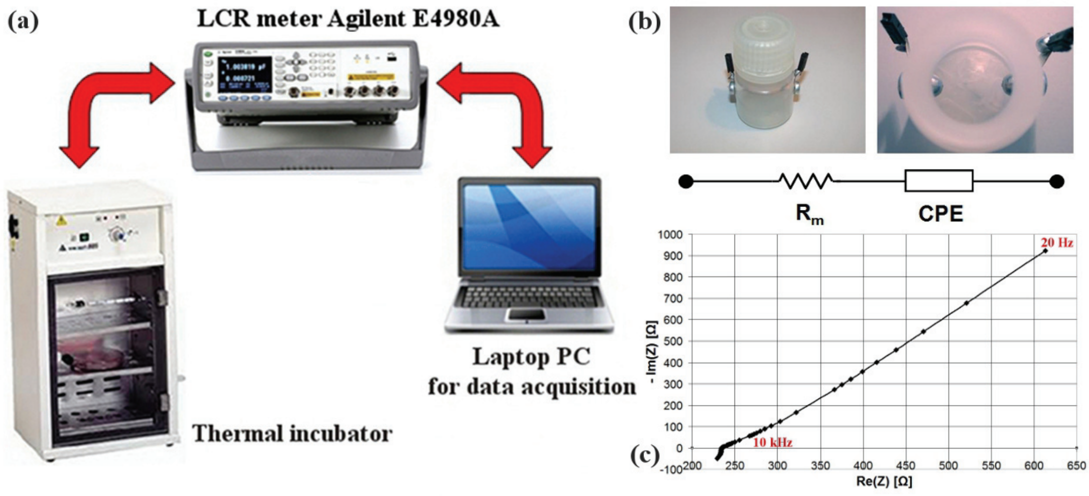

Fig. 1. Measurement setup used in the study: (a). Sensor hosting the sample under test and electrical circuit used to model the electrical response (b). Nyquist diagram for a sample under test (c)

The impedance of the electrical model can thus be expressed as:

$$Z = R_m + Z_{CPE} = R_m + \frac{1}{Q(j\omega)^\alpha} = R_m + \frac{e^{-j\frac{\pi}{2}\alpha}}{Q\omega^\alpha} = R_m + \frac{\cos(\frac{\alpha\pi}{2})}{Q\omega^\alpha} - j\frac{\sin(\frac{\alpha\pi}{2})}{Q\omega^\alpha} \qquad (1)$$

hence:

$$\mathrm{Re}(Z) = R_m - ctg(\frac{\alpha\pi}{2}) \times \mathrm{Im}(Z) \qquad (2)$$

The electrical parameters R_m, Q and α have been extracted from the measured data using the software Multiple Electrochemical Impedance Spectra Parameterization (MEISP) v3.0, by Kumho Chemical Laboratories.

Results and discussion

Different MWF samples have been tested to investigate the correlation between the measured electrical parameters (R_m, Q and α) and the bacterial concentration determined with the SPC procedure.

The capacitive component of the electrode-electrolyte interface (Q) has been found to be the parameter best suited to estimate the sample bacterial concentration, since it provides better repeatability and stronger correlation with the data of the SPC method.

Fig. 2 (a) shows the percent increase of Q vs. time for SUTs featuring different values of bacterial concentration (determined by SPC), with the stronger ones resulting in lower values of DT. In Fig. 2 (b) the measured DT values are plotted vs. the bacterial concentration, and a good linear relationship is obtained between DT and logarithm of the bacterial concentration. The corresponding linear regression can be written as

$$DT = -266.71 \cdot Log_{10}(C_0) + 2397.4 \qquad (3)$$

and the coefficient of determination is $R^2 = 0.975$.

These results prove that the ImpTech can be reliably used to estimate bacterial concentration with electronic systems to be embedded either in industrial machineries or in mobile equipment for in-situ measurements not requiring trained personnel. In both cases, measurements can be carried out at regular intervals so that, when the measured DT corresponds to bacterial concentration > 10^6 cfu/mL, actions can be taken (in particular adding biocide).

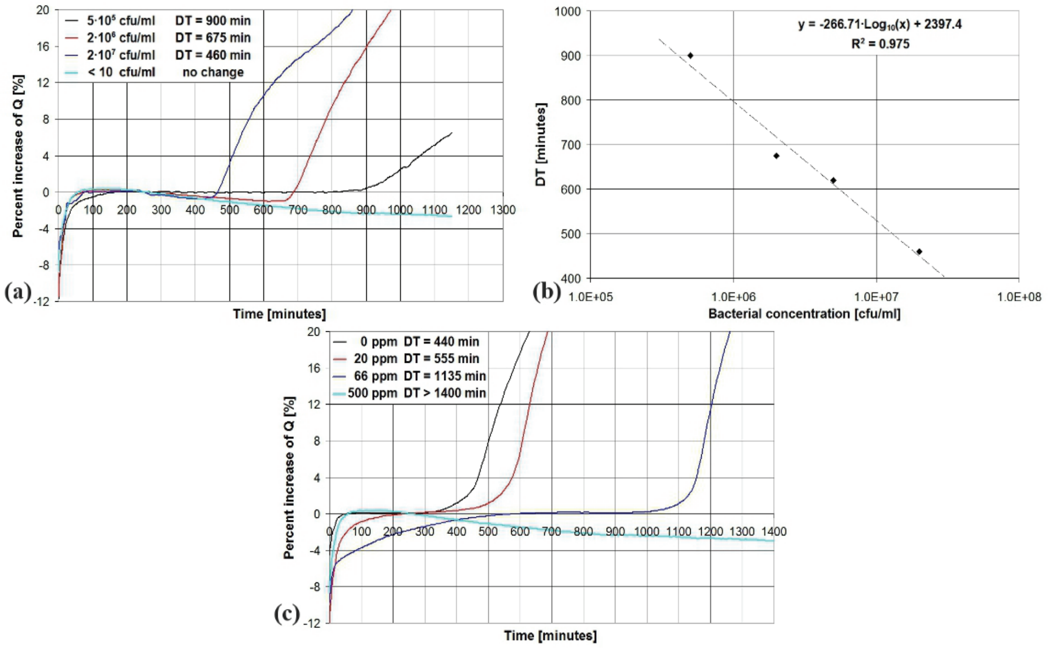

Fig. 2. Percent increase of Q vs. time for samples featuring different values of bacterial concentration (a). Scatter plot of the measured DT vs. bacterial concentration of the tested samples (b). Percent increase of Q vs. time for a sample inoculated with different amount of biocide (c)

The reliability of such an approach has been tested by adding known concentrations of biocide to strongly contaminated samples (10^6 – 10^7 cfu/mL) and the obtained results are presented in Fig. 2 (c).

As can be seen, increasing the amount of biocide the measured DT also increases because of decreased bacterial concentration: DT = 440 minutes for the untreated sample, DT = 555 and 1135 minutes with the addition of 20 ppm and 66 ppm of biocide, respectively; while with the addition of 500 ppm of biocide DT exceeds 1400 minutes.

Thus, starting with low biocide concentrations to be increased until the desired decrease in bacterial concentration is obtained, the minimum concentration of biocide (depending on the particular bacterial strains) able to stop bacteria proliferation can be determined.

Of course, minimizing biocide addition has beneficial effects on the health of exposed workers, besides leading to reduced costs of the material.

Concluding remarks

This work has shown the feasibility of measuring bacterial concentration in MWFs with the Impedance Technique, which offers the advantages of shorter time and possible implementation with electronic systems to become part of industrial machineries or used as portable instruments for in-situ measurements.

Regular monitoring of microbial concentration allows to add biocide once the contamination increases over a certain threshold. Moreover, the proposed approach provides information on biocide effectiveness, thus enabling to use the minimum concentration capable of stopping bacteria proliferation, with beneficial effects on the ambient, health of exposed workers and costs.

Keywords: bacteria, electronic system, impedance, metalworking fluids

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UNSORTED MUNICIPAL WASTE TREATMENT PLANT ANALYSIS: EMILIA-ROMAGNA REGION CASE STUDY

Extended abstract

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Background

Better knowledge of complete Municipal Solid Waste (MSW) cycle dynamics could allow MSW plan decision makers to reach the waste management goals that are, at present, still far from being achieved (Bianchini et al., 2011). Thus, in order to identify characteristics of the existing and/or planned MSW treatment plants, Emilia-Romagna started a deep analysis to optimize energy consumption, energy production, environmental impact and management costs of whole MSW system in comparison with the final "Regional plan for waste management" (PRGR, *Piano Regionale di Gestione dei Rifiuti*, in Italian) goal. New Emilia-Romagna PRGR is now under definition. MSW collection can be divided into two main streams: separate collection and unsorted collection. Law Decree 152/2006 defined separate collection as "the collection where a stream of waste is kept separate depending on kind and nature of the waste in order to facilitate a specific treatment". In 2011 Emilia-Romagna reached 52.9% separate collection on total MSW collection, which means about 356 kg/year collected per inhabitant (ARPA and Emilia-Romagna, 2012). Separate collections are not recoverable at all; moreover, the percentage of unrecoverable inside separate collection increases with separate collection increasing (Consonni et al., 2011). So, treatment plant for unsorted MSW must be properly designed taking into account also contribution from separate collection discards.

In 08/98/CEE MSW hierarchy landfill disposal is the last step.

Therefore, an effective and efficient MSW management is one that ensures the minimization of the waste in landfills. Nevertheless, a quantity as marginal of waste will still be in landfill (i.e. waste produced by selection and/or recycling plant, waste products from energy recovery plants). Furthermore, it is desirable to ensure a residual capacity greater than that strictly necessary in such a way operating safety, for example, relating to shutdown of Waste-To-Energy (WTE) plants. Energy recovery from waste is part of the additional forms of waste recovery and different from recycling. Thus, MSW energy recovery is a solution both for waste valorization and landfill disposal minimization. Mechanical-Biological Treatment (MBT) of residual MSW was born to achieve the target of reducing biodegradable waste that goes to landfills, according to 99/31/CEE. Over the years MBT has been developed to improve also the sorting of recyclable materials. MBT generally consists of a mechanical pre-processing stages followed by biological stages that reduce and stabilize biodegradable matter under controlled aerobic and /or anaerobic conditions. MBT with anaerobic stabilization process has the further advantage of energy recovery thanks to biogas production. The mechanical pre-processing is designed both for sorting recyclable materials and particle size fractionation and homogenization of waste, thus optimizing the following biological process. Therefore, MBT plants can represent an interesting alternative to direct unsorted MSW landfill disposal and, in certain condition, also to WTE (Cimpan and Wenzel, 2013).

Objectives

Regional unsorted MSW treatment plants were investigated by Prevention and Environment Regional Agency (ARPA) and Department of Industrial Engineering (DIN) of Bologna University. Final objective is a complete map

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of regional unsorted MSW treatment plants performance that will be an useful instruments for PRGR decision makers.

Outline of the work

This work is divided in three main parts:

- The first part covers data collection about regional unsorted MSW treatment plants.
- The second part covers data analysis and definition of different kind of performance indicators, to evaluate efficiency and environmental impact of the plants.
- The third part covers unsorted MSW plants system critical analysis.

Methods

ARPA and DIN drafted three technical forms, differentiated by kind of plant, to be compiled by plants managers. Generally, each forms contain information requests about mass flow, energy production and consumption and environmental emissions. The forms help DIN and ARPA to analyze each plant as a closed system and reconstruct the input and outputs flows of matter and energy, also including stack emissions and the possible consumption of solid or liquid substances used for MSW treatment. Once the forms were written off, ARPA and DIN collected the data. A general screening allows ARPA and DIN to identify data problems and inconsistencies. Moreover, new data were requested for further analysis. Thus, depending on data quality and quantity, different kinds of parameter were defined to compare the plants in terms of efficiency and environmental impact. All collected data refers to year 2011, except for WTE plants emission one that refer to year 2012.

Some parameters are the same for the three kind of plants. First of all, location must be considered. A homogeneous distribution over the region of plants is important for the optimization of the waste streams and for containment of costs; furthermore, it guarantees waste treatment or disposal in a scope of legality, especially with regard to landfill disposal. Another general parameter is defined as logistic and functional efficiency and it is measured by plant size (residual size is considered for landfill). In general, the greater the size of the system, the greater the margin of plant technical and economical optimization (Consonni et al., 2011). Moreover, the third and fourth general parameters identify potential impacts on population (measured by exposed population in a certain round from the plant) and on environmental interference levels (estimated as a function of buffer percentage occupied by environmental constraints according to a progressive number that ranges from a minimum of 1 to a maximum of 1+n). In addition to the general parameters, more parameters were assessed for every kind of plants to measure their efficiency and effectiveness.

Results and discussion

Landfill was firstly analyzed. In addition to having sufficient spare capacity to ensure normal waste management, landfills act as the last element in the chain of waste management. Therefore, landfill is primarily used for the management of extraordinary but predictable events (such as shutdowns of WTE plant) as well as of extraordinary and unpredictable events. From this point of view, location (see Fig. 1) and residual size of the plants seems to be predominant with regard to other kinds of parameters, like efficiency or effectiveness, that can be useful in the case of matching at similar location and residual size conditions. Moreover, a logistics optimization in waste streams helps to minimize those distorted effects of using unlawful means for the final disposal of waste.

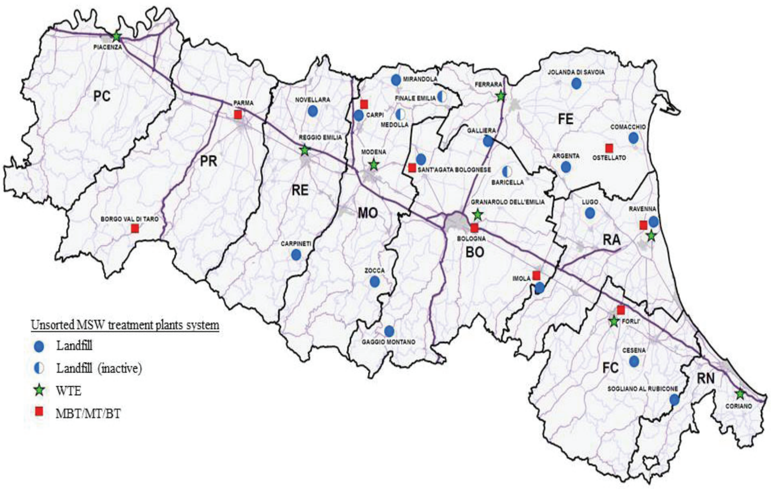

Fig. 1. Location of unsorted MSW treatment plants of Emilia-Romagna (year 2011).

The paper considers two parameters for efficiency determination of WTE plants: environmental impact and energy efficiency. Environmental impact is measured by annual emissions of different kind of pollutants (like powder, hydrochloric acid, nitrogen oxide, etc…). Pollutant emissions are also compared with emission level admitted by Italian legislation: if values are compared with emission limit ones, it can be found that plants emissions level are always under the limit. So, from the point of view of WTE flue gas treatment systems, Emilia-Romagna WTE plants show an average level of technology that corresponds to the highest standards in terms of performance. WTE plants are classified as energy recovery plant only if a certain value of energy efficiency R1, as defined in the 08/98/CE (acknowledged in Italy by Law Decree 205/2010), is reached. In particular, the value is 0.60 for installations in operation and permitted in accordance with applicable CE legislation before 1 January 2009, while for installations permitted after 31 December 2008 the value is 0.65. R1 does not measure the efficiency of the system calculated according to the classical criteria of thermodynamics, so it is an efficiency index useful to compare the capacity of energy recovery of different WTE plants. R1 definition is reported in Eq.1:

$$R1 = \frac{E_p - (E_f - E_i)}{0.97(E_w - E_f)} \tag{1}$$

where:
E_p means annual energy produced as heat or electricity (calculated with energy in the form of electricity being multiplied by 2.6 and heat produced for commercial use multiplied by 1.1), E_f means annual energy input to the system from fuels contributing to the production of steam, E_w means annual energy contained in the treated waste calculated using the net calorific value of the waste and E_i means annual energy imported (excluding E_w and E_f). R1 index has some critical aspects (i.e. the formula does not take into account climatic conditions of plant installed in areas where heat recovery capacity is limited) and is under analysis for a possible revision.

Nevertheless, now R1 index is the only European normative reference for the evaluation and comparison of the energy performance of WTE plants. Table 1 shows R1 index and the other general parameters for WTE plants analysis. In the CEWEP Energy Report (Reimann, 2012) the energetic yield of 314 WTE European plants was investigated: as a result, it can be stated that WTE plants installed in South-Western Europe have an average R1 index of 0.58, while WTE plants with size under 100,000 ton/year and between 100,000-250,000 ton/year have, independently from location, an average R1 of, respectively, 0.63 and 0.70. So, performance in terms of efficiency of the regional WTE plants amounted to values in line with the European average. R1 index was computed also for Ravenna WTE plant only for comparison purpose, even if the R1 formula is not properly applicable because the plant is fed by Refuse Derived Fuel (RDF), which is classified as special waste. Own the Ravenna WTE plant is the one that shows the most critical in terms of efficiency. Forlì and Rimini WTE plants could reach higher yield by increasing thermal recovery.

Table 1. Parameter for WTE plants evaluation (year 2011).

Plant	*Location (Province)*	*Size (ton/year)*	*Exposed population (inhab. in 3 km range)*	*Environmental interference level*	*Efficiency R1 index*
Bologna	Bologna	218,000	10,576	1	0.70
Forlì	Forlì-Cesena	120,000	18,049	7	0.50
Ferrara	Ferrara	130,000	6,680	4	0.68
Modena	Modena	240,000	26,579	6	0.60
Ravenna	Ravenna	56,500	464	3	0.21
Rimini	Rimini	150,000	21,653	2	0.51
Piacenza	Piacenza	120,000	21,439	5	0.64

Finally, MBT plants are analyzed. In 2011 there were 5 MBT plants (Carpi, Imola, Ostellato, Ravenna and S. Agata), to which 3 mechanical treatment (MT) plants are added (Forlì, Parma and Borgo Val di Taro). Bologna MT plant is not considered because it closed in 2012. MT plants separate organic from non-organic waste: the organic fraction is then sending to biological treatment plant for stabilization. All MBT plants are separate flow kind, where a mechanical treatment separates the humid fraction, destined to stabilization, from the dry fraction with high calorific power, destined to mechanical treatments of refinement for the production of RDF, to WTE plants or to landfill. A way to assess the performance of a MBT is to establish a mass balance.

Mass balances are generally expressed as a function of wet matter or dry matter, but it can be also interesting to express mass balances as a function of other parameters, such as organic matter or biodegradable organic matter (Morais et al., 2008). The quality of the collected data in terms of waste fraction analysis and characterization of individual waste fractions does not allow a so detailed analysis for the MBT and MT regional plants. So, performance of MBT and MT plants are measured with regard to global mass balances in the whole plant. Table 2 shows efficiency and environmental impact parameters based on mass balance of whole plant. The first one measures plant efficiency by electric energy in kWh consumed per ton of inlet waste.

The second one is expressed as percentage of inlet waste send to energetic valorization, while the third one is the percentage of inlet waste send to recycling. Two other parameters are used to measure plant impact on environment: the first one is percentage of inlet waste, stabilized organic matter (SOM) excluded, that is send to landfill, while the second one is percentage of inlet waste that is loss as flue gas (mainly composed by water steam and CO_2) during stabilization process.

Table 2. Parameter for MBT plants evaluation: efficiency and environmental impact (year 2011).

Plant	***Efficiency***			***Environmental impact***	
	Energy consumption [kWh/ton]	***WTE percentage***	***Recycled percentage***	***Landfill percentage (SOM excluded)***	***Matter loss percentage***
Carpi	34.0	0.0%	0.1%	34.6%	17.5%
Imola	19.3	0.0%	0.8%	47.6%	14.2%
Ostellato	11.0	48.1%	0.3%	1.1%	10.1%
Ravenna	36.8	27.0%	0.0%	45.1%	6.7%
Forlì	2.8	83.1%	0.0%	0.0%	-
Parma	12.9	25.5%	0.6%	31.8%	-
S.Agata	15.7	0.0%	0.1%	21.6%	37.5%
Borgo Val di Taro	22.3	36.8%	2.3%	20.6%	-

By analyzing Table 2 it can then be stated that the dry fraction separated and sent to the recycling is a marginal, if not negligible, fraction of the whole waste flow. Furthermore, in all the MBT plants the wet fraction is subjected to stabilization treatments that are exclusively based on aerobic processes. So, now there's no biogas production and no energy recovery from biological treatment (BT), besides a reduction of gas emissions due to matter loss during stabilization process. Another relevant observation is that three MBT plant (Carpi, Imola and S.Agata) addresses the whole dry fraction to landfill disposal. This fact can be explained if location of the three MBT plants near important landfill is considered. Secondary, it would be useful to evaluate lower heating value (LHV) of landfilled residual waste in order to assess a redirection to WTE plants, even if saturation of WTE plant can be a contributory cause to current landfill disposal.

Energy consumption varies in a very wide range, going from 2.8 kWh/year of Forlì (where MT plant is practically integrated with the WTE plant) to 36.8 kWh/year of Ravenna (where high energy consumption is mostly attributed to RDF production processes). If current plant efficiency is considered, only Ostellato and Forlì plants seem to match 08/98/CE hierarchy, which is landfill disposal minimization. Depending on MSW composition (in particular, organic fraction mass percentage) and kind of BT, MSW inlet mass reduction usually amounts to 20-40% (Morais et al., 2008). Emilia-Romagna MBT plants, with the exception of S.Agata plant, reveals values lower than 20%. Therefore, a further analysis is needed to analysis MSW inlet composition, because mass reduction could be low due to low mass percentage of organic fraction inside waste. Once MBT inlet stream composition is known, it will be possible to compare BT by mass reduction.

Concluding remarks

A complete map of Emilia-Romagna unsorted Municipal Waste treatment plants has been draft by ARPA and DIN, University of Bologna. Landfill, WTE and MBT-MT plants were deeply analyzed and match together, also by definition of evaluation parameters regarding efficiency, environmental impact and management optimization.

Keywords: landfill, mechanical-biological treatment, plant efficiency, unsorted MSW management, waste-to-energy.

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TECHNICAL SOLUTIONS TO IMPROVE RECOVERY OF SCRAPS DERIVED FROM TREATING GLASS PACKAGING WASTE

Extended abstract

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Background

Nowadays, the Italian industry is constantly oriented on innovation of products and processes in order to achieve a high level of economic and environmental sustainability. In this context, the waste management of Emilia Romagna region is very active on the Italian territory, thanks to over 2 thousand green companies engaged in such activities. This philosophy must be understood as a strategy to address current and future challenges and to strengthen our production system thanks to the support and commitment of citizens, consumers and entrepreneurs.

In 2010, in Italy about 32 million of municipal waste was produced, with a rate of separate collection of 35.3%. The waste glass collected in 2012 in Italy by separate collection of packaging waste amounted to approximately 1.6 million of tons of which 71% is sent to recovery (98% intended to glassworks, 2% to alternative recovery in ceramic or building industry (Co.Re.Ve, 2012). In Italy, the glass cullet is managed by Co.Re.Ve., the Italian Consortium for the recovery of packaging glass, since 1997. The cycle of collection and recovery of this glass can be implemented in 5 phases: collection of glass packaging in the container for recycling, withdrawal and transfer of glass cullet to the treatment plant, particle size selection and subdivision of cullet glass, obtainment of scrap suitable for the glassworks (maximum 0.068% of impurities (Co.Re.Ve., 2012), implementation of new packaging containing up to 90-95% of recycled glass. Specific treatments are performed on the glass cullet to obtain very low impurities values, such as manual sorting of pollutants, screening, separation of magnetic materials, suction of light-weight bodies and separation of non - magnetic bodies and opaque bodies are applied. Despite sophisticated equipment selection, total selection of "impure glass" is not guaranteed. In accordance with the Waste Framework Directive 98/2008/EC (landfill as a last form of disposal), the glass waste not sent to glassworks requires an alternative and innovative form of disposal.

Nowadays, in Italy, this fraction (contaminated by ceramic granules and high degree of organic pollutants and coarse scraps) is collected and, in particularly in the North of Italy, treated by technological plant in order to obtain secondary raw materials for both glassworks and ceramics. However, these treatments are very expansive and the materials obtained (in particular glass or ceramic sand) have high economic value sometimes not economically sustainable.

Objectives

On the basis of the well known benefits of the use of the glass inside the ceramic process, the main objective of this work was to identify strategic applications that allow efficient recovery and quality, both in economic and environmental terms, of scraps from treating glass packaging waste. The goal is to bypass the "secondary" treatments described above, reducing the costs associated with these additional activities and search solutions that allow the direct use of scrap within different manufacturing processes, ensuring performance and environmental benefits on the process and the final product. Several studies have highlighted the effects of using cullet in ceramics (Youssef et al., 1998; Maschio et al., 2009), bricks (Smith, 2004) or in the production of foam glass (Fernandes et al., 2009).

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In this paper we reported the results of studies carried out to obtain mixtures for bricks, cement pavement and foam glass with high content of waste glass, in order to evaluate the effects that of the use of glass scraps can lead on preparation and firing steps, and features of the final products.

Outline of the work

This work reports three case studies regarding building materials in which the glassy scraps are introduced in the bodies in different concentration:

- the first part covers the tailoring and characterization of cement pavement containing up to 85wt% of glassy waste;
- the second part is related to the tailoring and characterization of bricks containing up to 20wt% of glassy waste;
- the third part report a preliminary study in order to check the possibility to obtain glass foam with glass waste and an inorganic or organic residue as foaming agent.

Methods

The scraps used are sodium - calcium - silicate glass and the chemical composition (wt %) is 66.57 SiO_2, 16.47 Na_2O, 11.15 CaO, 2.16 MgO, 2.11 Al_2O_3, 0.86 K_2O, 0.37 Fe_2O_3, 0.07 Cr_2O_3, 0.05 PbO, 0.19 other, obtained by X-Ray Fluorescent Analysis (XRF). The presence of lead and chromium oxides is indicative of a contamination due to an uncorrected collection of the glass packaging to the container for recycling.

Beside, the elementary analysis demonstrates the presence of low percentage of Carbon (0.38%) associated to impurities such as rubber or plastic inside the sample, confirmed by DTA analysis (not here reported). In fact, this last method evidences one exothermic peak at 350°C associated to the decomposition of the organic materials. The characteristic temperatures (glass transition (Tg); sintering (Ts); softening (Tsf) and melting (Tm)) of waste glass were determined by DTA analysis (Tg = 530 – 580 °C) and optical heating microscopy (Ts = 698 °C, Tsf = 827 °C, Tm = 1048 °C). The scraps, available as granules with a diameter in the range about 5 – 20 mm, were ground at different particle size depending on the specific use, relatively coarse particle size for bricks and pavement mixtures and very fine particle size for foam glass. The glass used presents 5 – 6 % impurities such as plastic, paper and inert. These materials were not eliminated, because the purpose of this work is the direct use of scrap bypassing other treatments often expensive.

Several studies were carried out in order to use significant amounts of glass scraps within mixtures for the production of building materials. In particular 13 mixtures for preparation of pavement and 16 mixtures for bricks were prepared. Besides, regarding foam glass, a preliminary study was performed using both inorganic (glass cutting sludge) and organic (tyre pyrolysis residue) as foaming agent.

Up to 85 wt % of glass was employed in order to obtain pavement mixtures which were compared to a standard sample containing 100 % of Portland cement. This last was replaced with glass scrap ground into two different sizes (< 0.5 mm and 0.5 - 2 mm).

The effect of glass particle size on the adhesion degree between glass particles and cement paste was studied by porosity test and water absorption analysis. Rectangular samples of about 105 mm x 55 mm x 20 mm were obtained by pressing at 38 bar. After the moulding, the samples were dried at room temperature for 28 days to reach over 90% of the final strength during setting process. After this period, the samples were characterized by mechanical strength, water absorption and porosity tests. The mechanical analysis has allowed us to determine the compressive strength, peculiar property of these materials. The water absorption was obtained by procedure described into UNI EN 1338:2004. Finally, porosity was determined by mercury porosimetry.

Bricks containing up to 20 % of scraps slightly ground (< 1mm) to replace clay were obtained by traditional cycle of furnace. Samples were prepared by manual formation, dried at 80 °C for 48 hours and fired at 930 °C (maximum temperature of cycle) for 36 hours. The mixtures were made starting from the traditional body which contains two types of clays (80 wt %) and ceramic sludge (20 wt %). The glass powder was used as partially substituted of the lower performance clay in order to both improve technological properties of the final product and reduce environmental impact of virgin material use. Specific analyses of bricks were performed on the lab - scale in order to measure linear shrinkage and weight loss during drying and firing phases and water absorption after firing, employing samples of about 140 mm x 60 mm x 10 mm, and mechanical strength of the final product employing samples of about 140 mm x 15 mm x 10 mm.

The preliminary study on foam glass was developed preparing mixtures containing between 25-50 % of glass scrap. The scraps from treating glass packaging waste were dry ball milled for 30 minutes in order to obtain particle size into the range 75 - 180 µm. The cylindrical samples of 40 mm of diameter were realized by pressing at 40 MPa and dried at 110 °C for 2 hours, then subjected to heat treatment at 800 °C or 850 °C for 30 or 60 minutes. Glass cutting sludge composed of 6 - 7% calcium carbonate was used as inorganic foaming agent. The glass foams obtained were characterized by apparent (envelope density analyzer Geo Pyc 1360, Micromeritics) and absolute density (gas (He) pycnometer (AccyPy1330, Micromeritic), and measures of shrinkage/expansion during foaming process. The other samples were prepared using 50 – 90 % of glass scrap as matrix and as organic foaming agent, a residue from tyres pyrolisis, containing ~ 90 % of carbon.

The preparation procedure and firing conditions were similar to the other foam glass above reported.

Results and discussion

The pavement containing up to 75 wt% of small size glass shows the values of compressive strength comparable to the portland cement sample, but the progressive increase of glass percentage in the mixture produces a reduction of this property. On the contrary, the coarse glass size influences negatively the mechanical properties of manufact. In agreement with literature data regarding the use of glass in concrete products, there is a gradually worsening of resistance increasing the percentage of glass, explainable by the weak bond between the glass powder and the cement paste. The water absorption test provides an indirect indication of the material open porosity and the adhesion between glass particles and cement, obtaining an indication of compactness and resistance of the pavement in relation to its classic outdoor use. The water absorption decreases thanks to the presence of glass into the mixture for all the tested samples and independently of the particle size of the glass. Samples containing glass at different size particles, tested by mercury porosimetry, show comparable or less porosity values than the standard sample, confirming the positive effect of the glass. Fig. 1 shows the pore size distribution for the sample with 75 wt % of glass which presented the best performances. It is possible to observe that the majority of the pores have size of about 10 µm and micropores of size next at 0.07 µm are present.

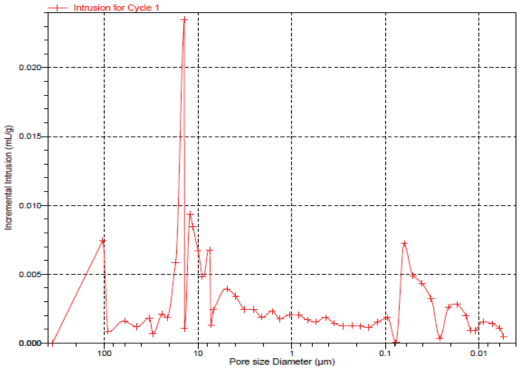

Fig. 1. Pore size distribution versus mercury intrusion volume for the sample containing 75 wt % of glass

The progressive addition of glass powder into bricks influences the properties of these products. The results are reported in Table 1.

Table 1. Technological properties of glass-containing bricks compared to standard ones

	Drying and firing shrinkage [%]			***Water absorption [%]***		***Mechanical strength [kg cm⁻]***
Sample	***Wet-dry***	***Dry-fired***	***Total shrinkage***	***Immediate***	***24h***	***Flexural strength***
Standard	7.47	0.70	8.17	13.48	15.48	118.61 ± 7.10
5% scraps	7.30	0.63	7.93	13.24	15.46	114.63 ± 6.60
10% scraps	6.75	0.98	7.73	13.65	15.24	108.04 ± 9.67
15% scraps	6.17	0.78	6.95	12.49	14.29	115.94 ± 3.27
20% scraps	6.73	0.74	7.47	12.53	13.97	109.18 ± 10.91

From the results it is clear as glass, acting as an inert in the drying step, allows to reduce the shrinkage of the sample (up to 1 % less than the standard sample) resulting in minor dimensional changes of the material and the reduction of the movements of the bricks in the kiln. Instead of clays, which tend to have plastic behaviour and shrink due to the water loss by evaporation, the glass powder reduces the shrinkage in drying step thus avoiding possible cases of cracking. Also, firing shrinkage is comparable to standard value. This is an important result because a high reduction of brick dimensions would result in the need to use a larger quantity of starting material with consequent economic burden. The decrease of linear shrinkage is in agreement with bricks made with soda - lime glass to particle size 0.1 - 0.6 mm and added up to 45 wt % in the body (Loryuenyong et al., 2009). The open porosity of bricks was evaluated by immediate water absorption. After firing, the open porosity is directly influenced by the composition of the mixture, in particular the presence of carbonates or substances that decompose provokes an increase of the porosity. The addition of glass replacing of clay constitutes a reduction of these compounds which results in a lower contribution to the formation of porosity and a consequent greater compaction of the material. In fact, the results show after 24 h and immediate water absorption values comparable or less than the standard. Low water absorptions provoke an increase in mechanical strength and resistance to freeze / thaw cycles, moreover, are also indicative of lower firing temperatures of clay bodies. The results of mechanical strength test show variable value but comparable to standard sample. These results suggest that during the firing phase the glass acts only as inert inside the mixture. There fore, it is not possible to affirm that the addition of glass is responsible of significant improvements in terms of mechanical performance of the product, but these features have been perfectly retained even after the partial replacement of clay, obtaining a product comparable to the standard bricks. The ESEM analysis confirms that the glass powder acts as inert component during sintering step. Finally, all samples have good aesthetic characteristics: no apparent defects of surface and same color of brick without glass.

Glass foams are cellular materials obtained by sintering of glass powder in the presence of a foaming agent. The peculiar properties of these materials, such as low density (~ 0.1 - 0.5 g/cm^{-3}) and high porosity (80 – 95 %), consent their use as lightweight aggregate in thermally and acoustically insulating concretes. In the performed preliminary study the foams glass has been prepared using only waste materials and sintered at relatively low temperatures (700 – 900 ºC), important aspects from the environmental point of view. In the first case in which we used cutting glass sludge as inorganic foaming agent, the apparent density measures showed that the best composition contains 50 wt % of glass scraps and 50 wt % cutting sludge and is treated at 800 °C for 30 min (0.48 g/cm^3). The porosity values calculated from apparent and absolute density are around 80 %. These data are promising due to showed properties comparable to those of typical commercial foam glass. Regarding the use of a tyre pyrolysis residue as organic foaming agent which its decomposition begins around 450 °C, the mixtures permits to obtain light - weight ceramic materials with apparent density values lower than 1 g/cm^3 using energy saving thermal treatments (< 900 °C) with respect to the traditional ceramic cycles (1100 – 1250 °C). The best composition obtained contains 50 wt % of glass scraps and 50 wt % of pyrolysis residue with an apparent density value of 0.60 g/cm^3 and firing condition of 800 °C and 30 min.

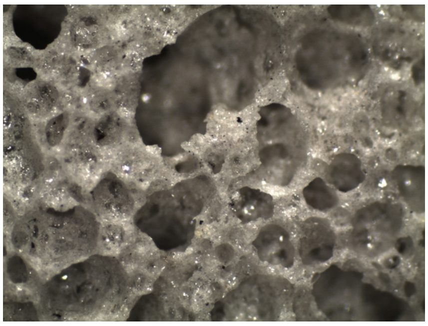

Fig. 2. Optical micrograph for the foam glass containing 50 wt % of glass scraps and 50 wt % cutting sludge treated at 800 °C for 30 min

Concluding remarks

This paper reports the results of three case studies regarding the possibility to valorize glass packaging waste substituting significant amounts of raw materials in different bodies as a function of the chemical nature and crystallinity degree of the matrix components (silicates or cement).

By obtained results it has been showed the feasibility of innovative uses in building industry in alternative to the landfill for the glass packaging waste. It is important to remark that the environmental sustainability of the new eco-products derives from the following key items: reduction of the use of virgin raw materials, valorization of waste and saving energy cycles

Keywords: ceramic, foam glass, glass packaging waste, recovery

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TYRES RECOVERY WITH THERMODYNAMIC CRACKING TECHNOLOGY

Extended abstract

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Background

In 2009, 3,400,000 tonnes of tyres were classified as waste in the European Union, with comparable quantities arising in North America and Asia (Shulman, 2011; Ondrey, 2011). Moreover, about 1 million tons of scrap tyres are generated annually in Japan (Fukumori et al., 2002; Ondrey, 2011). Tyres represent so far a valuable waste stream that, if not correctly managed, can cause important harm to the environment, and a loss of profit to the recycling industry. As an average, passengers car tyres are made of 45% rubber/elastomers, 23% carbon black, 16% steel, 6% textiles, 1-2% sulphur and the remaining percentage consist of additives (Shulman, 2011). Each car can contain up to 40kg of tires. The challenge for recyclers is that the same properties that makes tyres such durable and safe products, also make it difficult to recover the components in reusable form (Ondrey, 2011).

Tha fate of used tires depends heavily on each producer Country regulations. In Japan, for instance, about 62% of the used tires were used as an alternative fuel in various industries, such as paper manufacturing or cement production and steel manufacturing. Only 10% of the tires were recycled for rubber crumb and powder reclamation (Fukumori et al., 2002). In the U.S., about 76% of the end of life tires enters into the recycling scheme, whith roughly an half of this number being upgraded to tyre derived fuel (TDF). In the EU, due to a landfill ban was imposed to tyres and to waste with more than 13 MJ/kg LHV, material recycling reaches little less than 40%, exploiting a wide array of technologies (Ondrey, 2011; Shulman, 2011).

The first method to recycle tires involves mechanical separation of the materials by cutting, grinding and shredding the tyre itself at ambient temperature or in a cryogenic mill, followed by sorting of steel, by magnets, and textiles, with an air suck. In this way, it is possible to obtain: rubber crumbs, rubber powder, steel (in some case low grade), and fluff. Rubber crumbs can be then recycled back into the rubber industry, used for energy recovery, in road pavement or, for instance, undergo a de-vulcanization process (Fukumori et al., 2002). The second recycling option it is the thermo-chemical upgrade of the organic part by means of pyrolysis that aims at producing basically three main streams: a cracking oil, a gas and a solid carbon residue named char. The pyrolysis process consists of hating the material in absence of oxygen. In this condition, carbon bonds break up but, since there is no oxygen, there is no production of CO_2 and water as in a normal combustion, and hydrocarbons are generated by cracking high molecular weight chains into shorter fragments. Depending on reaction conditions, such as temperature, pressure and the inert gas used, the product share may vary, as well as may vary their chemical composition.

Many studies have been performed worldwide to improve tyres pyrolysis both on bench scale and pilot plant scale (Cachaço et al., 2013; Lopez et al., 2011; Murillo et al., 2006; Ondrey, 2012; Yehia et al., 2012; 4R, 2011).

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Objectives

This study was performed in order to assess the potential of a new pilot scale tyres-to-oil technology developed by CEML (Cracking Energy Machines Ltd) (patent no. BO2006A603 and BO2006A613). This work reports the preliminary results of thermodynamic cracking of pelletized used tyre feedstock. Particular attention was given to chemical and physical properties of the end products produced by the process in order to recovery energy.

Thermodynamic Cracking technology

The reactor is composed of two longitudinal rotors, supported in the upper part in order to ensure mechanical strength. In their first part, the axes of rotors have a helical profile to feed, heat and speed up the material towards the decomposition chamber. A thermal insulated cover separates the rotors from outside. Such cover is heated with a temperature gradient ranging from 350°C -at the output of the auger- to 400°C -in the decomposition chamber -. The tolerance of the cover is extremely precise and therefore it correctly adjusts the fiction of the material against walls and rotors. The profile of the axes of rotors changes in the decomposition chamber, thus favouring the friction of the material, now viscous, with moving mechanical parts. The difference with a traditional pyrolysis process is that this system allows the cracking of the material at lower temperatures and a higher heat transmission.

Friction turns kinetic energy into thermal energy which spreads in the material by means of direct conduction instead of irradiation from outside the reactor. Hence, it allows a considerably rapid heading (flash) which favours the production of unsaturated liquid molecules at room temperature, namely the cracking oil.

The material is firstly loaded up into a hopper and subsequently sucked into two feed tanks. Such procedure enables both the transport and monitoring of materials that may not be complying with the requirements or be potentially dangerous for the reactor, e.g. spring steel contained in tyres. By means of a auger at an adjustable speed, the rubber is sent to the reactor in which thermal decomposition takes place

Once the transformation process has finished, products move through a distiller provided with two self-cleaning twin augers which remove char, allowing gas to go into two condensers located one after the other. The liquid products that are collected in the condensers and the gases are stocked in special tanks. Char is cooled down and collected in a big bag. In

Fig. the plant operating scheme is reported, completed by standard working parameters. Reactors temperatures are reported both as set by the user (Ti) and as recorded (Tr).

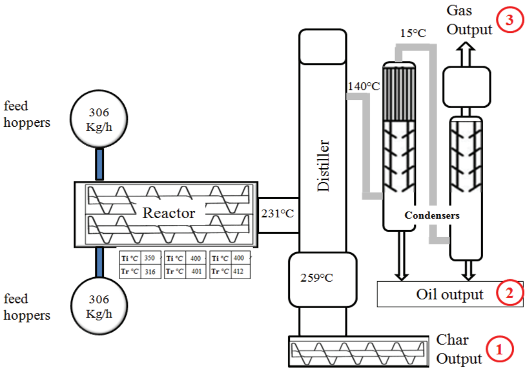

Fig. 1. Thermodynamic Cracking pilot plant worksheet (output: 1 char; 2 distilled oil; 3 incondensable gas).

In this worksheet, from left to right, the first box represents the main motor and RPM indicates the speed of the main motor powering the reactor shaft. The black circles indicates the two feed hoppers and the material flow rate. The three temperatures in the reactor indicates respectively the temperature at which the input material enters into the reactor heater, the temperature at which the cracking begins in the cracking chamber and finally the temperature at which the reaction ends.

Other parameters are represented by temperature (T) and pressure (P) registered at distiller, coolers and carbon collecting systems. In the distiller and in the carbon drying drum, RPM indicates the carbon cleaning and recovery auger operational speed.

Materials and methods

During the trial test, the reactor and the distiller have been heated up to the working temperature. Due to the limits stated by authorizations and to feed availability, it was not possible to run long term tests (more than 24h). The starting phase is very critical for this kind of system because reactor and distiller temperature are critical parameters for both cracking itself and recovered product quality.

Feeding rate has been fixed at around 611 kg/h of tyre crumbs. Samples of char, oil and gas have been collected once the system reached the stationary state (see the red collection points 1,2 and 3 respectively in Fig.). The samples have been kept in adequate vessels and analyzed. Chemical analyses were performed using international standard methods.

Results and discussion

Products mass balance

At the stationary state, solid and liquid samples have been recollected during one operating hour. Gas mass was calculated by difference (Fig. 2). Conversion rate is 79.1%, (50% oil, 29% gas) and it is in line with other plastic to fuel (PTF) technologies results (4R, 2011).

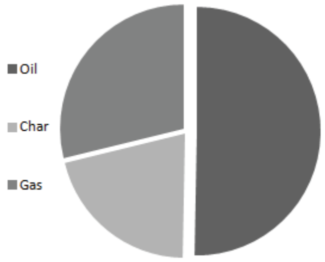

Fig. 2. Thermal cracking treatment products mass balance

In terms of yield, the share of products indicates that *Thermodynamic Cracking* is very efficient in breaking down polymeric chains because the gaseous fraction is very high compared to a traditional pyrolysis process operating at the same temperature. This result is even more satisfying when considering that no catalyst neither inert gas (such as Nitrogen) are used in this process. The main difference between this technology and other PTF is the oil and gas production rate. Usually, at 400°C, tyres oil production rate is lower in standard pyrolysis processes and char share is higher, meaning that cracking is not completed. With this technology it is possible to obtain roughly 50% oil ready to be used into a power generator. This is mainly due to the kinetic energy that this technology transmits to the softened rubber that, in addition to the external heat, enables cracking to happen at lower temperature.

Differences in products share can rise from the peculiar mechanical stress, which is the basis of this technology, applied to the rubber material, which is a thermosetting material. In fact, with respect to other pyrolysis systems, gas yield is more than 2 times higher with Thermodynamic Cracking. Being the main goal of this system power generation, a higher share of gas can be attractive due to its high power conversion efficiency.

Table 1. Analytical results: oil and gas characterization

OIL				*Gas*			
Parameters	***Method***	***Results***	***Unit***	***Parameters***	***Method***	***Results***	***Unit***
Gross calorific value	ASTM D240-07	10486	kcal/kg	Nett calorific value	ASTM D5865	35920	kJ/kg
Water content	EN ISO 12937	548	mg/kg	Hydrogen	ISO 6974-6	6.2	% v/v
Ash content	EN 6245	0.018	% wt	Hydrogen Sulphide	ISO 6974-6	0.55	% v/v
Total contamination	EN 12662	82	mg/kg	Nitrogen	ISO 6974-6	8.0	% v/v
Copper strip corrosion	EN ISO 2160	1b		1.3 Butadiene	ISO 6974-6	4.0	% v/v
Density at 15°C	UNI EN ISO 3675	0.8536	kg/l	Acetylene	ISO 6974-6	0.006	% v/v
Flash point	UNI EN ISO 2719	4	°C	Methane	ISO 6974-6	16	% v/v
Cetane index (calc)	EN ISO 4264	35		Ethane	ISO 6974-6	4.3	% v/v
Distillation curve				Propane	ISO 6974-6	2.3	% v/v
-I.B.P.	EN ISO 3405	42.3	°C	n-Butane	ISO 6974-6	0.39	% v/v
-5%	EN ISO 3405	83.4	°C	Carbon monoxide	ISO 6974-6	8.6	% v/v
-10%	EN ISO 3405	111.9	°C	Carbon dioxide	ISO 6974-6	12	% v/v
-20%	EN ISO 3405	148.5	°C	n-Hexane	ISO 6974-6	0.011	% v/v
-30%	EN ISO 3405	167	°C	n-Pentane	ISO 6974-6	0.077	% v/v
-40%	EN ISO 3405	178.5	°C	Oxygen	ISO 6974-6	0.17	% v/v
-50%	EN ISO 3405	190.1	°C	Ethylene	ISO 6974-6	7.5	% v/v
-60%	EN ISO 3405	219	°C	Propylene	ISO 6974-6	2.9	% v/v
-70%	EN ISO 3405	247.8	°C	Isobutane	ISO 6974-6	0.79	% v/v
-80%	EN ISO 3405	278.5	°C	1 Butene	ISO 6974-6	0.67	% v/v
-90%	EN ISO 3405	312.9	°C	Isobutene	ISO 6974-6	<0.0005	% v/v
-95%	EN ISO 3405	338.6	°C	2 trans Butene	ISO 6974-6	0.69	% v/v
-F.B.P.	EN ISO 3405		°C	2 cis Butene	ISO 6974-6	<0.0005	% v/v
recovered at 250°C	EN ISO 3405	67.4	% v/v	Ethylacetylene	ISO 6974-6	0.051	% v/v
recovered at 350°C	EN ISO 3405	97.6	% v/v	Methylacetylene	ISO 6974-6	0.14	% v/v
recovered at 370°C	EN ISO 3405	N.R.	% v/v	other hydrocarbons	ISO 6974-6	24	% v/v
Sulphur content	UNI EN ISO 20846	7820	mg/kg	Sulphur content	ASTM D5504-09	9555	mg/m3

Pour point	ASTM D97-08	< -66	°C				
Carbon Residue	ISO 10370	0.05	% wt				

Analytical results are reported in table 1. Critical parameters for oil classification and combustion are: gross heat value (GCV), distillation curve and sulphur content. GCV (10486 kcal/kg equal to 43.8 MJ/kg) is in line with other liquid hydrocarbon fuels, like diesel, and it is suitable for power generation in diesel engines. The distillation curve reveals the liquid to be quite light and together with sulphur content lower than 1% and low viscosity, allow this product to be classified as a "low sulphur content fuel" according to UNI 6579:2009. Also the density (0.85 kg/m^3) and the kinematic viscosity of the oil at 40°C (usually below 3 mm^2/s), are similar to those of diesel fuel, indicating that this product could be suitable for diesel generators. Gas composition reveals almost 70% hydrocarbon content, with a high methane concentration. Other C2 like ethane and ethylene are present in good concentration along with hydrogen. Gas GCV is high and in line with natural gas one conventionally used in power generation.

Energy balance

The Energy balance is calculated as net power production, by summing up liquid and gaseous product contributions based on each specific heat value, minus the internal electric consumptions. Solid carbon combustion is not considered in this energy balance, even though it could follow energy recovery route as coke or coal. Internal electric consumption is the sum of main drive motor, hoppers, pumps, heaters, compressors and all other utilities, and it amounts at 98 kWh.

- Oil production: 360 L *x* 0.85 kg/L =(306 kg/h x 10486 kcal/kg x 4.186 J/cal) / 3600 kJ/kW*h = 3731 kW*h thermal
- Gas production: (176 kg x 35920 kJ/kg) / 3600 kJ/kWh = 1756 kW*h thermal
- Total energy generation could be 5487 kW*h thermal
- Net energy generation could be 5389 kW*h thermal

Finally, with an input of 611 kg/h of crumb rubber, the system can produce 5389 MW*h of thermal energy which could be converted into electrical energy. More in detail, a note of the power generation builder (http://www.cat.com low BSFC 400 kW*h) indicates that for each liter of oil feeding conventional reciprocating engines it is possible to produce about 4.83kWh.

This means that during one hour operation, if the produced liquid fuel is completely used for generation, it is possible to obtain 360 l x3.86 kW*h/l = 1.39 MW*h of electric energy, assuming a power factor of 0.8.

Concluding remarks

The complex nature of tyres, which include several rubbers, carbon blacks, steel cord and other organic and inorganic minor components, makes it difficult to recycle them. Furthermore, the main component of tyres, rubber, is a chemically cross-linked polymer and, therefore, is neither fusible nor soluble and, consequently, cannot be remoulded into other shapes without serious degradation.

Even thought, this is a preliminary study and it is necessary to operate the machinery for a longer time in duration stress tests, the results are encouraging and further improvements are expected.

This trial showed that with this plant it is possible to obtain about 50% cracking oil ready to be burnt into a power diesel generator. Another product obtained during the test has been a gaseous fraction accounting for about 30% suitable for energy recovery. Moreover, the process produced a solid carbon powder which could be used as carbon black or for energy recovery.

Keywords: tyre recycling, pyrolysis, plastics to oil.

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WASTE PLASTICS MANAGEMENT IN MUNICIPALITIES: LOGISTICS AND PROCESSES IN LOMBARDIA (NORTHERN ITALY)

Extended abstract

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Background

A partnership of 49 Municipalities lying in Lombardia (Northern Italy) and belonging to the District "Monza and Brianza" has entrusted the management of the Municipal Solid Waste (MSW) to two Public Companies: "C.E.M. Ambiente S.p.A." - which owns and operates a *transfer station* and a *multi-material centre* - and "SERUSO S.p.A.", whose single facility is set up and equipped for a high performance factory sorting of the dry fraction of the urban waste.

The catchment area is populated by 448 000, living in an area of 366 km^2. The management system starts with household sorting for multi-bin curbside collection; followed by hauling to selection and physical treatment facilities; and last, transport of the selected fractions to final destinations.

The yearly throughput of "C.E.M. Ambiente" is about 296 000 t, of which over 70% home-sorted. Extra-CEM customers add to this amount about 40 000 t/yr. When calculated on the partner municipalities, the waste generation rate is almost 1.8 kg/capita per day including waste from craftsmen and workshops.

Less than 1% of the collected waste goes to landfill and about 8% to incineration with energy recovery (WTE). Since "C.E.M. Ambiente" operates mainly the logistics, however; and part of the materials recovery is actually made downstream its gate at "SERUSO" facility, where some by-products are unavoidably generated; the overall share of WTE will be slightly higher.

Electric energy produced from the combustible by-products of "C.E.M. Ambiente" and "SERUSO" covers largely the energy needs of the recovery and cleaning processes.

It is worthwhile stressing that in this district also waste from street sweeping – as much as 8 200 t/yr – is turned into sand, gravel and like for civil works.

"C.E.M. Ambiente" uses also fuel energy, to operate collection and hauling vehicles and factory handling machines, all of them powered by Diesel engines. Fuel requirements for TS and MMC in 2011 were 78 405 and 14 605 litres, respectively. Regrettably, these needs cannot be satisfied in any way with recovered energy.

This article describes the MSW management system in Year 2011, as the core of three; and reports on its materials, fuel and electric energy flows, with particular emphasis on waste plastics. The calculation of embedded energy and carbon footprint, assumed as ecological indicators, has been shifted to a following paper. Materials and energy balances are obviously the basis for evaluating the performance of the system in terms of ecological and economical benefits

Objectives

In this context, the main objective of the present study was to simulate and evaluate the performances of water scrubbing technology with regeneration and recirculation of water applied for the removal of pollutants from biogas,

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in particular CO_2, and to generate new data for scale-up calculation and techno-economic analysis of the process. There are two main approaches to modeling absorber and stripper: equilibrium and rate-based approaches. Both approaches are used in this study.

In particular, another objective of this work was to obtain reliable phase equilibrium data in binary systems (CO_2+H_2O, CH_4+H_2O, H_2S+H_2O, N_2+ H_2O, O_2+ H_2O) and quaternary system (CO_2 – CH_4 – H_2S - H_2O) based on data collected from literature. Further, the reliable experimental data will be further used to test the ability of various thermodynamic models to calculate the solubilities of gases in water. All the simulations were developed by commercial Software tool Aspen Plus (V.7.1., 2009).

Methods and results

The data to draw the materials flows and balances were taken from the ordinary records of the two Public Companies "C.E.M. Ambiente S.p.A." (Canzi, 2012) and "SERUSO S.p.A." (SERUSO, 2013) and worked. The Fig.s of the integrated system for year 2011 are shown in Fig. 1.

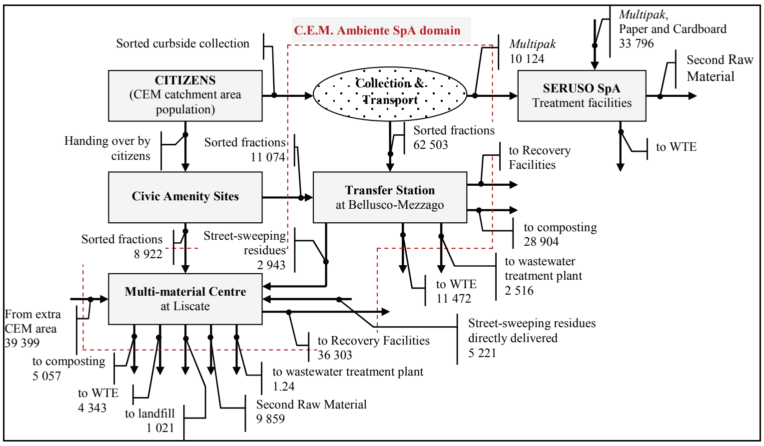

Fig. 1. Fluxes of urban waste in the District of Monza and Brianza, Lombardia (IT) – Year 2011 (figures in tons)

More than 73 000 tons of MSW were carried to the *transfer station* (TS) at Bellusco Mezzago. The output of the plant was constituted mainly by the following fractions: almost 9 000 tons of glass, 18 000 of wood and 29 000 of wet waste; 3 000 tons of earth from street sweeping were salvaged. Destinations of this output fractions were: 40 % to recovery and to composting; 15.6 % to incineration with energy recovery (WTE).

The *multi-material centre* (MMC) at Liscate received more than 56 400 tons of MSW; its more valuable output was almost 27 400 tons of glass and 5 800 of glass and tins mixed. Destinations of the output fractions were approximately: 64 % to recovery, 9 to composting, 7.7 to WTE facilities, 1.8 to landfill and 17.5 % to sale as secondary raw materials. The electric energy needs amount to about 412 800 kWh.

On the whole, the MMC at Liscate carries out more sophisticated and selective operations; while the TS at Bellusco - Mezzago makes – among others - the heavy work of shredding and grinding bulky and tough waste.

A source-sorted fraction of MSW of special interest is the one made up by plastics and metals packaging, paper and cardboard which is named *multipak*. In the last three years about 10 000 tons per year have been generated, that gives a mean value of 61 g per capita and day. The absolute amounts of *multipak* produced in the CEM service district – along with their breakdown into fractions - are drawn in Fig. 2.

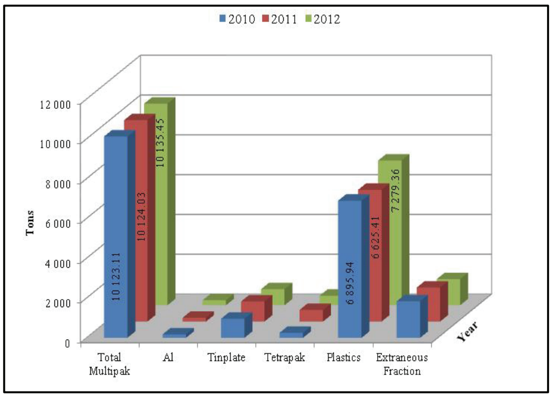

Fig. 2. Amounts of *multipak* and of its fractions produced in the CEM service district

Processing *multipack* is the duty of SERUSO, and will be treated in detail later in this paper. Table 1 below shows the integrated routing of waste fractions made by the two MMCs of the District.

Table 1. Waste output from Transfer Station and Multi-material Centre

Description	***Source***	***EWC Codes for the Output from the Selection Facility of:***		***Destination***
		Liscate	***Bellusco - Mezzago***	
Mixed munic. waste	Non sorted urban waste	20 03 01	20 03 01	Incineration
Street sweeping residues	Materials from street sweeping	---	20 03 03	Recovery plants
Wet waste	Biodegradable kitchen waste		20 01 08	Composting
Glass	Glass packaging curbside collection	15 01 07	15 01 07	*Co.Re.Ve.(°)*
Wood	Wood non containing dangerous substances		20 01 38 19 12 07	*Rilegno (°°)*
Leachate Rain water	Leachate from various sources First flush water Leachate from glass-tins heaps	19 07 03 19 09 02	19 07 03 19 09 02	Wastewater treatment plant
Plastic packaging	Bulky waste from Civic Amenity Sites		15 01 02	Recovery facilities
Metals			20 01 40	
Paper and cardboard			20 01 01	
Wood Mattress			20 01 11	
Other waste			19 12 12	WTE
Plastics			20 01 39	Recovery facilities
Lubricating oils	Used oils from fork lifts		13 02 08	Recovery facilities
Aluminium and tinplate	*multipak* from curbside collection	15 01 04	15 01 04	Recovery facilities with *CIAL (°°°) and C.N.A. ($^+$)*
End-of-life tyres	Sorted urban waste		16 01 03	Recovery facilities
Non-ferrous metal	Waste from maintenance		16 01 18	
Aluminium	Sorted urban waste		17 04 02	
Waste from sewage	Waste from sewer cleaning		20 03 06	Wastewater treatment plant
Inorganic production scraps	Residues from treatment of glass and street sweeping materials	19 12 12	---	Recovery facilities
Organic production scraps	As above	19 12 12	---	WTE
Glass	Glass from neon tubes treatment	19 12 05	---	Recovery facilities
Ferrous metals	Material from glass, tins, neon tubes treatments	19 12 02	---	C.N.A. Recovery facilities
Non-ferrous metal	Material from neon tubes treatments	19 12 03	---	CIAL
Sludges from treatment of industrial waste water	Material from street-cleaning activities	19 08 14	---	Landfill / Recovery facilities
Inorganic waste (rocks)	Material from street-cleaning treatments	19 12 09	---	Recovery facilities
Hg powders	Material from neon tubes treatments	19 12 11*	---	Landfill
Waste batteries	Sorted urban waste	20 01 34*	---	Landfill
Expired drugs		20 01 32*	---	WTE
Syringes		18 01 03*	---	WTE
TV monitor		20 01 35*	---	WEEE disassembling and recovery
Refrigerator		20 01 23*	---	
Electronic compon.		20 01 36	---	
Sand, gravel	Treatments o f materials from street sweeping	sold	---	Asphalt production
Glass “oven-ready”	Material from glass treatment	sold	---	Glassworks
Toner		08 03 18	---	Recovery
Lead batteries		16 06 01*	---	Recycle facilities

(°),(°°),(°°°), ($^+$) are institutional Syndicates aimed at standardizing quality and prices of recovered materials in Italy. In order: glass; wood; aluminium; and steel.

Sorting *multipak* is the main task of the SERUSO facilities, where also selected paper and cardboard are delivered from extra-CEM customers. This source - sorted dry waste stream is made of: plastics cutlery and tableware; bottles and food boxes labelled PE, PET, PVC, PP; caps of PE, PET, PP and silicone; *tetrapak*; steel as spray cans; aluminium foil and like (Rigamonti and Grosso, 2009). Fractions of *multipack* delivered from CEM area are illustrated in Fig. 2: plastics represent the major fraction, 68%, followed by *extraneous fraction*, 16%, and tinplate, 9%. If paper and cardboard are considered, *multipak* composition entering SERUSO facilities becomes: 60% plastics, 14% paper and cardboard, 12% extraneous fraction, 8% tinplate, almost 4% Tetrapak and almost 2% Aluminium.

In the SERUSO plant, *multipak* is machine processed to two output streams: homogeneous plastics fractions sent to recycling industries as secondary raw materials; and *extraneous fraction* sent to energy recovery. The principal unit operations put in practice are: screening by rotary and ballistic screens; followed by magnetic and optical separation; and finally baling of the selected materials. The activities carried out by SERUSO have consumed, in year 2011, about 2 100 MWh of electrical energy and about 63 000 litres of diesel fuel, used by mechanical equipments for handling the material to be processed.

The extraneous fraction (EWC Code 19 12 12) has a LHV (Lower Heating Value) of about 10 000 kJ/kg, up to 15 000; it is delivered to a near WTE facility to produce electrical energy and heat. The amount was 6 316 tons in year 2011 and 4 886 in the year 2012, with a decreasing trend all over the last three years. In the year 2012, the incineration plant has produced about 708.5 kWh_{el} per ton of waste processed. Since the plant receives waste also from extra-CEM catchment area, this Fig. comes out considering the total waste delivered to the plant (86 100 tons) and the total electrical energy produced (61 000 MWh_{el}).

The virtual amount of electrical energy produced at the incineration plant from SERUSO extraneous fraction only – apart from heat for district heating – is estimated 4 670 MWh, largely sufficient to satisfy the energy requirements of the selection plants. A resource use too often underrated in the eagerness for zero-waste is that of water. In the TS only, in year 2011, there was a water consumption of about 43 073 m^3.

Discussion

The data recorded by the two Companies and worked in this research demonstrated that source-sorted MSW is a good basis to get second raw materials with high efficiencies: i.e., 53% of materials recovery; 23% organic waste processed to compost, and 11% energy recovery (weighted averages). Minor amounts of valuable materials were directly sold.

The unit electric energy needs for mechanical separation at CMM amount to about 7.3 kWh/t; those at SERUSO are just 0.05. All these can be satisfied with energy coming from combustion of non-recyclables. The same does not hold for transport, although all the sites making up this integrated system lie within a less than 30 km reach.

Water use corresponds to 0.76 m^3 per ton of waste processed. Treated wastewater reuse accounted for about 70 % of the supply, the remaining being groundwater.

Concluding remarks

The high recovery MSW management in the District investigated is made possible by the circumstance that within a few dozen kilometres reach the treatment facilities and the industrial factories lie, to which materials are delivered. WTE plants – when limited in throughput to 10 – 20% of waste generated – are not competitors with recycling, and contribute to the sustainability of the system. All these data will be used in a following paper to calculate the CO_2 emissions and to quantify the environmental benefits of this integrated waste management system.

Keywords: municipal dry waste; waste plastics; waste treatment sustainability

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URBAN MINING: A SUCCESSFUL EXPERIENCE OF THE EU-FP7 *HYDROWEEE* PROJECT

Extended abstract

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Background

The final disposal of electrical and electronic devices is an issue of current worldwide concern. Disposal and incineration can pose threats to the whole environment, from the atmospheric to the aquatic and terrestrial compartments. Indeed, gases produced during thermal treatments (e.g. dioxins, furans, polybrominated organic pollutants and polycyclic aromatic hydrocarbons) can be released into the environment if adequate flue gas cleaning systems are not implemented. Similarly metals can be released from waste electrical and electronic equipment (WEEE) disposed of in landfill sites by leaching processes. As man-made devices such as electrical and electronic equipment, accumulators and fluorescent lamps are rich in valuable metals (e.g. Au, Ag, Cu, Zn, Co, Y), WEEE recycling for the production of secondary materials needs to be encouraged (Ongondo et al., 2011)

In the current scenario, recycling policies are gaining more attention, and many countries have drawn up regulations for the management of WEEE, including European Union, the United Kingdom, China, Japan, South Korea, Taiwan, some states of the U.S.A. In particular, the European WEEE Directive (EC Directive, 2012) aims at WEEE recycling, to reduce the disposal of waste and "to contribute to the efficient use of resources and the retrieval of valuable secondary raw materials". WEEE represents a source of metals, which have been mined from ore minerals, where they are often present at low concentrations: indeed, these are included at higher concentrations as the pure metals or metallic alloys in electrical and electronic equipment. Considering this context, "urban mining" looks more attractive than the conventional one.

Objectives

The main objective of this manuscript is the presentation of a successful case study of urban mining dealing with two research projects funded within the European FP7 framework: HydroWEEE (2009-2012) and its follow up HydroWEEE-DEMO (2012-2016).

Outline of the work

This manuscript is addressed at presenting a successful example of urban mining, achieved within EU-FP7 funded projects. The first FP7-Research for SMEs project HydroWEEE (2009 – 2012) dealt with the recovery of rare and precious metals from WEEE including lamps and spent batteries. Innovative processes feasible for SMEs were developed and a mobile prototype was performed; this was fed with a metal rich fraction, residual of widely applied

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physical processes for the recycling of metals from fluorescent lamps, cathode ray tubes (CRTs), spent Li-ion accumulators, printed circuit boards (PCBs), liquid crystal displays (LCD). Recovered metals were yttrium, zinc, cobalt, indium, copper, gold and silver. The objective of the follow-up FP7 - Environment project HydroWEEE Demo (2012 - 2016) is to build 2 industrial demonstration plants (1 stationary and 1 mobile) in order to test the performance and prove the viability of the processes from an integrated point of view (technical, economical, operational, social) including the assessment of its risks (including health) and benefits to the society and the environment.

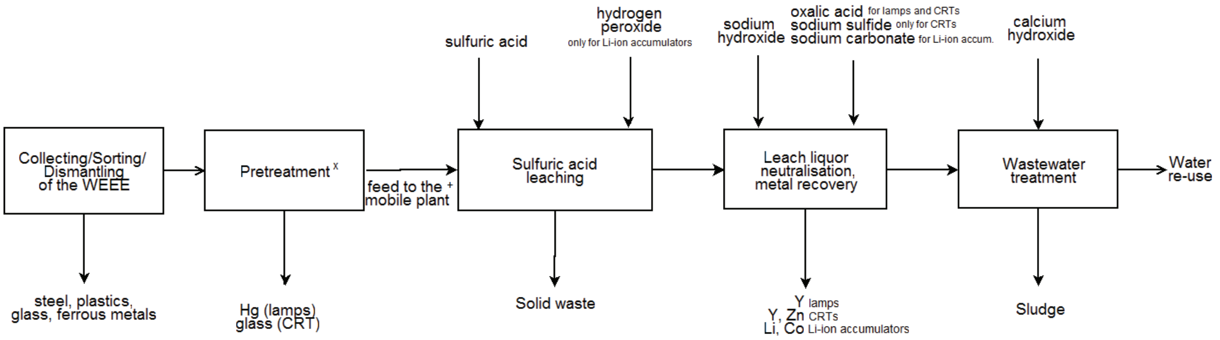

Fig. 1. Block diagram of the processes carried out in the HydroWEEE portable plant.
^{x} Pretreatment: Hg distillation (fluorescent lamps)/CRT recycling process/grinding (Li-ion accumulators, LCD)
$^{+}$ WEEE residues that enter the portable plant: fluorescent powders (fluorescent lamps and CRTs)/ ground electrode material (Li-ion accumulators), ground panel (LCDs).

Results and discussion

The processes addressed for the exploitation of WEEE residues (from fluorescent lamps, CRTs, Li-ion accumulators, PCBs and LCDs) were carried out in the portable plant from the HydroWEEE research project. Specific, essentially physical, pretreatments were carried out according to the kind of WEEE, which were aimed at the recovery of the main fractions (e.g. glass, plastics, metals) and at the production of the WEEE residues that are not treated by most small and medium enterprise (SME) recyclers at present . I

In particular, the pretreatments included crushing, sieving and Hg removal by distillation, for the fluorescent lamps (Fig. 1); disassembly and CRT recycling (e.g. with diamond cutting technology), for the CRTs (Fig. 1); sorting, dismantling and grinding for the Li-ion accumulators (Fig. 1); dismantling and panel shredding/milling for the LCDs (Fig.1) and sorting, shredding, magnetic separation and aluminium separation, for the PCBs (Fig. 2). The initial characterization and preliminary tests of the WEEE residues were carried out on the powders produced from these pretreatments.

From the fluorescent tubes, these contained 5 % to 7 % Y, as oxides, with rare earth elements also present, such as Eu (although these were not targets of the purification within the HydroWEEE project). From the CRTs, there were 15 % to 20 % Y and 30 % to 35 % Zn, which were present as oxides and sulfur compounds. The ground electrode material produced after the Li-ion accumulator pretreatment contained 23 % to 25 % Li and 2 % to 3 % Co. As concerns LCDs, the ground panel had around 200 g/tonne In content. Finally, for the PCBs, there were 25 % to 28 % Cu, 400 g/tonne to 800 g/tonne Au, and 1400 g/tonne to 1900 g/tonne Ag. These were thus the starting point for achieving the most suitable and effective treatments for metal extraction and recovery. The feed materials for the portable plant were thus the WEEE residues: fluorescent powders from fluorescent lamps and CRTs , ground electrode material from Li-ion accumulators, ground panel for LCDs and waste granulate material from PCBs. A leaching operation with sulfuric acid was a common unit operation for metal extraction (Y, Zn, Cu, Li, Co, In) from WEEE residues. For the Li-ion accumulator and PCB WEEE residues, hydrogen peroxide was also added under acidic conditions, as a reducing agent. In the case of PCBs, this was followed by a thiourea leaching step (for Au and Ag dissolution). The metal recovery from the leach liquor was carried out by selective precipitation operations, according to each of the specific metals to be recovered. The products were recovered here with extraction efficiencies of around 90 % for Y, Cu, Au, Ag, 93 % for Li, and >97 % for Co and In, with respective purities of 95 % , 99.5 %, 80 % (Au+Ag) , 18 % and 43 % .

These relatively low purities are not suitable for direct commercialization (where at least 99 % would be needed), but these products are marketable to companies that use them as feed for a final purification. A final step of wastewater treatment was also considered, based on the use of lime for precipitation and neutralization processes. Figs. 1 and 2 show the block diagram of the processes. All of the details concerning the processes developed can be found elsewhere (De Michelis et al., 2011; Granata et al., 2012; Innocenzi et al., 2013; Kamberovic et al., 2011; Rocchetti et al., 2013). Figs. 3, 4 show images of the mobile prototype.

A life cycle assessment (LCA) was applied to the hydrometallurgical treatments carried out using the new portable prototype plant. The category of global warming potential was the most critical one considering the specifications for southern European territories, with 13.3 kg CO_2/kg recovered metal from the powders/residues from fluorescent lamps, 19.2 kg CO_2/kg from CRTs, 27.0 kg CO_2/kg from Li-ion accumulators and 25.9 kg CO_2/kg from PCBs (Table 1). In general, these processes appear beneficial for the environment in terms of CO_2 emissions, especially for fluorescent lamps and CRTs. Further details can be found elsewhere (Rocchetti et al., 2013).

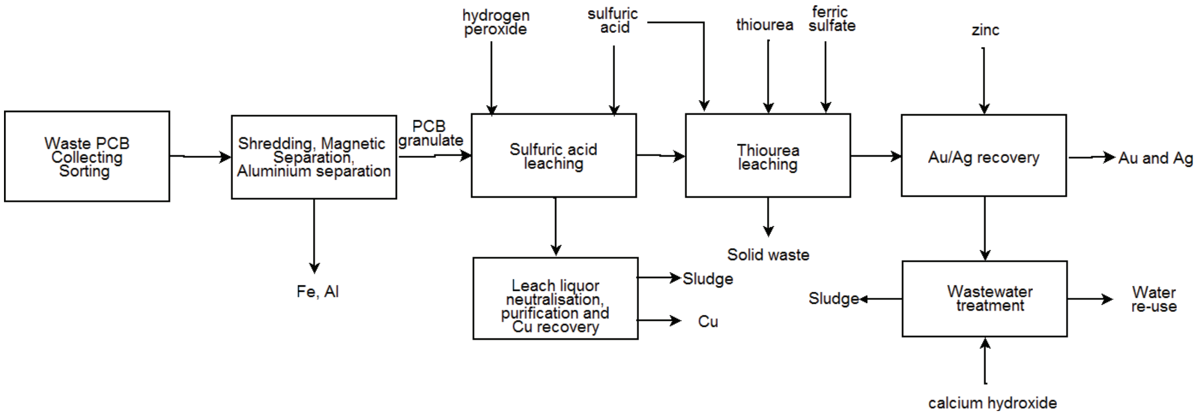

Fig. 2. Block diagram of the process carried out in the HydroWEEE portable plant aimed at metal recovery from PCB granulate

Table 1. Carbon dioxide emissions from the treatment of selected fractions of the WEEE residues

	HydroWEEE process		**Primary process**
	g CO_2/g WEEE residue	g CO_2/g metal	g CO_2/g metal
Fluorescent powder from lamps	0.9	13.3 g CO_2/g Y	144.9
Fluorescent powder from CRTs	2.0	19.2 g CO_2/g metals (13.7 g for Y ; 5.5 g for Zn)	104.5
Ground electrodic material (Li-ion accumulators)	5.4	27.0 g CO_2/g metals (24.5 g for Li; 2.5 g for Co)	27.4
PCB granulate	7.8	25.8 g CO_2/g metals (0.1 g for Au; 0.2 g for Ag; 25.5 g for Cu)	55.7

Fig. 3. Images of the portable prototype realized under the EU-FP7 HydroWEEE project - outside view

Fig. 4. Images of the portable prototype realized under the EU-FP7 HydroWEEE project - inside view

Concluding remarks

Waste from Electrical and Electronic Equipment (WEEE) is the fastest growing waste stream in Europe, that contains a high amount of valuable metals. In 2010 the Raw Materials Initiative of the European Commission (2010) defined 14 critical raw materials, most of rare metals which are used for electronic devices belong to this category. Hence innovative processes feasible for SMEs were developed and a mobile prototype was realized within the previous FP7-Research for SMEs project HydroWEEE (2009 – 2012).

The follow up HydroWEEE-DEMO has been running for less than one year: processes are being improved, also addressing additional metals leading to the "critical raw material" list.

Two industrial scale, real-life demonstration plants (one stationary and one mobile) are in the construction phase and will be delivered soon, in order to test the performance and prove the viability of the processes from an integrated point of view (technical, economical, operational, social) including the assessment of its risks (including health) and benefits to the society and the environment as well as remove the barriers for a wide market uptake later on.

Keywords: electronic waste, hydrometallurgy, recycling, urban mining

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SORBENT MATERIALS FOR THE CLEANING OF SEWAGE BIOGAS IN HIGH TEMPERATURE FUEL CELL PLANTS

Extended abstract

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Background

A good solution to reduce greenhouse gas emissions is represented by the micro-cogeneration locally distributed with fuel cell systems. Fuel cells directly transform efficiently fuel into electrical energy by electro-chemical reactions. Amongst fuel cells, SOFCs achieve the highest electrical conversion efficiencies (Buono and Simeone, 2010; Cresson, 1999) with wide fuel flexibility. Extensive research has been performed on fuel cells (Andujar and Segura, 2009; Austergard et al., 2006; Caserini et al., 2004). The integration between SOFCs in domestic and locally distributed systems however represents in theory and in practice a possible solution to reduce pollutant emissions improving also the fuel exploitability. One of the main challenges with SOFCs is the low tolerability with contaminants (VOCs) contained in biogenous fuel, such as biogas from the anaerobic digestion of waste water treatment plant sludge. Main compounds found in this biogas are methane and carbon dioxide, while trace compounds are sulphur, chlorine and higher hydrocarbon compounds (from tens to hundreds ppm(v)).

Mainly cell voltage decreases, cell power drop and fuel cell degradation are the main consequences of fuel impurities for the anode compartment (Lanzini et al., 2013) as well as carbon deposition phenomena (Lanzini and Leone, 2010). The problem of VOCs tolerability is addressed by making fuel cells more tolerant against these compounds (Wu and Liu, 2002), or by reducing the amount of VOCs in the fuels (Song, 2002). The most relevant volatile contaminants are sulfur, aromatic, carbonyl and chloro-compounds (Papurello et al., 2012; Sasaki et al., 2006), and siloxanes. The latter two groups are derived from the starting biomass loaded into the digester (Papurello et al., 2012). Hence, it is necessary to implement a cleaning section which effectively removes at ultra-low level VOCs from the biogas in order to feed SOFC systems. To achieve such stringent requirements, commercial sorbent materials are investigated in laboratory conditions.

Objectives

The main objective of this work was to investigate on the effectiveness of commercial filter: ZnO, RST3 and Carb-ox activated carbon. The effect of biogas water content was tested according to measurements done in a real waste water treatment plant (WWTP) (around 7.28 %vol.). At SMAT site H_2S contained in the biogas is one of the main pollutant compounds. Contaminant concentrations, GHSV values and water percentages affect the breakthrough time decreasing the filter removal performance. To know in which way these performances are affected was developed this preliminary work. Especially water content on equal terms affect strongly the removal performance of the sorbent filters, as previously described by Hernandez et al. (2008). In this work we focused on the water content effect on the sulfur removal performance of sorbent materials for SOFC applications. Preliminary considerations on the filter optimization are also reported in order to design a real scale gas cleaning unit for a SOFC stack (SOFCOM project). SOFCOM is an applied research project devoted to demonstrate the technical feasibility,

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the efficiency and environmental advantages of CCHP plants based on SOFC fed by different typologies of biogenous primary fuels (locally produced) also integrated by a process for the CO_2 separation from the anode exhaust gases.

Outline of the work

This work is divided in two main parts:

- The first part covers the biogas characterization made at SMAT waste water treatment plant site.
- The second part covers the investigation on the gas cleaning section at the laboratory conditions, controlling the methane, carbon dioxide volume percentage, the hydrogen sulfide concentration and the water content.

Methods

This paper presents the experimental results achieved for three different sorbent materials for the biogas cleaning for SOFC applications. Characteristics of sorbent materials adopted are indicated in Table 1.

Gas analysis of the biogas produced from the SMAT site, adopting waste derived biomass, was registered monthly (from January to July). For the chlorine, fluorine and bromine compounds it was adopted a method published on DM 25/08/2000 All.2; for the siloxanes and mercaptanes the EPA-TO-15-1999 method; for the sulfur it was adopted the adsorption on an activated carbon cartridge following the EPA 9056A 2007 method with the Mahler bomb. The experimental set-up adopted for the sorbent material test with simulated biogas ($CH_4/CO_2 = 1.5$), H_2S at 30.72 ppm(v) and demineralized water at 7.28% vol. is reported in Fig. 1. The biogas mixture and pollutant compound were inserted to the experimental set-up with mass flow controllers (Bronkhorst, The Netherlands) whereas the cylinder gas are prepared from (Siad spa, Italy). The demineralized water was added to the main stream using a liquid mass flow controller and a controlled evaporator mixer (Bronkhorst, The Netherlands). Fig. 1 depicts the experimental set-up adopted, red color represents the heated lines at 50°C with heater strings (isopad Thermocoax, Germany) controlled via a PID regulator (Horst, Germany). A PDMS (20 µm) membrane filter, to protect the mass spectrometer from the carbon particles, was inserted between the filter line and the heated trap before the capillary line of the mass spectrometer HPR 20 (Hiden Ltd., UK). The sorbent materials were grounded up to 100-180 µm with a vibratory sieve shaker (Fritsch, Germany). The filter cartridges were prepared with Teflon tubes with around 0,12 g of sorbent material.

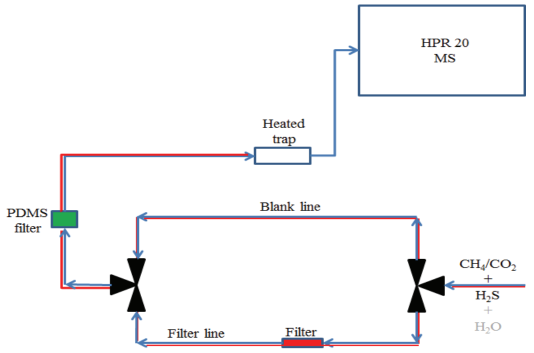

Fig. 1. Experimental set-up

Table 1. Characteristics of sorbent materials tested

Sorbent material	***Apparent density (kg m^{-3})***	***Relative density (kg m^{-3})***	***Note***
Activated carbon, *RST3 Norit*	200-600	2100	
Zinc oxide, *Actisorb S2 ZnO Clariant*		1090	
Activated carbon, *Carb-OX Air dep*	520	1650	The best performance are achieved with low fraction of oxygen and water – manufacturer

Results and discussion

This paper presents results of the gas cleaning removal with commercial sorbent materials. This work was focused in particular on the sulfur compound removal with and without the contemporary presence of water.

Biogenous gas from the anaerobic digestion of sewage sludge from a waste water treatment plant (SMAT spa), showed the principal contaminants: sulfur, chlorine, siloxane compounds and hydrocarbons. Fig. 2 depicts the concentration for siloxanes (2.a) and halogens (2.b). Organic silicon compounds are in the range of 2.5 and 10 mg/Nm^3 with a highest concentration of D5, D4, D3. Halogen (namely HCl) concentration is around 0.25 mg/Nm^3. Halocarbon concentration is around 1 mg/Nm^3 with dicholoroethylene being the most abundant compound. Total sulfur, not reported in Fig. 2, has on average a total concentration below 120 ppm(v) in the as produced biogas.

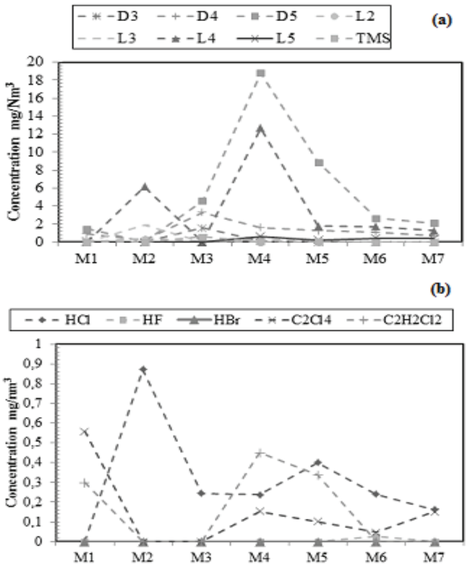

Fig. 2. Siloxanes (a) and Chlorine compounds in the as produced biogas from the SMAT WWTP plant

Considering the H_2S as the principal sulfur compound its concentration trend is reported below, with the maximum concentration around 100 ppm(v).

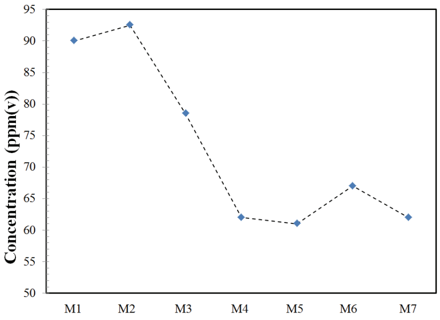

Fig. 3. Hydrogen sulfide in the as produced biogas from the SMAT WWTP plant

Resuming the maximum concentration monitored are: H_2S 95 ppm(v), HCl 0.6 ppm(v), D5 1.25 ppm(v) and D4 0.33 ppm(v). These concentrations are extremely detrimental for fuel cells as reported by Sasaki et al., 2011. For this reason further work is needed especially on the siloxane removal with sorbent materials, due to the low limits for SOFCs detrimental effect is reported around 100 ppb(v) (Sasaki et al., 2011).

Three different sorbent materials were tested for the H_2S removal with simulated biogas mixture CH_4/CO_2. Fig. 4 depicts the removal performance as the ratio between the outlet concentration (C) and the inlet concentration (C_0) of the filter cartridge. The best performance are achieved by ZnO and RST3 activated carbon for the sulfur removal. Carb-ox activated carbon decreases the filer performance around 9% in dry conditions. At stationary conditions this material removes only 30% whereas the other two sorbents 60%.

The impact of the biogas water content on the H_2S removal was investigated for the three different sorbent materials. At the SMAT plant the water contained in the biogas was monitored, a mean value was registered around 7% vol. Considering a humid biogas the filter performance trend changes accordingly to Fig. 4. Zinc oxide and RST3 still show a similar trend even if after the removal of 70% the ZnO allows to have better performance. Carb-ox with water content (7.28 %vol.) shows the best performance for the sulfur removal. An increasing of 50% on the removal performance respect to RST3 at 80% of the concentration removed is depicted in Fig. 4. Under humid conditions the filter performance decrease for RST3 and ZnO around 36% and 28% respectively, whereas in case of Carb-ox they improve of +17%.

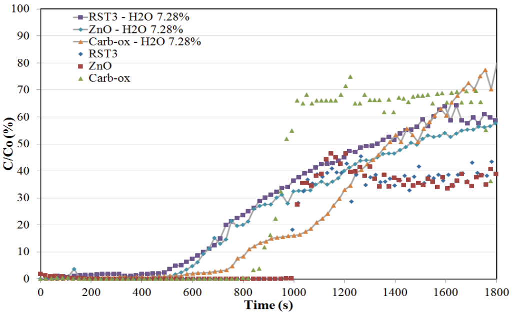

Fig. 4. Hydrogen sulfide removal for sorbent materials in dry and humid conditions

Concluding remarks

This paper describes the removal performance of different sorbent materials for SOFC applications. A biogas mixture and a sulfur pollutant compound was considered for the filter performance in dry and humid conditions according to the measurements done in a real WWTP (SMAT site). According to experimental results, Zinc Oxide and RST3 activated carbon show the best performance in dry conditions. Considering the presence of water in the biogas, the filter performance would decrease with around 30%. A new activated carbon made from air-dep shows a performance increases, around 17% in humid conditions even if in dry conditions presents the worst performance. For a gas cleaning section not only considerations on the biogas water content has to be done, but also on the other pollutant compound concentrations. An our previous study, results not reported here, showed how even only 1 ppm(v) of co-vapors concentration affect the filter performance.

A decreasing in the performance around 30-40% was reported. Co-vapors considered were: aromatic (toluene, xylene) carbonyl (2-butanone) and chlorine (chloroethane) compounds. In conclusion, to design a proper gas cleaning section for SOFC related applications, further work on the pollutants removal is needed, especially considering chlorine and siloxane compounds effect and the contemporary presence of water.

Keywords: biogas, cleaning sorbent material, hydrogen sulfide, SOFC

Acknowledgements

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BMP ANALYSIS AND DECISION TOOLS FOR THE COMPARISON OF DIFFERENT MANAGEMENT AND TREATMENT SCENARIOS OF FOOD WASTE FORM LARGE RETAILERS

Extended abstract

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Background

The new strategies in waste management, i.e., source-separate collection of the organic fraction and the need to reduce the biodegradable-Municipal Solid Waste (MSW) allocated in landfill, have favoured the development of composting and anaerobic digestion as useful biotechnologies for transforming organic waste into suitable agricultural products. Moreover, given that the attention to the environmental impacts is becoming all the time more important, the possibility to recover energy from waste has encouraged the spread of the anaerobic digestion processes of organic fraction of waste as way to provide a clean fuel from renewable energy.

In the frame of a research project between this important supermarket chains and the Department of Industrial Engineering of the University of Florence (DIEF), some strategies for the waste management from food departments of the stores spread in Tuscany were compared in a life cycling perspective.

In particular it was considered a reference scenario in which the Food Waste (FW) are delivered to the existing MSW treatment plants and some innovative scenarios in which waste are used for energy production in a anaerobic digestion plant dedicated and directly managed by the company.

Methodology

For the comparison between the two scenarios, the Life Cycle Assessment methodology was used, according with the ISO 14040 regulations.

The main objective of this assessment is the comparison of the environmental impacts of alternative management scenarios of the FW produced in a year by the surplus from an important company of retrials.

In particular, three scenarios were studied:

- Scenario1: reference scenario in which the FW produced by each store is delivered and treated in the nearest existing MSW treatment plant, currently only composting facilities;
- Scenario 2: the total amount of FW produced is treated in an anaerobic digestion plant directly managed from the distribution company, two possible plant locations are considered (scenario 2A and scenario 2B);
- Scenario 3: only the FW produced by the bigger store are treated in the new anaerobic digestion plant while the waste from the smaller shops are composted in the nearer facilities, always two possible plant locations are considered (scenario 3A and scenario 3B).

The functional unit of the assessment is the management of the amount of FW produced in a year by the food departments of a big distribution company.

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As defined before, the aim of this study is to investigate the impacts of the biological treatment of food waste from retail trade occurring in the FW life cycling: from their production as long as the organic fraction is stabilized as compost. A simple model of an activated sludge process is considered to model the treatment of the wastewaters from biological process and the impact due to transports is included too. In the system modeled the processing waste are landfilled but the impacts are not considered in this assessment, given that it is assumed that the amount is about the same in the scenarios compared. The same it is assumed for metals that usually are recovered and recycled by means of simply pre-treatment.

The impacts considered, according with the Eco-indicator 95, are Greenhouse Effect, Ozone Layer Depletion, Acidification, Eutrophication, Heavy Metals, Carcinogens, Winter Smog, Summer Smog, Pesticides, Primary Energy and Residuals to landfill. Reuse of organic fraction through compost production and energy recovery with biogas utilization are included in the model, therefore, in order to avoid allocation, a system expansion is done. However, given that the quantities of compost produced in the two scenarios could be considered the same, the benefits from the compost recovery is not consider in the study.

Regarding the biogas utilization, it is assumed to recover energy by means of an internal combustion engine for both electricity and thermal energy production.

Inventory

The data about the waste composition and characterization were obtained performing several analysis. In particular four type of store, depending on their size, and three fraction of FW were considered.

Each store, 103 in total, took note for one year of the quantity of leftover produced:

- from bakery (BW),
- from fruit and vegetable department (FVW),
- from deli counter, butcher and fishmonger, mainly meat and fish (MFW).

The average FW compositions recorded every mouth show that there are no significant differences during the year. Furthermore, form the comparison between the average FW composition recoded for a year for each store typology, results that fruit and vegetable residues mainly compose the food waste from the store typology 3, that correspond to the smaller one.

In terms of quantities produced it is estimated that more than the 62% of the total FW comes from the store of the typology 2; for this it was studied the scenario 3, in which only FW from these store are treated in the anaerobic digestion plant of the company. Therefore, to model the scenario 2 it was considered an average FW composition (AC), while in scenario 3 the FW composition of the store of typology 2 was considered (2C). Total Solids (TS), Total Volatile Solids (TVS) and pH for each sample of the previous waste fractions were measured. Since in the aerobic stabilization process modeled a fixed quantity of garden waste is added to the digestate or to FW, a sample of this fraction was studied too. The anaerobic digestion process was modeled with reference to the wet technology using a pulper pre-treatment system. The main assumptions are show in Table 1.

Furthermore some Biochemical Methane Potential (BMP) tests were performed, according to the waste composition considered, in order to obtain specific results. BMP analysis were carried out in duplicate for the two waste composition and both the BMP21(biogas produced at 21 days) and the BMPf (when no significant biogas production is detected) were measured (Pecorini et al., 2012). The gas produced was routinely analyzed using an IR gas analyzer (ECOPROBE 5 - RS Dynamics). After every measurement the bottles were shaken to guarantee homogeneous conditions in the assay vessels (Angelidaki et al., 2009).

The composting and the aerobic stabilization were modeled as full scale windrow processes, in particular it was assumed a degradation efficiency of about 40% of input TVS, a wastewater process production of 0,4 m3 for each tonne of compost produced (Lombardi et al., 2011) and a compost water content at the end of the stabilization of about 55% (ANPA, 2002). About 21.5 kWh/t of treated waste was considered as electricity consumed in the process (ANPA, 2002).

As said before, the wastewater treatment was considered in the assessment too, in particular it was modelled as a simple activated sludge process; Table 1 shows the inventory (Costa, 2010).

The gas from the biological degradation process is assumed to be directly used as fuel in a internal combustion engine in cogeneration mode (with a thermal and an electric efficiency respectively of 0,53 and 0,35) and that the energy produced is partially used to supply the plants consumptions itself.

The emission factors in Table 1 were assumed (EPA, 1998). The electricity surplus is assumed to be sold to the electric grid while the thermal energy is given to external thermal users. To perform the system expansion, the electricity country-mix and heat from a natural gas boiler were extracted from Ecoinvent database, as well as other processes as industrial water, flocculants and methanol production.

Regarding the impact of transports, Corinair 2009 methodology was used to calculate the emission, assuming that the FW is transported by truck diesel, with a load of 14 to 20 tons with an average velocity of 60 km/h.

The fuel production process was considered, as well, by means of data extracted from Ecoinvent data base.

Table 1. Life Cycle Inventory

Parameter	***Assumed values***	***Source***
Digester TS	8.5%	Management data
Anaerobic digestion process inventory		
Wastewater TS	0.79%	Assumption
Digestate TS	29%	
Fresh water	18% input grit-send removal system	Management data
Flocculants	0.026% output digester	
Electricity Consumption	60.68 kWh/t	
Thermal Energy Consumption	115.64 kWh/t	
Wastewater treatment process inventory		
Oxygen demand	4.21 kgO_2/m^3	Costa, 2010
Electricity Consumption	3.50 kWh/m^3	
Methanol Consumption	0.58 kg/m^3	
Sludge Production	4.79 $kgTS/m^3$	
CO_2emissions	3.64 kg CO_2/m^3	
Biogas inventory		
NO_x	4000 kg/10^6 Nm^3CH_4	EPA,1998
CO	7500 kg/106 Nm3CH4	
PM	770 kg/106 Nm3CH4	
CO_2	2.75 kg/kg CH4	

Experimental results

The biogas production curves of the two FW compositions seem to be quite similar even if the BMP of the average composition sample (AC) was higher than the BMP if the 2C composition, especially in the first thirty days of incubation. Considering the typical hydraulic retention time of the anaerobic digesters, the Biochemical Methane Potential production at 21 days of 376 Nl/kgTS and of 481 Nl/kgTS for the 2C and the AC and an average biogas composition (5%H_2O, 33%CO_2 and 62%CH_4) was considered in the assessment.

Impact Assessment

The following table shows the normalized impacts for each scenario. In the assessment all the indicators were considered except the Pesticides impact as the values were found to be zero for each scenario. The impact indicators show that among the modeled scenarios, those in which the anaerobic digestion process is considered, are characterized by negative values that means avoided effect, mainly due to the energy recovery through biogas utilization. One of the indicators with a positive value is the Eutrophication that seems to be really sensitive to NO_X emissions, in this case from the combustion of biogas. The residual to landfill indicator is positive and higher for scenarios 2 and 3 because of the larger quantity of wastewater that has to be treated in the case of anaerobic digestion corresponding to an higher quantity of sludge.

Table 2. Environment impact for categories for each scenarios

		Scenario 1	***Scenario 2A***	***Scenario 2B***	***Scenario 3A***	***Scenario 3B***
Greenhouse Effect	t CO_2/t_FW	1.88E+02	-9.67E+02	-9.58E+02	-3.14E+02	-3.16E+02
Ozone Layer Depletion	t CFC11/ t_FW	4.73E-05	-2.71E-05	-1.25E-05	3.53E-05	3.19E-05
Acidification	t SO_2/ t_FW	1.07E+00	-1.52E+00	-1.47E+00	7.83E-02	6.79E-02
Eutrophication	t PO_4/ t_FW	7.51E-02	1.86E-01	1.93E-01	1.55E-01	1.53E-01
Heavy Metals	t Pb/ t_FW	4.80E-04	-2.15E-03	-2.14E-03	-6.55E-04	-6.59E-04
Carcinogens	t B(a)P/ t_FW	9.74E-03	-6.52E-02	-6.52E-02	-2.35E-02	-2.35E-02
Winter Smog	t PM/ t_FW	7.52E-01	-2.21E+00	-2.20E+00	-5.34E-01	-5.36E-01
Summer Smog	t C_2H_4/ t_FW	4.85E-02	-1.36E-01	-1.26E-01	-1.91E-02	-2.14E-02
Primary Energy	MJ LHV/ t _FW	3.20E+03	-1.71E+04	-1.70E+04	-5.66E+03	-5.69E+03
Residual to landfill	t/ t_FW	1.37E+01	3.52E+01	3.52E+01	2.62E+01	2.62E+01

Comparing the values obtained for the scenarios 2 and 3, higher savings result for the second scenario in which larger quantities of waste are treated with anaerobic digestion processes and therefore greater quantities of energy is produced. The comparison between the results with respect to the different location of the composting facility (scenario 2A vs. 2B and 3A vs. 3B scenarios), does not reveal great differences between the impacts, even if, as expected, the scenarios with shorter distances have lower impacts.

Furthermore, comparing the impacts due to the several sub-processes modelled in each scenario, almost all the impact categories show similar results: as in the case of the Greenhouse Effect (Fig.1) the anaerobic digestion process has the main impact (as savings), mainly because of the energy production, while for wastewater treatment and for transports impacts are almost negligible. Different results were obtained for the Ozone Layer Depletion and Eutrophication impact categories. In particular, the transport of FW has the main impact, in terms of kg of CFC11 in all the scenarios compared and, looking at the inventory, this is mainly due to the use of fuel that, in the case of study, is diesel. Regarding Eutrophication however, the highest impact is due to the anaerobic digestion process and mainly to the production of energy, process usually characterized by savings. In this case, in fact, the recovery of biogas involves higher emissions of NOx, characterized by a bigger impact factor among the other substances inventoried.

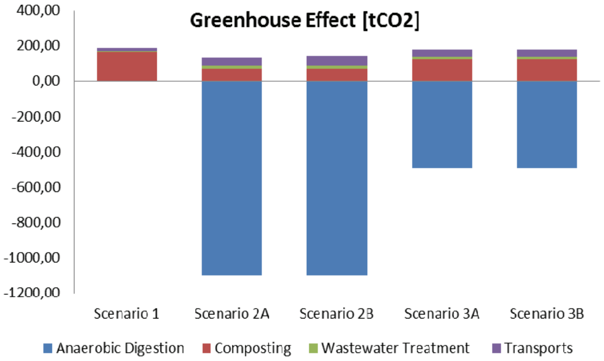

Fig. 1. Greenhouse Effect for each sub process

Concluding remarks

The comparison between scenario 1, the reference scenario in which the FW produced by each store is treated in the nearest existing MSW composting plant, and other scenarios, which consider the anaerobic treatment, shows that the innovative scenarios have the best performance thanks to the environmental impacts avoided with energy recovering. Between scenarios 2 and 3, it results that scenario 2 has the lower impacts due to a larger amount of waste for anaerobic digestion and therefore for energy production. However, focusing on the real application of the management scenarios compared, the scenario 3 seems to be more suitable, given that, with comparable environmental performance, the FW collection system is more practicable.

Keywords: anaerobic digestion, Biochemical Methane Potential, Food waste, Life Cycle Assessment

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IMPROVEMENT OF BEACHED *Posidonia* RESIDUES PERFORMANCE TO COMPOSTING

Extended abstract

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Background

Posidonia oceanica (L.) Del. is a marine monocotyledon endemic of the Mediterranean. The plant can produce up to 10 t·ha^{-1}·year^{-1} of biomass (in terms of dry weight), which in part (about 25%) is accumulated along the coast in the form of beached residues (leaves and fibers), often in characteristic piles ("*banquette*").

Accumulations could be huge: an investigations carried out in the framework of Life+ PRIME project, showed that in the coastal site of Mola di Bari (Bari, Italy), as an example, in August 2011 were found approximately 8,800 m^3 of posidonia residues in an area of about 7,400 m^2, while in a stretch of coast approximately 600 m long and 4-5 m wide, in Torre Canne (Fasano, Italy), were measured in the period from August to October 2011 about 2,600 m^3 of residues. The presence of such huge biomass along of the coast represents a complex problem for the coastal municipalities when the accumulation interferes with economic and recreational activities, first of all the touristic use of beaches. The presence of high amounts of residues close to urban centers may also represent a hardship because of the odors that develop from the accumulation, or even a danger because of the possibility of fires, with consequent problems of public health and safety. In all these cases, the coastal municipalities are forced to remove seagrass residues that, in the absence of alternative solutions, are disposed of in landfills resulting in both environmental charges, due to the significant amount of organic matter removed from the ecosystem, and economic due to disposal costs. In Italy the possibility of using the sea grass as a raw material for composting is fairly recent.

With the Legislative Decree no. 75 of 29 April 2010, this material is allowed in the composition of the mixtures, although at a maximum of 20% by weight (Decreteo Legislativo, 2010). Currently, however, the use in industrial composting is rather limited, despite the good attitude of the material for this use (Cocozza et al., 2011a, b). The major concerns are represented by the excessive presence of sand and the high concentration of salts (mainly sodium chloride) that the residues may contain. The collection phase, therefore, represents a critical step for the beached biomass management.

The methods used during the beach cleaning and seagrass residues removal have repercussions both on the environmental impact related to the intervention and on the possibility of reuse of the collected biomass. Indeed, the presence of extraneous components within such organic material (in particular the sandy sediment) can affect the acceptability of the biomass in the composting industry. The separation of the sandy sediment from posidonia residues is relatively difficult because the sand is often intimately interconnected with organic fraction. In a survey conducted in the PRIME project, has been found that 1 m^3 of sea grass residues can hold up to 150 kg of sand.

Moreover, the high salt content of the residues may lessen the attitude to composting for the influence it could have on the final compost properties (Lopez et al., 2011). The objectives of the present research were: i) to test different treatments to separate sand from posidonia beached residues and reduce the salinity of the material, with the aim to improve its attitude to composting; ii) to study the effects of those treatments on final properties of compost.

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Methods

1. Sand separation test

This operation was mechanized by means of a prototype ("Rotative Sieve"), realized by the partner of PRIME project Tecoma Drying Technology srl (Maranello-MO, Italy), consisting of a tank equipped with a stirrer and a movable cylindrical sieve with 2 mm holes. The principle of operation of the prototype for the separation of the sand consists in washing the residues with sea water and in subsequent sieving. The operation is conducted in two phases. In the first, residues of *Posidonia* are placed inside the tank containing the water, where, by means of a movable arm, the washing of residues takes place. Subsequently, the residues are run inside a movable cylindrical rotative sieve which completes the separation. Three duration of the treatment have been tested: 15+15, 10+10 and 5+5 minutes for the first and the second phase, respectively. In order to quantify the sand present in the material before and after the separation treatment, 3 samples (replications) were taken from each type of material. Samples were placed in containers of volume 1.25 L, standardizing the filling by the application of a constant pressure of 7.5 $g{\cdot}cm^{-2}$. Subsequently, the residues were separated from the sediment by wet sieving with a 2 mm sieve. After sieving, both the oversize and the undersize fraction (respectively, > 2 mm consisting of leaves, and <2mm consisting mainly of sandy sediment and a small part of posidonia fibers) were dried at 105 °C. In order to completely separate the organic fraction from the sediment, the undersize fraction was treated with H_2O_2 130 vol. at a temperature of 40 °C (ANPA, 2001). At the end of the oxidation (indicated by the stop of effervescence), the residues were repeatedly washed in running water, dried again in the oven and finally weighed.

2. Salinity reduction test

The possibility of reducing the salinity of the residues by storing the material under the action of rain was tested. The test involved the study of salt leaching from the stored material in relation to the time of storage and the amount of water distributed. About 140 m^3 of beached posidonia residues, manually collected on the coast of Mola di Bari (BA), were stored on July 27-2012 at the Experimental Farm La Noria of CNR-ISPA, in a pile of height 1-1.5 m, 8 m wide and 14 m long. During the period of storage, rainfall events were simulated, by means of water distribution devices with low intensity (20.6 $mm{\cdot}h^{-1}$). Daily distributions of 60 minutes with well water (pH 7.2, conductivity 5.5 $dS{\cdot}m^{-1}$) were provided. All the material was turned weekly in order to avoid putrefactive phenomena. During the test, the quantities of water distributed have been recorded; leaching fraction has been measured and leacheate has been sampled at every overturning of the material, by four sampling points inside the mass by means of special collection tanks. Electrical conductivity (EC), pH and the content of potassium (K), magnesium (Mg), sodium (Na) and chlorine (Cl) have been measured on leachate samples by means of ion chromatography (Dionex DX 120, Dionex Corporation, CA).

3. Compost production test

With the objective to test the influence of sand separation from *Posidonia* residues on their attitude to composting, two *Posidonia* -based green compost (GW) were produced at the experimental farm "La Noria". Two piles (each approx. 3 m^3) of *Posidonia* leaf residues, collected along Mola di Bari (BA) coast, mixed with tomato plant residues and olive tree pruning residues, were generated.

In the first compost, here referred as "GW Treat", *Posidonia* residues treated with the prototype "rotative sieve" to separate residues from sand were used; in the second compost, here referred as "GW NoTreat", posidonia residues just collected from the beach and not treated with the prototype were used. The two composting mixtures were produced using the following proportions of raw materials (on a % fresh weight basis): posidonia residues, pretreated or not-pretreated, (20%) + tomato plant residues (40%) + olive tree pruning residues (40%). The proportion of raw materials in the mixtures were designed to obtain a C:N ratio of 35-45, which is considered optimal for microbial growth (Michel et al., 1996; Kumar et al., 2010). The composting cycle started on July 19th 2012. The temperature of the piles was kept ≥55 °C for at least 3 days and then controlled by turning and irrigating the piles to obtain the pasteurization of the biomasses. The active phase of the biomass was considered completed after approximately 4 weeks, when the temperature of the piles decreased to values of 40-50 °C.

The curing phase was characterized by less frequent turning and continued until the 90th day to achieve further stabilization and obtain the final products. With the objective to test the influence of salinity reduction on the attitude to composting, residues of *Posidonia* subjected to storage and residues just removed from the coast were transferred to an industrial composting plant (ASECO srl, Ginosa-Ta, partner of PRIME project) and mixed (16-17% on a weight basis) with sewage sludge (28%) or organic fraction of urban solid waste (29%) in factorial combination. In all mixtures, to maintain the C/N ratio in the optimal range, wood, plant debris and food scraps (16-17%) were added. Four *Posidonia*-based compost were obtained: 1) with stored residues and sewage sludge (CSS PSt), 2) with stored residues and organic fraction of urban solid waste (CMSV PSt), 3) with not stored residues and sewage sludge (CSS PNoSt) and 4) with not stored residues and organic fraction of urban solid waste (CMSV PNoSt).The mixtures were placed inside biocells in piles of 4 m wide and 2 m high. The oxygenation was assured by forced ventilation system. The composting process took place from September 2012 to January 2013. On obtained compost, EC, pH, ash content (by combustion in a muffle a 550 °C), concentration of Na (by ion chromatography) in water soluble extract and heavy metal concentration (by OES ICP), have been determined.

Results and discussion

1. Sand separation test

Table 1 shows the sand content in the starting material used for the tests and in the one treated with the prototype, in function of the duration of treatment. The data indicate that the content of sandy sediment in posidonia residues undergoes an almost total abatement following the treatment, while the washing time does not significantly affect the fraction of the sediment removed. The almost total abatement of the sand obtained with the “Rotative Sieve”, is also reflected on the density of the material that, due to the loss of sediment, is significantly reduced compared to the starting material, despite the increase of moisture resulting from the washing, inconvenience the latter that can be solved by providing, after the treatment, an on-site storage for a variable period of time depending on the climate conditions.

Table 1. Density and content of sand in the starting material (beached *Posidonia* a residues) and in the material treated with the prototype “Rotative Sieve” using 3 duration of treatment

	Density (kg/ m^{-3})	***Content of sand (kg/ m^{-3})***
Starting material	426 a	153.2 a
15 + 15 min	268 c	0.37 b
10 + 10 min	281 bc	0.09 b
5 + 5 min	304 b	0.39 b
Significance[1]	***	***

[1] Data are means of three replications. Mean separation within columns by $LSD_{0.05}$. *** significant at P≤0.001.

2. Salinity reduction test

The exposure of *Posidonia* residues to water wash-out, by simulating a daily rainfall, made it possible to substantially reduce the presence of salts in the material. The EC measured in water drainage, which was on average 16% of the water distributed, in fact, has been gradually reduced over time from 55 to 7 dS·m^{-1} after 60 days (end of the storage period) (Fig. 1a). It can also be deduced that, in the conditions of the test, the duration of the storage period could have been be reduced by one or two weeks since the EC variations of the last weeks were very small. Parallel with the reduction of EC, it was reduced the concentration of major inorganic ions in water drainage; in particular, the Na and Cl, present in high quantities in the first weeks, have declined steadily during the test (Fig. 1b), demonstrating the ease with which they can be removed from the material. Similar trends have also presented other ions whose concentration values, however, have stabilized earlier than the previous two. The removal of the salts in the water drainage has led to the consequent reduction of EC in the material that decreased from 9.4 to 0.6 dS·m^{-1} at the end of the period (Fig. 1c). The action of run-off has considerably altered the chemical composition of the aqueous extract of the stored material. In particular, Na, Cl, Mg and K were reduced by 71, 45, 23 and 62%, respectively (Fig. 1d). These results indicate the opportunity to reduce the salinity of *Posidonia* residues through the temporary storage and exposure to the washing action of the rain, selecting appropriate period and seasons. Furthermore, it is preferable to select the storage site in areas very close to the coast, in order to avoid phenomena of salinization or contamination of the groundwater with the salts removed from the stored material.

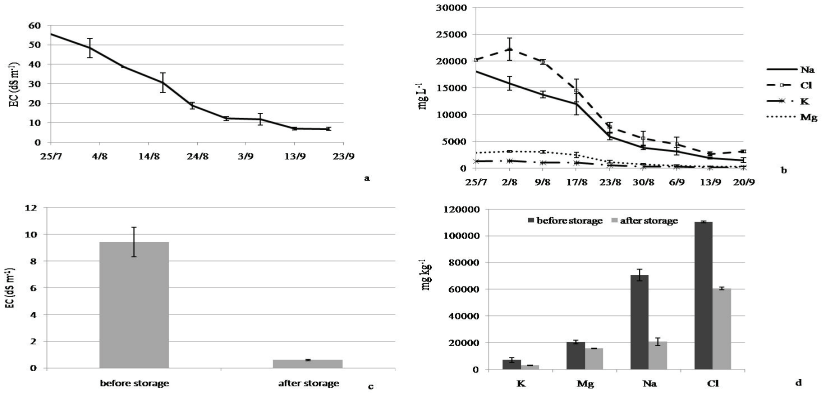

Fig. 1. Electrical conductivity (EC) and content of K, Mg, Na and Cl in the run-off fraction and in the aqueous extract of stored *Posidonia* residues (Vertical bars represent ± SE of mean (n=3)).

3. Compost production test

The EC, while not representing a parameter subject to limits by regulations, is essential for the agronomic evaluation of compost. Among the compost obtained, the EC was low in the two GW compared to other composts (Fig. 2). Using posidonia residues stored as raw material, the EC was reduced by almost 30% compared to when using not stored material, highlighting the effectiveness of an appropriate period of storage that guarantees at least the partial removal of the salts. The ash content was lower in GW compared to other composts and in particular in GW Treat with respect to GW NoTreat: that confirms the importance of removing the sand from the material before starting composting (Fig. 2). The concentration of Na in the compost obtained from posidonia residues subjected to storage was markedly lower than those just collected for the aforementioned effect of washout. Instead, the differences of EC found between the two GW are due to the process of separation from the sand that, using sea water, involves a partial enrichment in salt (Fig. 2).

From the point of view of the dangers related to heavy metals presence, all compost products have presented concentrations of heavy metals (in particular lead, cadmium, nickel, zinc, copper and mercury) well below the limits set by the Italian regulations (D. L. 75/2010) (data not shown), therefore the use of such compost products can be considered safe. Some of the *Posidonia* based composts described above have been used in cultivation trials of green bean and lettuce as soilless growing media component in replacement, partial or total, of peat. For the green bean were used, in comparison with peat alone used as a control, CMSW PSt , CSS PSt and GW Treat, alone and in mixture with peat (50:50 by volume). The substrates were placed in of 10 L volume pots. Plants grown in mixtures showed same yield than those grown in peat alone (547 g of commercial product per plant) while the compost used alone reduced yield of approximately 50% (432 g of commercial product per plant). For the cultivation of lettuce was used only the CMSV PSt in mixture with peat at 25, 50, 75% in volume, as well as alone.

Even in this case peat alone was used as a control. In this test, when used in the mixture compost allowed a higher plant growth which resulted in higher yield of almost 30% compared to the control (470 vs 369 g fresh weight/plant, respectively), while when used alone the production was lower but still greater than the peat alone (430 vs 369 g fresh weight per plant, respectively).

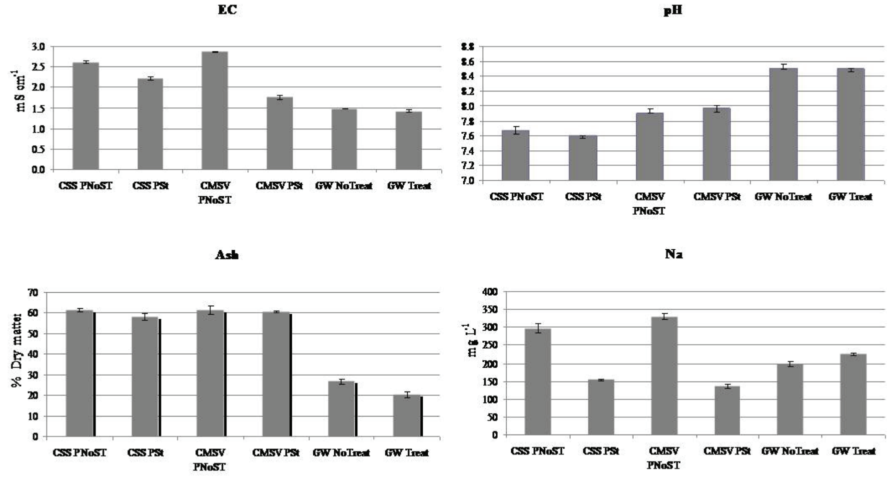

Fig. 2. Electrical conductivity (EC), pH, ash and content of Na in the acqueous extract of six posidonia-based compost. Vertical bars represent ± SE of mean (n=3).

Concluding remarks

The residues of beached *Posidonia* are often perceived as a waste. The experiences described in this research show that they can be turned into a resource for agriculture through the composting process, using proper preliminary treatments to increase their attitude to composting.

Keywords: compost, salinity, sand content, seagrass

Acknowledgements

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PRODUCTION OF BIOHYDROGEN AND VOLATILE FATTY ACIDS FROM DEPHENOLIZED OLIVE MILL WASTEWATERS IN A SEQUENTIAL TWO-STEP ANAEROBIC PROCESS

Extended abstract

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Background

A large variety of agro-wastes are actually investigated for their reliability as renewable sources: the possibility to employ some organic residues for the production of biomolecules, biofuels and biomaterials has fostered the born of the concept of second generation biorefineries, which differ from the first generation processes, since non dedicated crops are used as the feedstock.

To this aim, Olive Mill Wastewaters (OMWs) are the most investigated wastes, due to their high organic content and to a high concentration of polyphenols, compounds that are natural antioxidant.

If on the one hand OMWs are recalcitrant to biodegradation and their environmental impact can represent a serious issue, on the other hand these wastes show a biochemically interesting composition, rich of sugars, lipids, alcohols and organic acids. Recent studies have demonstrated that a lot of processes can be applied to OMWs, which can be exploited for the recovery of polyphenols, production of biofuels or chemicals such as Volatile Fatty Acids (VFAs).

The latter can be used as precursors for biopolymers intracellular accumulation (*i.e.* polyhydroxyalkanoates, PHAs) by mixed microbial consortia (Beccari et al., 2009). In this respect, a continuous Packed Bed Biofilm Reactor (PBBR) performing OMW organic matter bioconversion into VFAs was developed (Bertin et al., 2010); moreover, a preliminary recovery of polyphenolic fraction of OMWs before their feeding to acidogenic digestion was also assessed (Scoma et al., 2011).

In this way, a multi-target biorefinery scheme aimed at extensively valorizing OMWs has been designed: its backbone is represented by a two-step process dedicated to the recovery of polyphenols (by a fully eco-compatible procedure) and the anaerobic acidogenic digestion of the dephenolized effluent (OMW_{deph}).

Recent studies have shown the feasibility of an interesting production of biohydrogen together with accumulation of VFAs, obtained by changing the Hydraulic Retention Time (HRT) on the developed acidogenic process fed with a dephenolized OMW (Scoma et al., 2013).

Objectives

In this investigation, the possibility of including into the above mentioned developed biorefinery scheme a biofuel production (*i.e.*, biohydrogen) between polyphenols recovery and VFAs production has been attempted. The basic idea was to selectively use carbohydrates catabolism to sustain a dark fermentative H_2 gas production from OMW_{deph} during the first hydrolytic step of anaerobic digestion.

Then, in a second separate step, the resulting effluent would be employed as the feedstock (still rich in not fermented biomolecules, mainly lipids) to support an effective VFAs production.

In this way, the two sequential biological anaerobic steps should not compete for substrates.

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This experimental scheme is based on previous studies showing that, under continuous conditions, the use of longer HRTs enhanced VFAs accumulation (with a peak at an HRT of 5 days), whereas shorter HRTs improved biogas productivity, enriched in H_2 gas (Scoma et al., 2013).

Methods

2.1. Dephenolized olive mill wastewater

The OMW employed in this study was provided by the Sant'Agata d'Oneglia (Imperia, Italy) three phase olive mill; phenols were removed according to a solid phase extraction (SPE) procedure developed and applied in previous investigations (Scoma et al., 2011). The OMW employed had, after polyphenols removal, the following characteristics: COD about 32 g_{COD} L^{-1}; VFAs about 4 g_{COD} L^{-1}; phenols about 1 g L^{-1}.

2.2. Microbial consortium

The acidogenic microbial consortium employed as the inoculum was obtained and microbiologically characterized within a previous investigation dedicated to the development of an acidogenic process fed with OMW_{deph} (Scoma et al., 2011). The inoculum was stored at 4°C before being used in this study.

2.3. Packed Bed Biofilm Reactors (PBBRs)

The two PBBRs used in the present investigation had the same configuration; they consisted of a hermetically closed glass column (40 cm in height, 5 cm outer diameter) with an empty volume of about 0.8 L and they was operated under continuous anaerobic mode. The columns were packed with Ceramic cubes of Vukopor S10® (Lanik, Boskovice, CZ) whose dimensions, porosity and density were 25 x 25 x 18 mm, 10 ppi and 2.38 g/mL, respectively; the use of this support relied on previous investigation (Bertin et al., 2010). The reactors were equipped with a recycle line: the recycling ratio, expressed as the ratio between the recycled broth flow and the whole flow entering the column, was about 0.95. PBBRs were fed according to an up-flow scheme with HRTs equal to 1 and 5 days. The system was provided with a mixture of OMW_{deph} and microbial inoculum (10% v:v): the mixture was pumped up in the columns while nitrogen was fluxed into the head space. Process temperature was maintained at 35°C with silicon tubing serpentine continuously recycling thermostated water; pH was maintained to 7 by periodically dropping a 10 M NaOH solution. The two processes were daily monitored for biogas production and composition, VFAs and COD concentrations.

2.4. Analytical procedures

VFAs concentration was monitored through a GC-7890A (Agilent Technologies, Milano, Italy) with a Flame Ionization Detector (FID) under the following conditions: column temperature 170°C, inlet temperature 250°C, detector temperature 280°C, pressure 5 psi and using hydrogen as gas carrier. Before the analyses the sample were diluted with a 60 mM oxalic acid solution. VFAs concentration was reported as COD equivalents (g_{COD} L^{-1}) by using stoichiometric calculations. COD and total carbohydrates concentration were determined spectrophotometrically using *COD Vario Tube Test* (Aqualytic, Dortmund, Germany), following the producer's instructions, and phenol respectively (Chaplin et al., 1986); the standard employed for the calibrations was glucose (Sigma-Aldrich, Milano, Italy). Biogas amount was measured as reported elsewhere (Bertin et al., 2004), while its composition was gas-chromatographically determined (Scoma et al., 2011). Bioconversion of OMW_{deph} organic matter into VFAs was calculated as the ratio between produced VFAs and influent net COD excluding its VFA fraction.

Results and discussion

OMW previously dephenolized was initially fed to a packed bed biofilm reactor config.d as explained above, which was operated with an HRT of 1 day. The influent OMW_{deph} had 4.14 ± 1.38 g_{COD} L^{-1} of VFAs, containing mainly acetic acid (about 3.9 g_{COD} L^{-1}) and butyric acid (about 0.5 g_{COD} L^{-1}) (Fig. 1); after this first step hydrogen gas production was about 170 mL L^{-1} d^{-1} while final VFAs concentration was 5.46 ± 1.15 g_{COD} L^{-1} (thus, VFAs net production was only 1.5 g_{COD} L^{-1}). The total carbohydrates concentration was abated from 7.14 ± 0.60 g L^{-1} to 1.57 ± 0.07 g L^{-1} (Table 1).

Table 1. VFAs concentration, H_2 production and total carbohydrates concentration in PBBRs influents ("IN") end effluents ("OUT").

	units	**HRT 1 IN**	**HRT 1 OUT = HRT 5 IN**	**HRT 5 OUT**
VFAs	g_{COD} L^{-1}	4.14 ± 1.38	5.46 ± 1.15	12.06 ± 2.36
H_2 production	mL L^{-1} d^{-1}	-	170	n.d.
Total carbohydrates	g L^{-1}	7.14 ± 0.60	1.57 ± 0.07	0.88 ± 0.06

The effluent resulting from this first process was fed to a second separate reactor (with the same configuration) which was operated with an HRT of 5 days. In this second PBBR H_2 gas was released only in traces, while CO_2 was the first biogas constituent; at the same time, the net consumption of monitored total sugars was, in this second separated step, very low. Nevertheless, VFAs net production was about 7.5 g_{COD} L^{-1} (final VFAs concentration was 12.06 ± 2.36 g_{COD} L^{-1}) and, since OMW_{deph} fed to HRT1 reactor had a COD of about 32 g L^{-1}, the final bioconversion yelds into VFAs after the two-step anaerobic process was 31.6%. It can be observed that acetic and butyric acids were the major constituents of the VFAs mixture (about 6.3 and 2.7 g_{COD} L^{-1} respectively) as in influent OMW_{deph}, but in effluent we had also an interesting increase in the concentration of propionic and isobutyric acids (Fig. 1).

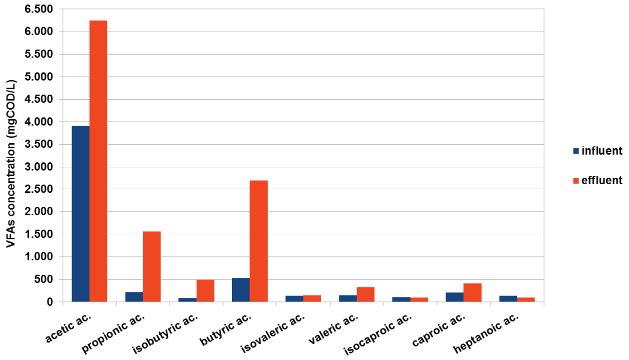

Fig. 1. VFAs concentration in second step influent end effluent

In the present work the possibility of separately and consecutively obtaining a H_2-rich biogas and a VFAs-rich stream by anaerobically digesting a dephenolized OMW under hydrolytic and acidogenic condition, respectively, was evaluated. Considering the first PBBR (HRT1), the high total sugars consumption confirms that carbohydrates catabolism sustained a dark fermentative H_2 gas production during the first hydrolytic step. Then, in the second reactor, the final bioconversion yields of OMW_{deph} into VFAs after the two-step anaerobic process was about 31.6%. This value is equal to what previously seen with identically operated reactors fed with an HRT equal to 7 days (Scoma et al., 2011) and slightly lower than what obtained with reactors fed with an HRT of 5 days (Scoma et al., 2013), when all of them were operated in a single step.

Those findings seem to confirm that the efficiency of the acidogenic process was not substantially affected by physically separating the first hydrolytic step. Furthermore, the relative composition of the produced VFA mixture was comparable to that observed within one-step experiments carried out previously. In particular, acetate and butyrate were confirmed to be predominant. Probably, in the second acidogenic process, other compounds such as lipids, which are more slowly degraded with respect to sugars, fermented to VFAs.

Concluding remarks

In this work, the possibility of separating the biological anaerobic acidogenesis of a dephenolized OMW from the production of a H_2-rich biogas, previously obtained from the same OMW_{deph}, was evaluated. The efficiency of the acidogenic process was not affected by previously processing the substrate under dark fermentation conditions for H_2 production. These results look promising in the prospective of developing robust biorefinery processes, with the possibility to realize a continuous process, coupling serially wastewater acidogenesis to the production of biohydrogen.

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CHARACTERIZATION OF FRUIT AND VEGETABLE WASTES AS A SINGLE SUBSTRATE FOR THE ANAEROBIC DIGESTION

Extended abstract

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Background

Fruit and vegetable wastes (FVWs) represent a specific waste produced by all the wholesale markets and by many companies in the food industry. Due to their high perishability their handling and disposal are quite critical to community acceptance.

Since they have very high moisture contents, biochemical processes, such as anaerobic digestion, are the most suitable conversion technologies to treat FVWs. To ensure process stability and good conversion efficiencies, it is of fundamental importance to accurately characterize the feedstock properties, especially physical and chemical characteristics like the Total Solid (TS), Volatile Solid (VS), Carbon, Nitrogen, macro, micro and trace elements contents. Moreover, on the basis of such parameters, a decision on whether using FVWs as a single feedstock or as co-substrate in the anaerobic digestion process can be made.

Most of the studies on a complete residues' characterization focus on the organic fraction of the municipal solid waste (Hanc et al., 2011), on biomass produced by the forestry, agriculture, municipality and industry sectors (Chiang et al., 2012), or on food waste (Zhang et al., 2007). On the counterpart, to the authors' knowledge, most of the studies on fruit and vegetable wastes focus on their use as a co - substrate in the anaerobic digestion process (Garcia-Peña et al., 2011).

This work presents a detailed characterization study of the chemical and physical properties of representative varieties of fruits and vegetables' residues produced by the Vegetable Wholesale Market of Sardinia (Mercato Ortofrutticolo della Sardegna - Italy). In addition, this study comments the feasibility of using FVWs as a single substrate in anaerobic digestion, on the basis of the existing scholarly literature (Deublein and Steinhauser, 2008) and the results from the present analysis. More over, the study estimates the expected biogas composition from the anaerobic digestion of FVWs.

Methods

The investigated properties of FVWs were Total Solid (TS), Volatile Solid (VS), Ash, Fixed Carbon, Carbon, Hydrogen, Nitrogen, Sulphur, macro, micro, trace elements and the energy contents.

The samples of the most common varieties of fruits and vegetables produced by the Vegetable Wholesale Market of Sardinia were collected during a period of six months (from March to September). In accordance with the commercial distinction between fruits and vegetables, the samples consisted in 10 kinds of fruits (Apricot, Banana, Clementine, Lemon, Melon, Orange, Peach, Pear, Pineapple, Watermelon), 13 kinds of vegetables (Aubergine, Broccoli, Cabbage, Carrot, Cauliflower, Courgette, Cucumber, Endive, Fennel, Lettuce, Onion, Pepper, Tomato) and one of Potato. The samples were shredded and homogenised with a cutter, then were dried at 65°C in a thermostatic oven and, finally, the obtained dried samples were ground to obtain a fine powder. The Carbon, Hydrogen, Nitrogen and Sulphur contents were determined with a LECO (Leco Corporation, St. Joseph, MI) TRUSPEC CHN analyser according to the ASTM D 5373 method, and the Oxygen content was calculated as a difference. The proximate

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analysis (TS, VS, Ash and Fixed Carbon contents) was performed with a LECO (Leco Corporation, St. Joseph, MI) TGA 701 thermo gravimetric analyzer according to the ASTM D 5142 Moisture Volatile Ash method. The energy content was analysed only for the samples representative of some selected FVWs families with a LECO (Leco Corporation, St. Joseph, MI) AC500 Isoperibolic Calorimeter according to the UNI EN 14918:2009 method. The results, given in terms of Higher Heating Value, were expressed as Lower Heating Value using the formula (UNI EN 14918, 2009)(Eq 1):

$$q_{p,net,d} = q_{V,gr,d} - 212{,}2 \cdot w(H)_d - 0{,}8 \cdot \left[w(O)_d + w(N)_d\right] \tag{1}$$

where: $q_{p,net,d}$ is the net calorific value at constant pressure of the moisture - free sample [kJ/kg]; $q_{V,gr,d}$ is the gross calorific value at constant volume of the moisture - free sample; $w(H)_d$ is the Hydrogen content, in percentage by mass of the moisture - free sample; $w(O)_d$ is the Oxygen content, in percentage by mass of the moisture - free sample; $w(N)_d$ is the Nitrogen content, in percentage by mass of the moisture - free sample;

The macro, micro and trace elements contents were determined with a simultaneous atomic emission spectrometer ICP - OES Varian Vista - MPX (Varian Inc., Palo Alto, CA) with axial viewed plasma. To dissolve fruit and vegetables samples for elemental analysis, microwave - assisted acid decomposition was performed at high pressure and temperature. An amount of approximately 0.2 g of sample, weighed accurately, was transferred into microwave teflon vessels; 3 ml of aqua regia and 1 ml of hydrogen peroxide at 30 % were added. All samples were placed in the microwave carousel together with a blank prepared with a solvent of analytical - reagent grade. A CEM model MarsX Microwave - Assisted system was used.

Finally, the expected composition of the biogas produced by the anaerobic digestion has been calculated using the following formula of the methane formation (Deublein and Steinhauser, 2008))(Eq 2 - 4):

$$C_cH_hO_oN_nS_s + yH_2O + xCH_4 + nNH_3 + sH_2S + (c-x)CO_2 \tag{2}$$

with:

$$x = \frac{1}{8} \cdot (4c + h - 20 - 3n - 2s) \tag{3}$$

$$y = \frac{1}{4} \cdot (4c - h - 20 - 3n - 3s) \tag{4}$$

Results and discussion

The TS content and its percentage in VS indicate the fraction of organic matter that can be converted into biogas by the microorganisms, while the C/N ratio represents the availability of organic substrate in comparison to the availability of the main nutrient. Macro, micro and trace elements are the fundamental nutrients required by the microorganisms' metabolism.

Fruits residues have higher TS, VS and C/N ratio compared to the vegetable wastes. Indeed, the Total Solids of fruits are in average 14% (minimum 7.5% and maximum 23%), while in the vegetables they are 6.7% (3-11%). Volatile Solids on wet basis in the fruits are in average 10.3% (5-12%), while in the vegetables they are 4.7% (2-9%). C/N ratio is in average 40 (19-53) in the fruits residues and 13.4 (10-21) in the vegetables. Potatoes represent a separate category that reported 21.8% of TS, 17.4% of VS on wet basis, and a C/N ratio of 23.

Fig. 1 shows the qualitative descriptive profiles in terms of the C/N ratio, TS and VS contents on wet basis for fruits, vegetables and Potatoes. Fruits have generally C/N ratios in average three times and VS on wet basis two times higher than vegetables. Potatoes show TS and VS on wet basis contents higher than both fruits and vegetables, while their C/N ratio is in between.

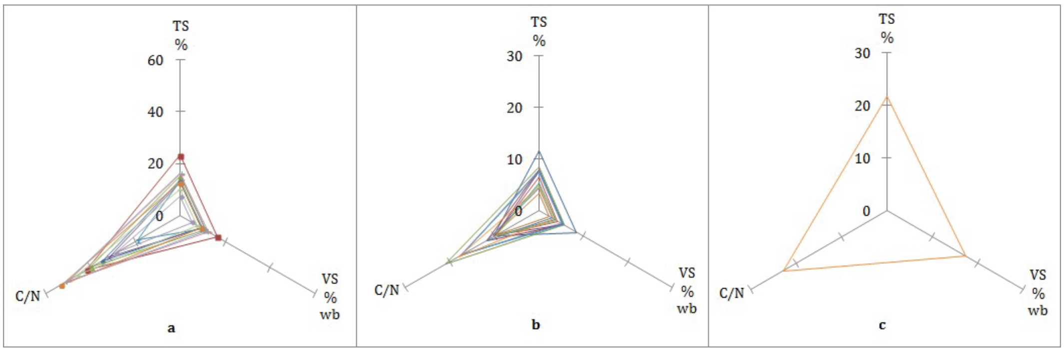

Fig. 1. Qualitative descriptive profiles of the Total Solid (TS) content, Volatile Solid (VS) content and C/N ratio: 1a – Fruits, 1b – Vegetables, 1c – Potatoes

The distribution of C/N ratio, Volatile Solids and Sulphur contents are also reported in the bar graphs in Fig. 2, that shows fruits and vegetables grouped together in terms of VS and C/N. In addition, Sulphur content is also pictured, as it is a relevant characteristic of the feedstock. Sulphur concentration in fruits is generally lower than in vegetables.

In particular, Broccoli, Cauliflower, Cabbage and Onion have the highest Sulphur contents on dry basis (0.7 - 1.1 %). As for the Carbon and Nitrogen ratio, Sulphur in Potatoes is approximately in between fruits and vegetables.

The analytical determinations showed no substantial differences in the fixed Carbon, Hydrogen and Oxygen contents on dry basis in fruits (22 %, 6.5 % and 44 % respectively), vegetables (20 %, 6.5 %, 40 %) and Potatoes (15 %, 6.5 %, 43 %), while the ash content on dry basis is different depending on fruits (minimum 2 % and maximum 9 %), vegetables (0.7 – 16 %) and Potatoes (5 %).

The energy content analysis reported a LHV on wet basis ranging between 0.7 and 1.9 MJ/kg for the vegetables and between 1.2 and 3.9 MJ/kg for the fruits. The LHV on wet basis of Potatoes is 3.5 MJ/kg. The energetic analysis allows to quantify the total energy introduced in the anaerobic digestion reactor and, thus, the energy that can be obtained in the form of biogas and that remains in the digestate.

Macro, micro and trace elements determination is shown in Table 1. No particular differences between the content of nutrients and metals in fruits and vegetables have been found. Calcium, Potassium, Magnesium and Sodium are the most abundant.

Arsenic, Cadmium, Mercury, Lithium, Selenium, Tin, Vanadium are present at trace concentration or absent, while heavy metals like Copper, Nickel, Lead and Zinc are higher in all the samples and occasionally overcome the minimum concentration required as trace elements.

Few high values are found (for instance, Nickel, Lead and Zinc in the Peach), that could be related to isolated cases of pollution. Finally, depending on the examined fruit or vegetable, the expected methane concentration in biogas ranges between 43 % and 70 %, the carbon dioxide between 30 % and 57 %. In particular, the highest methane contents (> 60 %) are expected from the anaerobic digestion of fruits rather than of potatoes and vegetables.

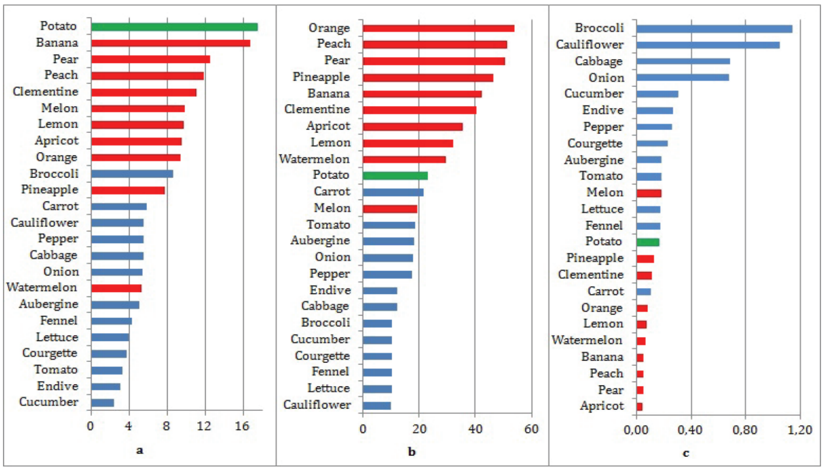

Fig. 2. Distribution of the main substrate properties among fruits, vegetables and Potatoes.
2a - Volatile Solids content on wet basis. 2b - C/N ratio. 2c - Sulphur content on dry basis

The analytical results of this study allow to make some considerations on the FVWs main properties. Fruits and vegetables show different characteristics in terms of C/N ratio, TS, VS and Sulphur contents.

In particular, all samples have high moisture and Volatile Solids contents, with Potatoes having in average the highest VS% on wet basis. Not all samples show optimal Nitrogen and Sulphur contents as feedstock for anaerobic digestion.

According to literature (Deublein and Steinhauser, 2008), the optimal Carbon and Nitrogen ratio should be lower than 25 and the N/S ratio should be 15-20:3. C/N ratio in fruits is generally higher than 30, while most of the FVWs have a Nitrogen/Sulphur ratio higher than 6.

Vegetables show a lower C/N ratio (13 in average) instead, while only Broccoli, Cauliflower, Cabbage and Onion have a N/S ratio lower than 6. Nutrients such as Sodium, Potassium, Calcium, Magnesium and the main micro and trace elements are present at sufficient concentration to limit or avoid the adding of external sources.

As a conclusion, all the FVWs varieties examined in this study contain a high percentage of organic matter that can be converted into biogas.

Due to the presence of the main macro, micro, and trace elements, the use of FVWs in anaerobic digestion without adding additives or other organic materials as co-substrate is possible, while heavy metals are generally lacking. The calculated biogas composition shows that fruits are expected to produce the highest methane content. Nevertheless, it is important that fruits and vegetables are mixed together in order to balance the possible excess or deficiency of nutrients, like Sulphur, and dilute occasional inhibitive elements' peaks.

Table 1. The macro, micro and trace elements in the fruit and vegetable wastes

	Al	*As*	*B*	*Ba*	*Ca*	*Cd*	*Co*	*Cr*	*Cu*	*Fe*	*Hg*	*K*	*Li*	*Mg*	*Mn*	*Mo*	*Na*	*Ni*	*Pb*	*Se*	*Sn*	*Sr*	*V*	*Zn*
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Apricot	0.95	<0.05	0.10	0.014	3.67	0.002	0.029	0.648	0.04	2.37	<0.05	29.81	<0.005	1.31	0.31	0.022	0.08	2.88	0.04	<0.1	<0.25	0.01	0.007	0.08
Aubergin	3.40	<0.05	0.03	0.006	2.68	<0.001	<0.004	0.001	0.42	0.07	<0.05	20.75	<0.005	1.80	0.02	0.001	0.30	0.22	0.13	<0.1	<0.25	0.02	<0.001	0.49
Banana	0.68	<0.05	0.06	0.005	1.79	<0.001	0.015	0.033	0.44	0.26	<0.05	51.70	<0.005	4.35	0.08	0.012	0.08	2.58	0.08	<0.1	<0.25	0.03	<0.002	0.46
Broccoli	0.07	<0.05	0.06	0.015	14.03	<0.001	<0.006	0.002	0.31	0.11	<0.05	27.46	<0.005	4.36	0.02	0.008	3.28	0.27	0.06	<0.1	<0.25	0.08	<0.001	0.30
Cabbage	0.09	<0.05	0.04	0.006	7.96	<0.001	0.004	0.001	0.18	0.08	<0.05	21.15	<0.005	3.02	0.02	0.002	3.43	0.51	0.04	<0.1	<0.25	0.04	<0.001	0.22
Carrot	1.01	<0.05	0.03	0.021	6.27	<0.001	<0.004	0.004	0.15	0.12	<0.05	14.27	<0.005	2.24	0.03	0.003	8.75	0.16	0.02	<0.1	<0.25	0.03	<0.001	0.10
Cauliflow	0.12	<0.05	0.03	0.006	4.22	<0.001	0.005	0.000	0.37	0.08	<0.05	23.04	<0.005	2.87	0.02	0.003	2.89	0.72	0.03	<0.1	<0.25	0.02	<0.001	0.29
Clementin	1.07	<0.05	0.13	0.014	16.53	<0.001	<0.008	0.005	0.98	0.14	<0.05	16.78	<0.005	2.17	0.02	0.003	0.22	1.24	0.19	<0.1	<0.25	0.15	<0.002	0.98
Courgett	0.14	<0.05	0.02	0.002	2.38	<0.001	0.003	0.002	1.68	0.08	<0.05	18.51	<0.005	1.96	0.01	0.002	0.18	0.66	0.07	<0.1	<0.25	0.01	<0.001	1.16
Cucumbe	2.28	<0.05	0.02	0.004	3.78	<0.001	<0.002	0.001	0.05	0.05	<0.05	12.41	<0.005	1.85	0.01	0.002	1.19	0.07	0.01	<0.1	<0.25	0.02	<0.001	0.06
Endive	1.02	<0.05	0.01	0.000	3.68	<0.001	0.002	0.025	0.08	0.14	<0.05	12.49	<0.005	1.30	0.03	0.001	0.19	0.31	0.02	<0.1	<0.25	0.00	<0.001	0.08
Fennel	1.74	<0.05	0.02	0.007	5.47	<0.001	0.018	0.080	0.35	0.52	<0.05	21.62	<0.005	1.38	0.09	0.005	5.59	0.37	0.12	<0.1	<0.25	0.03	0.001	0.54
Lemon	3.16	<0.05	0.04	0.021	13.56	<0.001	<0.006	0.005	0.69	0.10	<0.05	19.71	<0.005	1.64	0.03	<0.001	0.42	0.41	0.31	<0.1	<0.25	0.07	<0.001	1.14
Lettuce	3.05	<0.05	0.01	0.005	6.93	<0.001	0.026	0.038	0.31	0.42	<0.05	30.11	<0.005	1.67	0.08	0.001	1.26	0.28	0.17	<0.1	<0.25	0.02	<0.001	1.13
Melon	3.43	<0.05	0.03	0.001	3.70	<0.001	0.010	0.001	0.80	0.19	<0.05	37.60	<0.005	3.60	0.02	<0.001	1.15	0.59	0.11	<0.1	<0.25	0.02	<0.001	0.93
Onion	0.78	<0.05	0.07	0.021	9.26	<0.001	0.004	0.001	0.51	0.11	<0.05	12.21	<0.005	1.73	0.02	0.002	0.97	0.54	0.13	<0.1	<0.25	0.05	<0.001	0.80
Orange	0.39	<0.05	0.05	0.016	17.61	<0.001	0.012	0.029	0.05	0.25	<0.05	11.85	<0.005	1.63	0.03	0.007	0.11	2.43	0.02	<0.1	<0.25	0.23	<0.001	0.05
Peach	0.68	<0.05	0.04	<0.002	1.28	0.001	0.020	0.001	1.31	0.24	<0.05	19.06	<0.005	1.28	0.01	<0.002	0.11	3.25	1.50	<0.1	<0.25	0.02	<0.002	8.40
Pear	0.12	<0.05	0.06	0.001	0.94	<0.001	0.007	0.006	0.49	0.08	<0.05	7.86	<0.005	0.68	0.01	<0.002	0.29	0.98	0.31	<0.1	<0.25	0.01	<0.002	1.25
Pepper	0.34	<0.05	0.01	0.001	0.61	<0.001	<0.004	<0.001	0.83	0.09	<0.05	15.84	<0.005	1.10	0.01	<0.001	0.18	0.77	0.09	<0.1	<0.25	0.00	<0.001	0.76
Pineapple	4.86	<0.05	0.02	0.009	3.08	<0.001	0.005	0.001	1.99	0.07	<0.05	12.90	<0.005	1.33	0.16	<0.001	0.08	0.51	0.05	<0.1	<0.25	0.02	<0.001	1.53
Potato	5.48	<0.05	0.07	0.017	4.86	<0.001	0.012	<0.001	0.41	0.19	<0.05	45.30	<0.005	3.33	0.03	<0.002	0.35	0.24	0.13	<0.1	<0.25	0.01	<0.002	0.70
Tomato	0.48	<0.05	0.01	0.000	1.23	<0.001	0.003	0.001	0.35	0.07	<0.05	9.97	<0.005	0.64	0.01	0.001	0.21	0.68	0.04	<0.1	<0.25	0.00	<0.001	0.39
Watermel	2.08	<0.05	0.03	0.006	1.57	0.001	0.013	0.203	0.004	0.81	<0.05	17.13	<0.005	1.65	0.16	0.007	0.08	2.29	0.01	<0.1	<0.25	0.01	0.002	0.02

Concluding remarks

The results of the characterization presented in this study demonstrate that FVWs are an eligible single feedstock for anaerobic digestion. Indeed, they have optimal moisture and Volatile Solid contents and, in accordance with their chemical composition, the maximum expected methane concentration in the biogas produced is 70 %.

Proper mixtures of fruits and vegetables allow having a feedstock with balanced properties in terms of macro, micro and trace elements that prevent the instability of the anaerobic digestion process. The practice of adding external sources of nutrients can be avoided, generating cost savings for the anaerobic digestion plants.

Keywords: Anaerobic digestion, chemical and physical properties, fruits and vegetables waste, nutrients.

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ANAEROBIC DIGESTION OF POTATO INDUSTRY BY-PRODUCTS ON A PILOT-SCALE PLANT UNDER THERMOPHILIC CONDITIONS

Extended abstract

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Background

Potato industry by-products are typically produced in industrial processing such as freezing, drying, canning and frying. This kind of waste includes, for instance, skins and tubers with defects and mechanical damages that are rejected in the process of potato chips production.

These residues have a high perishability and their quick removal and disposal is therefore mandatory, with consequent high costs for the food companies. Since these materials have a high moisture content, they are an eligible feedstock for anaerobic digestion (AD). Nevertheless, because of their high soluble organic compounds content, the anaerobic digestion of potato by-products as a single substrate is considered very critical. Scientific literature contains some studies on anaerobic digestion of potato tuber and its industrial by-products (Kaparaju et al., 2005; Parawira et al., 2004, 2005).

Many authors have reported unstable process conditions when treating this kind of substrate in mesophilic conditions. In fact potato industrial by-products contain high amounts of soluble substances that can be easily degraded to volatile fatty acid and inhibit the methanogenic microorganisms in single stage anaerobic digesters, as shown by Kaparaju et al., 2005. To overcome this problem, these authors used pig manure as co-substrate. Another study reports the results of the batch anaerobic digestion of potato waste alone and in combination with sugar beet leaves (Parawira et al., 2004). In this case the authors obtained an improved methane yield when applying the co-digestion compared to the digestion of the single substrates.

They studied the anaerobic digestion of solid potato waste in two double-stage mesophilic anaerobic digestion systems. The first consisted of a solid-bed reactor connected to an upflow anaerobic sludge blanket reactor (UASB), while the second was a solid-bed reactor connected to a methanogenic reactor packed with a wheat straw biofilm. The configuration with the packed straw bed had a greater speed of degradation compared to an UASB system. The methane yield was the same for both systems (Parawira et al., 2005).

The anaerobic treatment of potato processing solid waste was also studied in completely stirred tank reactors (CSTR) under thermophilic conditions (55°C) and on lab-scale equipments. In particular a kinetic study to find simple model equations for the design of completely stirred tank reactors (CSTR) was carried out (Linke, 2006).

The study shows that an increase in the organic loading rate (OLR) causes a decrease in both biogas yield and CH_4 content. To the authors' knowledge, all the experiments described were performed on laboratory scale reactors, while experiments at large scale have not been performed yet.

Actually, anaerobic digestion of potato industrial by-products as a single substrate is a challenging process due to the high biodegradability of this material which can lead to the rapid and strong acidification inside the reactor with a consequent inhibition of the methanogenic bacteria activity.

In this paper an experimental assessment of biogas production from potato industrial wastes at thermophilic conditions is presented.

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In particular, the study is based on the experimental performance of a pilot scale anaerobic digestion reactor (1.13 m^3 of volume) fed with potato industrial by-products as a single substrate derived from a Potato Chips Line (Terrantica Srl) located in Sardinia (Italy).

Scanning Electron Microscopy (SEM) was used to the preliminary study of the morphology of the microbial species involved in the anaerobic digestion process, as this technique was recently demonstrated to be suitable for this purpose (Molinuevo-Salces et al., 2012).

Methods

In this experiment, a pilot plant (RES Italia) was used. The plant includes: a cutter for substrate pre-treatment, a feeding hopper, a tubular horizontal reactor, a pneumatic feeding pump, a pneumatic digestate discharge pump, a biogas measuring and a treatment unit, a digestate storage tank, an air compression unit, a gas holder and a control and supervision system (PLC). After cutting, the potato wastes are delivered to the feeding hopper, where they are mixed by means of a vertical stirrer before being pumped inside the reactor. The feeding hopper is mounted on load cells, is thermally insulated and can be heated with an electrical heater. The tubular horizontal reactor has an overall volume of 1.13 m^3, it is partially insulated with a polymeric layer and equipped with a radial stirrer and an electrical heating system which allows working at temperatures up to 60°C. The biogas composition, the total solid contents (TS%), the pH and the ratio between volatile organic acids and alkaline buffer capacity (FOS/TAC) were daily monitored.

Scanning electron microscope (SEM) images of the micro-organisms inside the feeding hopper and the reactor were also obtained by using a FEI Helios Nanolab 600 dualbeam (SEM/FIB).

The substrate materials used for the experimental assessment were sampled weekly at the potato chips line of Terrantica Srl (Italy) for the full duration of the experiment.

Once received in the laboratory, every sample was ground and homogenized by means of the cutter. If not immediately processed, the samples were stored in a refrigerator at 4 °C for a few days or frozen and stored at -18°C for later use. All samples were characterized in terms of chemical and physical properties. In particular, the Total Solid (TS) content, the Volatile Solid (VS) content, the ash content and the ultimate composition (C, H, N, and S contents) were determined. The TS and VS contents of the substrate were determined with a LECO TGA701 Thermo Gravimetric Analyzer according to the ASTM D5142 Moisture Volatile Ash method. The same instrument was used for the determination of TS and VS contents in the digestate. The Higher Heating Value (HHV) of both substrate and digestate was measured according to the UNI EN 14918:2009 method with a LECO AC500 Isoperibolic Calorimeter. The contents of C, H, N and S were determined with a LECO TRUSPEC CHN according to the ASTM D5373 method. The biogas composition (amount of methane, carbon dioxide, Oxygen, hydrogen sulphide) was determined with a *Geotech GA2000 Gas Analyser*.

Experimental

The experiment was started by inoculating the reactor with 935 kg of digestate from anaerobic digestion of fruit and vegetable wastes to provide the starting population of microorganisms. The temperature of the reactor was then gradually raised up to thermophilic conditions (50 °C ± 0.5 °C) and this temperature was kept constant for the full duration of the experiment. Overall, the monitoring period lasted 72 days. It included a start-up period, which lasted 48 days and during which the complete substitution of the initial fruits and vegetables digestate with the potato wastes was achieved, and a stationary phase, called phase 1 in the following sections, which lasted 24 days .

The goal of the experimental study was to optimise the AD process operating parameters, to achieve an efficient conversion of potato wastes into biogas. The control of the process was carried out by monitoring the reactor mass content and the most important operating parameters, such as: TS and VS of both substrate and digestate, Organic Loading Rate (OLR), FOS/TAC ratio, pH, biogas composition, Gas Production Rate (GPR), Hydraulic Residence Time (HRT).

Results and discussion

The average analytical composition of potato industrial by-products shows a moisture content ranging from 75% to 85% depending on the particular type of waste (whole tubers, skins), a C/N ratio around 30 and a volatile solids content on dry basis ranging from 82% to 90%.

Fig. 1a-d summarizes the most important results of the study in terms of biogas composition (Fig. 1a), FOS/TAC ratio and organic loading rate (Fig. 1b), mass and VS daily loading rate (Fig. 1c), biogas production rate and methane content (Fig. 1d). As shown in Fig. 1a, the mass flow rate was increased constantly during the whole start-up phase, in order to achieve a complete substitution of the initial inoculum. In the following phase fluctuations in the daily loading rate can be observed. They were caused by corrective actions required to control the organic loading rate (OLR). As shown in Fig. 1b, in the start-up phase the OLR was increased up to about 2 $kg_{VS}/d{\cdot}m^3$, with a corresponding increase of the FOS/TAC ratio. The FOS/TAC ratio of anaerobic digestion processes should be in the range of 0.3-0.4 and that FOS/TAC ratios above 0.4 could indicate instability process conditions (Lossie et al., 2008). This normally leads to a decrease in biogas production. For this reason, once the FOS/TAC ratio reached values above 0.4, the OLR was reduced to about 1.5-2.0 $kg_{VS}/d{\cdot}m^3$. However, our experimental results demonstrate that even for FOS/TAC ratios up to 0.5, the AD process still maintained high yields (in terms of biogas production and methane content). Fig. 1c shows the biogas composition trend. As can be noted, the CH_4 content ranged between 43.4% and 63.1 % with an average value of 54.7 % in the phase 1, while CO_2 ranged between 37.4% and 56.8%. During the whole experimental study the hydrogen sulphide (H_2S) content in the biogas reached a maximum value of 363 ppm, that is lower than the limit values (about 1000 ppm) suggested for the direct use of biogas in internal combustion engines. Fig. 1d shows the trend of the Gas Production Rate (GPR). In particular, it demonstrates that in good process conditions (FOS/TAC ratio around 0.4 and OLR not above 2.0 $kg_{VS}/d{\cdot}m^3$), the GPR varied from 1.1 to 1.3 $Nm^3_{biogas}/(m^3_{reactor}{\cdot}d)$, while in suboptimal conditions the GPR was below 1.0 $Nm^3_{biogas}/(m^3_{reactor}{\cdot}d)$.

The process stability was reached with an organic loading rate (OLR) of about 2.0 $(kg_{VS}/m^3)/d$. This corresponded to a loading rate of 40 kg/d with a hydraulic retention time of 24 days. The maximum GPR was 1.3 Nm^3/d with a specific methane production of 0.429 Nm^3/kg_{VS}. In stable process conditions, about 70% of the volatile solid content of the feeding substrate was converted into biogas.

Fig. 2 shows SEM pictures of the material in the feeding hopper (A), at the head (B) and at the end of the anaerobic reactor (C). For each of the three samples two images at different magnifications are presented. In the hopper bacteria of the cocci and rod-shaped types were predominant. At the reactor head, long rod-shaped bacteria seemed to be predominant. At the reactor end long rod-shaped bacteria and other shape bacteria were present. However an in-depth study is necessary for a correct identification of the various kinds of bacteria involved.

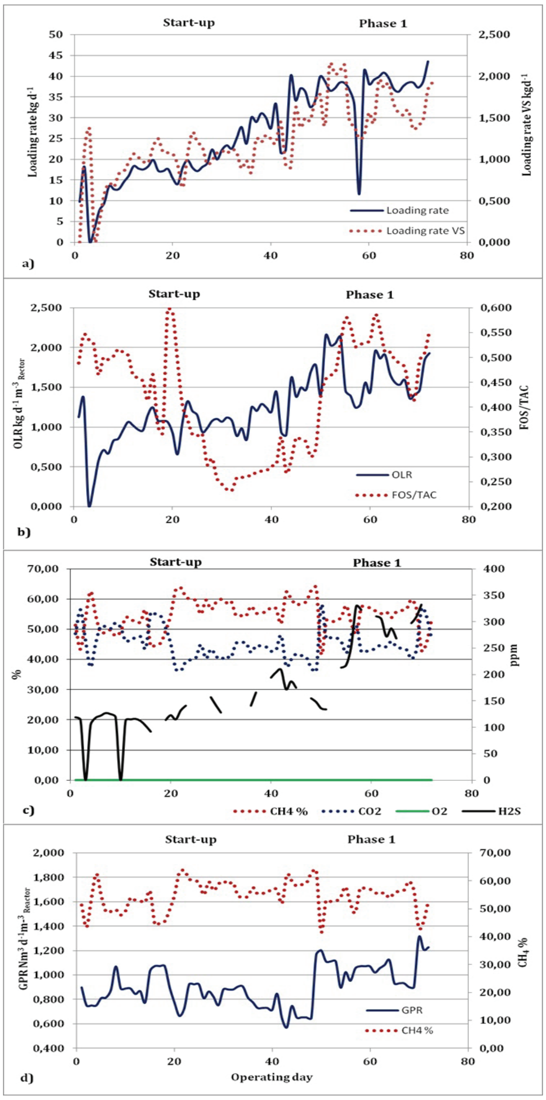

Fig. 1. Main experimental results of the pilot-scale system. a) Loading rate and VS Loading rate. b) Organic loading rate trend. c) Biogas composition. d) Biogas production rate and CH_4 % content

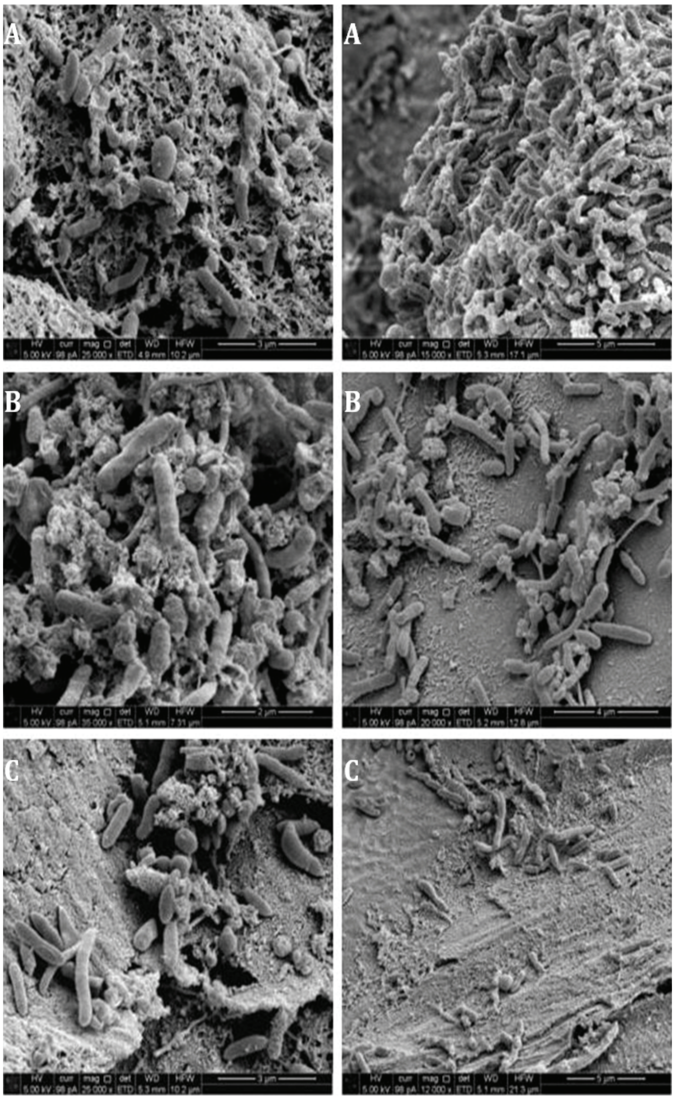

Fig. 2. SEM images ad two different magnifications of the material in the feeding hopper (A), at the reactor head (B) and at the reactor end (C)

Table 1 summarizes the average values of the specific gas production and the specific methane production (i.e. the volume of biogas and methane produced per kg of volatile solids fed to the pilot plant) during the two experimental phases. It is interesting to observe that the reported values are high if compared to the ones obtained with other kinds of wastes such as fruits and vegetables. For this reason the thermophilic anaerobic digestion of potatoes industrial by-products as a single substrate can be a useful and advantageous technology from both environmental and the energetic point of view.

Scanning electron microscopy was then been used to perform a rough identification of the kinds of bacteria that are present in different parts of the anaerobic digestion plant.

Table 1. Average values of the specific gas production and the specific methane production

Experimental period	Specific gas production	Specific methane yield
Start- up	0.91 Nm^3/kg_{VS}	0.50 Nm^3/kg_{VS}
Phase 1	0.68 Nm^3/kg_{VS}	0.37 Nm^3/kg_{VS}

Concluding remarks

In this paper we demonstrated that potato industrial by-products are suitable materials for biogas production by means of single substrate AD. However the result of the experiment showed that it is essential to perform a tight control of the process parameters.

The maximum daily loading rate of wastes was 40 kg/d, with a corresponding hydraulic residence time of 24 days. Higher values of the daily loading can cause process instability. The optimum organic loading rate was around 2.0 $kg_{VS}/d \cdot m^3$ and the average specific biogas production was about 0.68 Nm^3/kg_{VS}, with a specific methane yield of about 0.37 Nm^3/kg_{VS}. Moreover, a first rough identification of certain microbial forms was obtained.

Keywords: anaerobic digestion, biogas production, potatoes industrial by-products, scanning electron microscopy, thermophilic digestion

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PRODUCTION OF POLYHYDROXYALKANOATES BY *Cupriavidus necator* FROM TREATED OLIVE MILL WASTEWATER

Extended abstract

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Background

Nowadays the development and production of new polymers is of great interest, either when looking for a new property or a more eco-compatible material. In this sense, polyhydroxyalkanoates (PHAs) are one of the newcomer polymers, since they can exert similar or even better physicochemical properties than those of petrochemical-based polymers.

However, it is not easy to achieve an economic feasible process. Generally, main costs associated to PHA production processes are those due to the carbon source for the fermentation process and to the downstream step (biopolymer separation and purification), which affect total PHA production costs for approximately 30% each other (Choi and Lee, 1999).

The exploitation of a largely available organic agro-waste such as olive mill wastewater (OMW) -instead of costly refined sugars- could be persecuted for PHAs production. OMW is a dark brown-greenish effluent, with high phenols content, which abounds within the Mediterranean region. The first step of a hypothetical bio-refinery of OMWs should be represented by the waste dephenolization, which would both decrease its antimicrobial activity and allow the recovery of added-value natural antioxidants. Thereafter, in the perspective of developing a biotechnological PHA production process, the dephenolized OMW should undergo to an anaerobic acidogenic digestion dedicated to the production of a volatile fatty acids (VFAs)-rich stream, since VFAs are suitable substrates for PHA producing microorganisms.

The production of PHAs from acidified OMW (OMW_{Acid}) was already reported by using a mixed culture (Beccari*, et al.*, 2009). However, low PHAs content were obtained, as typically happens when mix cultures are employed, this implying high separation and purification costs for an industrial scale production. At the same time, studies on PHAs production from different treated wastewater with pure cultures were reported (*e.g.*, OMWs were employed with *Azotobacter* strains (Cerrone et al., 2010).

Objectives

The present work was dedicated to evaluate the feasibility of employing a pure culture of *Cupriavidus necator* in the development of a PHA production process fed with an OMW_{Acid}. This microorganism was chosen since it can accumulate till 80% of PHAs with respect to the cell dry weight and also has the capacity to degrade phenols.

Specifically, two particular aims were defined: the use of OMW as solvent for preparing the growing culture medium and the use of OMW_{Acid} as carbon source for the PHA accumulation phase. To the very best of our knowledge, this work represents the first attempt of singularly testing those strategies.

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Methods

Standards, salts and carbon sources

Fructose, acetic, propionic, butyric, valeric and caproic acids, salts for the E2 mineral medium and poly (3-hydroxybutyric acid-*co*-3-hydroxyvaleric acid) (12wt.% PHV; natural origin) were purchased from Sigma Aldrich.

Two kinds of OMWs were employed: a dephenolized OMW (OMW_{Deph}) and an OMW_{Acid}, which was the product stream of an anaerobic acidogenic immobilized cells process developed in our laboratories to obtain a volatile fatty acids (VFAs)-rich effluent (Scoma*, et al.*, 2011). The latter stream contained different short chain volatile fatty acids, namely (g/L): acetic (7), propionic (1.3), butyric (1.8), valeric (0.2) and caproic (0.3) acids. Cultural media were prepared by filtering OMW_{Deph} and OMW_{Acid} (Whatman N11, 11µm), dissolving the corresponded amount of E2 or E2 (ammonia free) salts into the filtered OMW_{Deph} and OMW_{Acid}, respectively, and sterilizing them in autoclave. Thereafter, centrifugation was performed (10,000 rpm and 4°C for 20 minutes) - maintaining sterilization- in order to obtain a clear sterilized solution.

Bacterial strain and inoculum

Cupriavidus necator (DSMS 545) inoculum was started from LB-Agar plates and grown within 24 hours in 500 mL Erlenmeyer flask containing 150 mL of LB medium; incubation conditions were 30ºC and 150RPM.

Analytical techniques

Sampling was performed periodically. The optical density (OD) measurement at 600nm, using a Cary-100 UV-Vis spectrophotometer, was implemented to detect cellular concentration variations. Cellular concentration, in terms of cell dry weight (CDW), can be determined by employing an OD vs. CDW calibration curve (data not shown). Thereafter, samples were centrifuged; the supernatant and pellet were separated and stocked for analyses.

Fructose was determined by HPLC-IR analysis, using a Varian Hi-Plex H column (300 x 7.7 mm); the mobile phase was sulfuric acid 5 mM at an elution rate of 0.6 mL/min and the operating temperature was 65°C.

VFAs and PHAs were determined by GC-FID analysis (Agilent 7890A). For the VFAs, it was employed a HP-INNOWAX column (ID 0.25 mm, length 30 m and film thickness 0.25 µm) and the method described in (Scoma*, et al.*, 2011). The PHAs were determined according to the methanolysis method described by (Braunegg*, et al.*, 1978) using a CP-Sil 5 CB column (ID 0.25 mm, length 30 m and film thickness 0.25 µm) with the temperature program described by (Bengtsson*, et al.*, 2008). The validity of this method was checked with thermo gravimetric analysis (TGA).

Experimental approach

OMW_{Deph} as solvent for C. necator growth

Balanced growth was carried out in different experimental E2 mineral media, which were prepared by using different relative proportions of OMW_{Deph} and distilled water, in order to determine the maximal OMW volume quantity that can be used as solvent before the occurrence of inhibition effects. To this aim, five different conditions were tested depending on the percentage of OMW_{Deph} used for preparing the culture media, namely: 0, 25, 50, 75 and 100%. The incubation conditions were the same previously described. Unique batch tests were started by inoculating 500 mL Erlenmeyer flasks containing 150 mL of E2 mineral medium prepared with the corresponded percentage amount of OMW_{Deph} and 10g/l of fructose, so that the initial absorbance (at 600nm) was 0.150.

OMW_{Acid} as carbon source for PHA accumulation

Balanced growth was carried out in about 24h under the same incubation conditions previously described, by using distilled water as the solvent and by adding 5 g/L of fructose as the carbon source, so that the initial absorbance (at 600nm) was 0.400. When the growth phase finished, the growth broth was centrifuged (6000 rpm for 6 minutes). The accumulation phase was started by re-suspending the obtained pellet in 150 mL of accumulation medium, which was composed by E2 (ammonia free) and OMW_{Acid} (source of VFAs, which represented the PHA precursors). In order to determine the maximal amount of OMW_{Acid} that could be used before detecting accumulation inhibition, four different conditions were tested depending on the OMW_{Acid} content in the accumulation medium, namely (%v/v): 25, 50, 75 and 100. A control test was carried out but using a water solution representing the mixture of VFAs inside OMW_{Acid} (SYN-OMW_{Acid}). It contained only the corresponding VFAs and it allowed to determine whether eventually observed inhibition effects were due to VFAs themselves or the wastewater matrix. Each condition was tested in triplicate. The experiments lasted about 50 hours.

Results and discussion

The results of the growth inhibition test are shown in Fig. 1. When the culture media was prepared using only distilled water (0% OMW_{Deph}) the maximal absorbance was 3.75 (A.U), with a specific growth rate of 0.219 h^{-1}. For 25% OMW_{Deph}, a smaller specific growth rate of 0.128^{-1} without any lag phase detection was calculated. The final OD for this condition was 3.66 (A.U.), which is a comparable value with respect to the former experimental control condition. At the contrary, a strong inhibition was observed when culture media contained 50% or more of OMW. On the other hand, it was observed that after 80 hours the OD related to 50% OMW_{Deph} experiment started to increase at a similar exponential rate to the previous mentioned. A possible explanation of this evidence is represented by the fact that the employed strain requires a critical cell concentration, which can be estimated in an OD of 0.6 (A.U.), approximately, to rich the exponential growth in the presence of inhibitors. In particular, polyphenols can be responsible for the growth inhibition, since about 1 g/L of total phenols (TPs) were found in the employed dephenolized wastewater (Scoma et al., 2011). Therefore, about 0.25 g/L and 0.50 g/L of TPs occurred in 25% and 50% OMW_{Deph}, respectively. Interestingly, *C. necator* was found to growth without inhibition effects at least below 0.25 g/L of polyphenols.

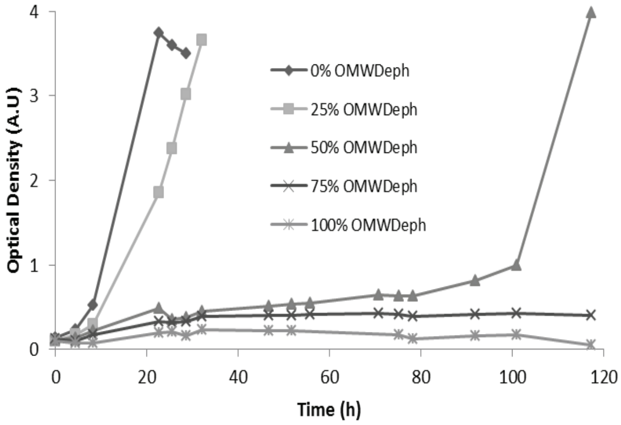

Fig. 1. Growth trend: a strong inhibition was detected when the culture media contains 50% of OMW_{Deph}

As for the feasibility test of PHAs production from OMW_{Acid}, PHA accumulation was detected for 25% OMW_{Acid} immediately after the accumulation phase started (Fig. 2); 40% of PHAs content in a cell dry weight base was obtained at the end of the experiment. When using 50% OMW_{Acid}, a significant “accumulation lag phase” (constant optical density), which lasted 23 hours, was observed before accumulation started. Both conditions represent, either because of the scarce final PHAs content or dilatory accumulation rate, low productivity and thus a difficulty to obtain a feasible industrial biotechnological process.

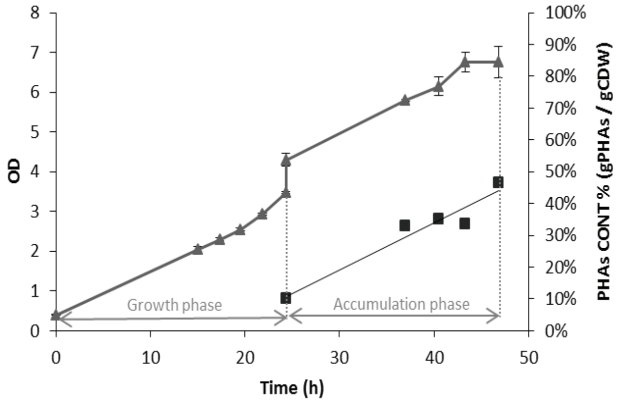

Fig. 2. Biomass (triangles) and total PHAs content (squares) during the sequential batch experiment.
This is for an accumulation culture media containing 25% of OMW_{Acid}

On the contrary, when using SYN-OMW_{Acid}, neither completely inhibition nor “accumulation lag phase” were detected; however, the same PHA content of about 40% of PHAs (on dry weight bases) was detected. Finally, VFAs were observed to contribute to the strain inhibition, since it was observed that the more SYN-OMW_{Acid} content was in the media the lowest was the accumulation rate. From this it can be inferred that something in the OMW_{Acid} matrix cause the observed inhibition.

Concluding remarks

The production of PHAs from treated OMW with *C. necator* is proposed as a strategy to achieve an economical feasible process.

Growth inhibition results suggested that 25% of the water required for preparing the growing culture media, can be saved by replacing it with OMW_{Deph}. Furthermore, if increasing the amount of inoculum it could be saved at least up to 50%.

As for the PHAs production from OMW_{Acid}, compromising results were obtained either because of the scarce final PHAs content (in the case 25% OMW_{Acid}) or dilatory accumulation rate (in the case 50% OMW_{Acid}).

All this considered, and still trying to obtain an economical feasible process, the implementation of three sequential batches is proposed: one dedicated to the cell growth (using 50% OMW_{Deph}) and two for PHAs accumulation (using 25% of OMW_{Acid}). In this way, the resulting increase in PHAs content would allow avoiding high separation and purification costs that compromise the economic feasibility.

Keywords: *Cupriavidus necator*, Olive mil wastewater, Polyhydroxyalkanoates, Pure culture, *Ralstonia eutropha*

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PRODUCTION OF VOLATILE FATTY ACIDS FROM CHEESE WHEY WITH IMMOBILIZED CELLS

Extended abstract

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Background

Dairy industry is practised all over the world for the production of milk, butter, yogurt, ice cream, cheese, and other milk derivates. This activity generates big amounts of highly COD containing effluents. Since their disposal requires a treatment step in dedicated plants aimed at abating the wastes organic content, their valorization within biorefinery schemes represents a valuable opportunity. In that frame, there is a strong interest on producing volatile fatty acids (VFAs) for the subsequent biotechnological production of biopolymers (namely, polyhydroxyalkanoates (PHAs)). Some investigations, which employed cheese whey (CW) as the PHA process feedstock, were reported in the literature (Pais et al., 2009).

Such a waste is one of the dairy industry effluents exerting higher organic contamination, mainly due to its high lactose content. Thus, it represents a good raw material candidate for biorefinery processes. Few experiences about CW anaerobic acidogenic digestion for the production of ethanol and lactic acid with immobilized cells by employing a membrane bioreactor or packed-bed column were already described (Kosseva et al., 2009). However, almost no experiments for VFAs production with immobilization, from CW, have been reported.

Objectives

The present work proposes the production of VFAs from cheese whey powder (CWP) by employing a packed-bed biofilm reactor (PBBR) filled with a ceramic support, which was operated continuously under anaerobic acidogenic conditions.

Outline of the work

This work is divided in two main parts:

- Preliminary batch experiment in small scale, 100-mL Pyrex bottles, was performed in order to study and define the main process parameters.
- The second part is the operation of a PBBR in batch and continuous state with a HRT of 9 days.

Methods

The inoculum used in the present work was an acidogenic mixed culture, which was recovered from a membrane bioreactor that was also producing VFAs from CWP. A concentrated sample of the consortia was cultured in a 500 mL-Pyrex bottle with a solution of CWP prepared according to what reported below, in order to have enough active biomass for all experiments. CWP was kindly provided by Lactogal (Portugal). Technically, it is

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lyophilized cheese whey used for animal feed. Its main composition was (w/w CWP): proteins, 13.6%; lactose, 78.4% and fat, 1.21%.

All experiments were done with the same culture media: a CWP solution (20 g/L) prepared with distilled water, corresponding to 15 g/L of lactose. All anaerobic microcosms were prepared in quadruplicate in 100-mL Pyrex bottles and had a packed and working volume of 45 and 55 mL, respectively. They were filled with a ceramic material supports (Vukopor S10, Lanik, CZ) and inoculated at 10% of the liquid volume. The incubation conditions were 37°C and 150 rpm; pH was maintained at 6 by adding drops of NaOH 10 M. The process was monitored every 2-3 days for VFAs and metabolites concentrations, pH, biogas production and composition.

Three sequential batches were performed for favouring biofilm formation, while a consecutive fourth batch test was lasted until VFAs accumulated. Each subsequent process was started, after lactose complete consumption, by taking out the liquid phase and by refilling the microcosms with an equal volume of the CWP solution.

An anaerobic packed-bed biofilm reactor (PBBR), filled with Vukopor S10 ceramic cubes, was developed. It Consisted of 1L-hermetically closed glass column wrapped with a silicon tubing serpentine continuously recycling thermostated water (37 °C) and equipped with down flow recycle line. It was packed with 118.36 g of support, and inoculated with the acidogenic mixed consortium 20% of the liquid volume of the reactor, which was filled with the experimental solution of CWP (20 g/L). The whole reactor working volume was 830 mL. The liquid and the gas effluents were collected in a 1-L bottle hydraulically connected to a 2.5-L “Marriotte” system. A preliminary batch experiment was performed for favouring biofilm formation.

Thereafter it was turn to continuous state operation with a hydraulic retention time (HRT) of 9 days. The VFAs concentrations were determined by gas chromatography using a GC (Agilent Technologies, Milano, Italy), which is coupled to a Flame Ionization Detector (GC-FID model 7890A) and equipped with a HP-INNOWAX column (length 30m, diameter 0.250 mm film 0.25 μm) (Bertin, 2010), The samples were centrifuged at 14,000 RPM for 10 minutes; supernatant was diluted with oxalic acid solution (60 mM) and filtered (0.45 μm membrane). The lactose and lactic acid concentrations were determined by HPLC using IR as detector and a Varian Hi-Plex H 300 x 7.7 mm column. 0.01 N sulfuric acid was used as eluent, with an elution rate of 0.6 mL/min and a 65°C operating temperature. The samples were centrifuged at 14,000 rpm for 10 minutes and filtered (0.45 μm membrane).

The produced biogas volume was determined by using a glass syringe of 50 mL for microcosm experiments while for the bioreactor was by a “Mariotte” system. The composition was measured applying gas chromatography using a μGC-FID, either microcosms as for the bioreactor (Scoma et al., 2011).

Results and discussion

The VFA production trend obtained in the fourth microcosm batch experiment is represented in Fig. 1. It was observed a typical behaviour, according to which lactose was converted to lactic acid, with a yield of 91% (C-mol lactic acid/C-mol lactose). When the latter reached its maximal concentration, VFAs started to be produced; therefore, their concentration increased till lactic acid was completely depleted. The total VFAs yield (9 days) was 77% (C-mol VFAs/C-mol lactose) (Table 1).

The experimental time is in concordance with the results obtained in a previous work (Bengtsson et al., 2008), but in this study the organic load was 4 times higher. The final VFAs mixture composition was also different with respect to the one obtained by Bengtsson and co-workers (Bengtsson et al., 2008), in particular, the concentration of propionic acid which in this study was higher with 3 g/L as maximum obtained. Since such parameter is directly linked to the type of PHA, which can be obtained within the subsequent PHA biotechnological production process, these evidences are of interest in the perspective of producing defined PHAs having specific chemical and mechanical features. From the profile obtained within microcosms and reported in Fig. 1, a HRT of 9 days was selected for the PBBR.

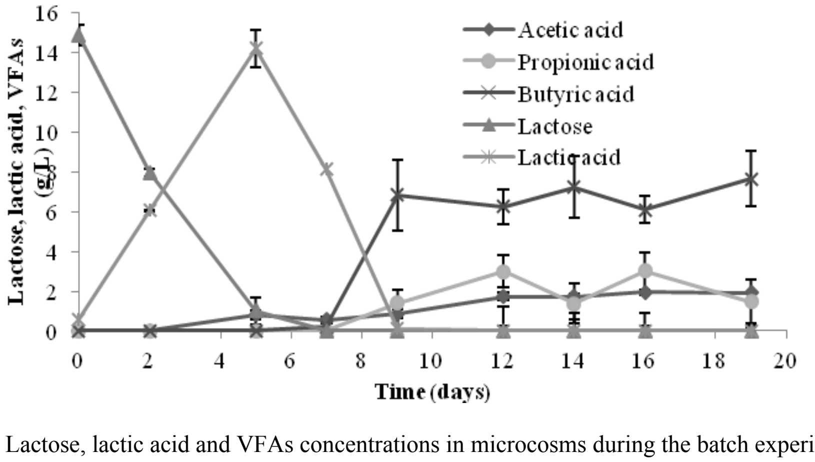

Fig.1. Lactose, lactic acid and VFAs concentrations in microcosms during the batch experiment

Interestingly, the preliminary batch experiment, which was carried out with the PBBR for favouring the biofilm formation, has shown the same behaviour in terms of sequential bioreactions trend than that observed within microcosm experiment. Nevertheless, it was obtained a different final VFAs mixture composition, whereas the lactic acid and VFAs yields were similar to the previous ones obtained at the smaller scale (Table 1).

The VFA concentrations as a function of the time for the continuous mode operation are shown in Fig 2. It can be said that an almost stationary state condition was reached after 9 days, which means after the bioreactor changed 1 time its liquid phase. From day 9, and during the whole stationary state, the VFAs yield was 79% (C-mol VFAs/C-mol lactose), which is similar to what previously obtained under batch conditions (Table 1).

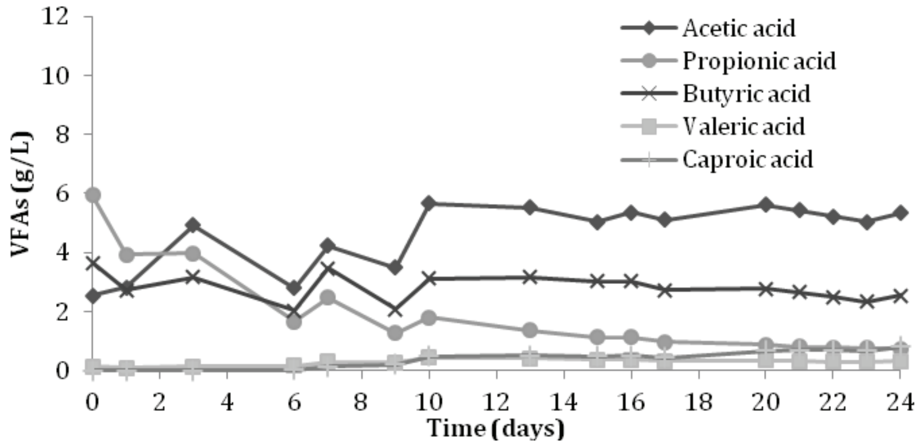

Fig. 2. VFAs concentrations observed during PBBR operation

Anyway, the VFAs mixture composition was not definitely constant: in particular, propionic acid concentration decreased drastically from 6 g/L at day 0, 1.3 g/L after 9 days of operation, until 0.8 g/L at stationary state. This could be attributed to a wash out of the microorganisms responsible for propionic acid accumulation. Thus, the process still needs to be optimized, with the aim of avoiding the loss of specific metabolic activities.

Table 1. Yields obtained in microcosm experiment and in the PBBR

	Microcosm	*Bioreactor batch*	*Bioreactor HRT 9*
Y lactic acid/lactose % (C-mol/C-mol)	91	93	-
Y VFAs/lactose % (C-mol/C-mol)	77	84	79

Concluding remarks

An anaerobic acidogenic immobilized-cells process for the production of VFAs from CWP was developed by employing a PBBR filled with Vukopor S10. All the lactose present in the solution of CWP was bioconverted producing a VFA mixture with a yield about 80%.

Despite it was obtained a good VFAs yield, during the operation with the PBBR a loss of capability of producing propionic acid was observed. Since the latter represents an interesting substrate in the perspectives of producing PHAs with specific features, and the employed inoculum presented the capacity to produce it in considerable amounts, the optimization of the biotechnological process for the obtainment of a VFA mix rich in propionic acid has to be persecuted.

Keywords: Acidogenic mixed culture, Ceramic support, Cheese Whey, Packed-bed bioreactor, Volatile Fatty Acids

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BIOMETHANE PRODUCTION FROM GRAPE POMACES: A TECHNICAL FEASIBILITY STUDY

Extended abstract

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Background

Agricultural wastes, obtaining by processing fruits and vegetables, nowadays are a huge environmental problem. On the other hand, they can represent sources for the production of high added value products, such as biofuels and fine chemicals. Winemaking is one of the most common fruit processing industries in the world: during the 2011 campaign 293 million hL of wine were produced, 46 million hL of which in Italy, which is the second producer of wine in the world after France (FAOSTAT, 2013). Vinification is a traditional and seasonal process which differs depending on the kind of wine to be produced. However, usually, it mainly consists of the same following phases: harvest, steaming, crushing, pressing, fermentation, sedimentation decanting, stabilization, bottling. The winemaking residues can be divided in liquid and solid ones. The former are composed by wastewaters used to clean and sterilize winery equipment.

The solid wastes consist mainly of grape stalks obtained from the destemmed grapes, pomaces or marcs obtained after pressing and lees from sedimentation of the fermented grape juice. Grape pomace (GP) is the most abundant winemaking waste, and it represents about the 20% (w/w) of grapes used for the production of wine (Schieber et al., 2001). During the 2011 campaign, about 1.1 Mt of GPs were produced in Italy (FAOSTAT, 2013). GP typically consist of skins (peels), stalks and seeds. Its composition depends on a lot of parameters, among which geographic production region, clime and winemaking process.

However, it is a fibrous solid waste rich in lignin, cellulose, hemicellulose and pectine due to the major presence of the fruit skin, usually characterized by 40% of TS and a low pH (around 4). GP is not rich in sugars, while it contains a high amount of tannins and polyphenols, which are high added value compounds well known for their antioxidant characteristics (Dinuccio et al. 2010; Bustamante et al. 2008). In Italy, GPs are sent to distilleries, where they are processed for the production of distillates. Alternatively, GPs could be valorized in different ways, by taking advantage of their chemical features and the presence of a lot of high added value substances.

According to literature, the main obtainable products and processes applicable to GPs can be summarized as follows: (a) polyphenols extraction; (b) animal feeding; (c) composting; (d) fermentation for the production of fine chemicals; (e) incineration; (f) biomethane. In particular, the last one is produced during anaerobic digestion, which is a biological process usually referring to an oxygen-free fermentation of biomass which lead to the production of biogas, i.e., a mix of gases represented by up to 70% of methane. The anaerobic digestion for the production of biogas from GPs can be a highly attractive process for the winery industry, by coupling the opportunity of generating income from waste with that of abating disposal costs.

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Objectives

The objective of this work was to evaluate the technical feasibility of producing biomethane by exploiting GPs as the substrate for anaerobic digestion processes. GPs obtained from both red and white grapes were tested. For this purpose, the experimental matrices biomethane potential (BMP), defined as the maximum amount of methane obtained from discontinued operating conditions (batch), was evaluated.

Methods

Experimental set up

Micro-batch anaerobic reactors (microcosms) with a total volume of approximately 110 mL were set up to determine the BMP of the experimental matrices. The microcosms consisted of a Pyrex glass bottle hermetically closed with a double silicon septum inside of a perforated cap, which was used for sampling the head space gas. All tests were conducted incubating the microcosms statically at the temperature of 55°C (termophilic conditions). Each bottle was filled under nitrogen purging with a total final mass amount of about 55 g. This was composted by substrate (GP), anaerobic inoculum and osmotic water in different percentages, as reported below. Employed Red GPs came from the production of wines "San Giovese" and "Montepulciano", while white GPs derived from Trebbiano and Verdicchio winemaking processes. Both GP types were obtained from Cantine Moncaro, Jesi, Italy. The methanogenic inoculum was previously selected and microbiologically characterized (Bertin et al., 2012), and it had a low content of total (3.15% w/w) and volatile solids (1.34% w/w).

A control experiment for each experimental condition was prepared within microcosms containing only water and inoculum, in order to subtract the amount of any eventually observed biogas to that produced in corresponding microcosms containing the GP, thus determining the BMP only relating to the pomace. At the same time the pH was correct with a NaOH solution moving from 4 (i.e., the initial pH of the broth), to a weakly alkaline pH (between 7 and 8), to promote the onset of methanogenic conditions.

1st Experiment

The objective of this experiment was to compare the experimental GPs in terms of BMP. GPs were dried and milled before being processed, to enhance the substrate bioavailability. The used GPs had high contents of TS and VS (White GP: TS 92.63 %, VS 87.53%; Red GP: TS 93.90 %, VS 84.35%). The microcosms were set up by filling them with 10 g of GP, 50 mL of water and 5 g of inoculum. All conditions were carried out in triplicate. The experiment lasted 12 weeks.

2nd Experiment

The influence of the ratio between inoculums and substrate was evaluated by employing the matrix, which gave rise to the best results during the first experiment (namely, the red GP). In particular, by keeping constant the amount of inoculum, different quantities of substrate were tested and vice versa. All conditions were carried out without varying the total amount of anaerobic digestion broth. The reproducibility of results obtained within the 1st experiment was also verified by repeating one experimental condition, which was set up during the 1st one. Table 1 summarizes the composition of the different developed microcosms and the used acronyms. The condition, which replaces the one of previous experiment is called I5S10. All conditions were carried on in duplicate. The experiment lasted 12 weeks.

Table 1. Composition of microcosms developed within the 2nd experiment

Acronym	***Inoculum*** **(g)**	***GP*** **(g)**	***Water*** **(ml)**	***TS*** **(g)**	***S*** **(g)**
I5S10	*5*	*10*	*40*	*9.5*	*8.5*
I5S5	*5*	*5*	*45*	*4.9*	*4.3*
I5S1	*5*	*1*	*49*	*1.1*	*0.9*
I5S15	*5*	*15*	*35*	*14.2*	*12.7*
I2S10	*2*	*10*	*43*	*9.5*	*8.5*
I10S10	*10*	*10*	*35*	*9.7*	*8.6*
I15S10	*15*	*10*	*30*	*9.9*	*8.6*
I20S10	*20*	*10*	*25*	*10.0*	*8.7*

Monitoring

Microcosms were monitored periodically, at the beginning every 2 days, then by higher growing time intervals, till monthly. Each monitoring consisted of the evaluation of the produced biogas, in terms of volume and composition, and of the volatile fatty acids (VFA) production, indices of acid-acetogenic fermentation that typically precedes the methanogenic respiration during the anaerobic digestion process. To those aims, microcosms were taken out from the incubator and let cool till ambient temperature.

The septum of the microcosms was perforated with a needle connected to a cilinder-Mariotte system to measure the produced biogas. Assuming that the composition of the biogas in the head of the bottle was still constant and no oxygen came inside, the septum were perforated another time by a needle connected to a microGC-TCD system, by which the composition of the produced biogas was determined. Afterwards, the cap was opened under a flux of nitrogen and an aliquot of the supernatant was sampled for VFA analyses. Then, if necessary, the pH was correct to the initial value (between 7 and 8). Finally, the end the bottle is closed with the cap and incubated again.

Analytical methods

Biogas composition was measured by a MicroGC 3000 Agilent Tecnologies coupled with a TCD detector (injector temperature 90 °C; column temperature 60 °C; sampling time 20 s; injection time 50 ms; column pressure 25 psi; run time 44 s; carrier gas, N2). Volatile Fatty Acids were analyzed by an Agilent GC-FID (model 7890A) equipped with an Agilent J&W GC column, 30 m x 0,25 mm x 0,25 µm (injection volume 1 µl; injector temperature 250°C; column head pressure 5 psi; column initial temperature 40 °C; 1 min isotherm; temperature rate 25°C/min; final temperature 150°C; 6 min isotherm; temperature rate 4°C/min; final temperature 180°C; temperature rate 25°C/min; final temperature 240°C; detector temperature 280°C). The samples were centrifuged for 5 min at 14000 rpm then the supernatant diluted with an oxalic acid solution (60 mM) in the ratio 1:4 or more in order to reduce all carboxyl terminations of VFAs. This method allowed the monitoring of the following VFAs: acetic, propionic, isobutyric, butyric, isovaleric, valeric, isocaproic, caproic and eptanoic acid.

Results and discussion

The 1st experimental set suggested that the matrix, which allowed a higher biomethane production, was the red drayed-milled GP. 573-mL of biogas, 62.5% of which represented by methane, were produced after 3 months of incubation; as a whole, this corresponds to 41 ml of CH_4 per g of VS. No methane production was observed within control microcosms, this meaning that all the above reported production was due to biomethanization of the substrates (GPs). Anyway, results were very low, if compared to available literature, where a BMP of 116 for red/white GPs was reported (Dinuccio et al., 2010).

Thus, with the proposal to enhance the biomethane production, a second set of experiment was carried out, with the aim of understanding the role of the ratio inocula/substrate. The profiles of BMPs and VFAs as a function of the time are shown in Figs. 1 and 2. BMPs are expressed as the cumulative amount of produced methane per the organic matter initially introduced in the microcosms (expressed as volatile solids).

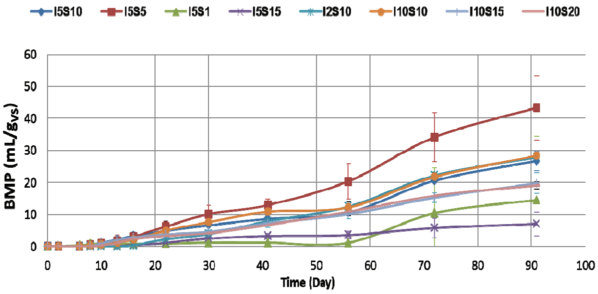

Fig. 1. BMPs of matrices employed in the 2nd experiment

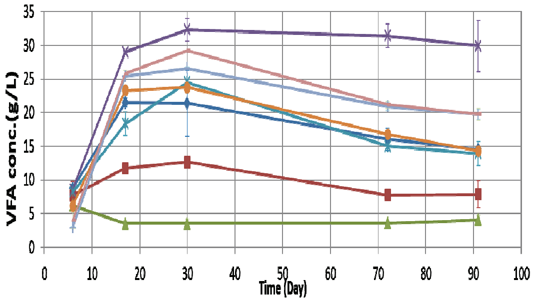

Fig. 2. Volatile Fatty Acids profile in the 2nd experiment

After 90 days of incubation, the best result was reached by the microcosms I5S5, where 43±10 mL/g_{VS} of CH_4 and 391±57 mL of biogas were produced. Then, the I5S10 microcosms reached a production of 26±3 mL/g_{VS} of CH_4 and 571±50 mL of biogas. The obtained methane corresponded to a percentage of the 48 and 41%, respectively, of the total produced biogas. The microcosms I5S1, which had the lower quantity of TS, i.e., 1.1 g, gave rise to the lowest production of VFAs (Fig. 2), but not to the lowest BMP, which was achieved by microcosms I5S15 containing the highest amount of TS, i.e., 14.7 g. In these bottles about 32 g/L of total VFAs were achieved after 30 days of incubation, and that amount remained constant over time.

The best condition was the I5S5, whose TS content was 4.5 g. In such microcosms, the maximum concentration of produced VFAs was about 12.5 g/L.

Both values were among the lowest. The other conditions were characterized by more or less similar TS contents (around 9.5 g) and showed a trend in terms of production of acids and BMP approximately similar, and intermediate between the best and worst situations mentioned above. In general, the results were not satisfactory, being BMP values very low if compared to those cited above (Dinuccio et al., 2010) and regarding other solid vegetable matrices (Raposo et al., 2011).

Actually, it was observed that during the phases of acid-acetogenesis, that precedes the methanogenesis, the production of acids was very high and the presence of such concentrations can not allow the achievement of suitable BMP. As for the concentration of single acids when maximum production of VFAs was reached, the mixture composition was about the same in each experiment and mainly consisted in about 60% of acetic acid, 30% of butyric acid, 5% of propionic acid and traces of the other acids.

In the I5S15 microcosms amounts of 19.6±2.8 g/L of acetic acid, 9.7±1.1 g/L butyric acid and 2.0±0.1 g/L propionic acid were observed after one month of incubation. Those data indicate that the acetogenesis was predominant with respect to the acidogenesis phase.

Concluding remarks

The anaerobic digestion for the production of methane was probably affected by the very high production of VFAs, which was closely related to the content of TS. Thus, the performance of the anaerobic digestion strictly depended on total solids content.

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A DETAILED MONITORING OF AN ANAEROBIC DIGESTION PLANT IN NORTHERN ITALY

Extended abstract

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Background

Throughout the years, the attention on the quantification of the environmental impacts derived from agricultural production systems has increased considerably. The agricultural contribution to greenhouse gases (GHG) emissions is incontestable (Intergovernmental Panel on Climate Change [IPCC], 2007). Agricultural activities are responsible for about 10 % of the total Europe GHG emissions (Bacenetti et.al, 2013). Furthermore, considering the European objectives regarding the reduction of fossil fuel consumption and GHG emissions, the production of energy from renewable sources is a priority (EC Directive, 2009).

In Italy, in 2011, the energy production from RES reached 11.6 % of the global energy consumption and the 23.5 % of the total electric consumption. In this framework, during the past 10 years, the agricultural biogas production was considerably increased. Nowadays, about 1000 agricultural biogas plants are running mainly in northern regions with a total electrical power of 756 MW. This Fig. corresponds to 1.65 % of the global electric consumption. Strong public incentives are granted for electricity produced from biogas. From 2013 with the (D.M. 6 July 2012) (Ministry of Economic Development, 2012) the public incentives framework has been changed giving more importance to heat and by-products valorization. Nevertheless, for the biogas plants put into operation before 31 December 2012 and with electrical power lower than 1 MW, 280 €/MWh are granted for the electricity fed into the grid without any consideration regarding heat and byproduct valorization. The granting of incentives only to the electricity has favored the building of several big AD plants with poor consideration for overall efficiency of the system. Regarding the feeding of digesters, although the anaerobic digestion (AD) of animal manure is one of the best techniques for an energetic valorization of these by-products the cereal silages are the main feedstock for biogas production, both in Italy and in other European countries (Dressler et al., 2012).

Although the AD of agricultural feedstock can be performed with different types of biogas plants (Fabbri et al., 2011), the most widespread technology is characterized by mesophilic conditions and single-stage digestion in continuous stirred-tank reactors [CSTR] (Fantozzi and Buratti, 2009). Considering that the biogas production involves important environmental issues, especially global warming, acidification, and eutrophication (Meyer-Aurich et al., 2012; Gonzalez et al., 2013) it must take place in an efficient way. Nevertheless, the increasing number of biogas plants, especially those larger than 500 kW electrical power, involves high consumptions of energy crops, large transportation distances (both for the biomass feedstock and the digestate), and difficulties with thermal energy valorization. The widespread of AD plants, beside environmental issues, involves also economic and social challenges. Over the years, the spread of biogas plants, often concentrated in specific areas (such as the provinces of Cremona, Lodi and Mantua), resulted in the considerable rising of biomass prices and concerns about the fact that more and more agricultural land is used to feed the digesters.

The achievement of high global efficiency of the biogas system is become a very important issue without which satisfactory economic and environmental results are hardly reached. In this contest, the monitoring of AD plant is the first step and it represents a useful tool capable to give information needed to well manage the plant itself.

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In this study an agricultural AD plant with an electrical power of 998 kW was monitored for 12 months. The aim of the monitoring was the evaluation of the global efficiency of the biogas plant and, in particular, to consider the exploitation of the biomass introduced into the digesters.

Methods

1. Description of the biogas plant

The AD plant is based on a single stage process, it has two CSTR (Completely Stirred Tank Reactor) digesters operating together with a total volume of 5300 m^3 (2750 m^3 per digester) The AD plant has an electric output of 998 kW (η_{EE} = 40.9 %). Since the heat is recovered only from engine water and oil cooling jacket, the thermal power of the plant is equal to 577 kW (η_{TE} = 45.0 %)

It works in mesophilic conditions (T = 40 °C). Over the year, it co-digests energy crops (maize silage, triticale silage, and ryegrass silage), pig and cattle slurry, poultry manure, by-products of maize industry and food wastes. Feeding systems and schedules are different for solid and liquid biomass: silages are put into the digesters by a screw placed on the bottom of the feeding hopper; the loading system is located between the two digesters. Slurry coming from the animal husbandry is stored in a tank and, from this, it is pumped into the digesters; the whole substrate is mixed with liquid fraction (LF) of digested matter. In this way, proper inlet Total Solid (TS) content is achieved. The AD microbial process operates at 40°C and it occurs in 2 cylindrical above-ground CSTR (Completely Stirred Tank Reactor) digestion reactors (diameter Ø = 20 m, height H = 8 m). They are made of iron-reinforced concrete and have an expanded polyurethane external insulation. Both the two digesters are covered by a gasometric dome with a spherical shaped cap.

In each reactor the mixing is obtained by 4 submerged long-axis mixers operating 5 minutes per hour. Mixers can be adjusted in height and internal angle. Regarding the heating system, the hot water (80 °C) coming from the CHP unit is used to heat the biomass inside the digestion reactors; 4 pumps circulate this hot water into in-vessel heat exchangers. Within a year, the 4 pumps have an average operating time of 5 h/day. Digestate is dumped by a lobe pump from the bottom part of the digesters. AD effluents are: (i) partly, accumulated in a storage tank and (ii) partly, separated into a liquid (LF) and solid (SF) fraction by using a screw separator. Biogas treatments (filtration, dehumidification and desulphurization) are always required before to feed the CHP i.c. engine. Filtration is carried out with a simple sand-filter. Produced biogas is filtered in a sand filter, dehumidified and desulphurizated. Dehumidification is carried out by a refrigeration unit (15 kW_e) that cools down the biogas temperature removing the water vapor while desulphurization by a wet scrubber (10 kW_e). Biogas treatment devices work in series with operating on the same biogas flow rate consumed by the CHP i. c. engine. After the treatments, biogas feeds a CHP unit. Thermal energy not used for heating the biomass inside the digesters is dissipated by fan-coolers. The cogeneration unit runs constantly at 1500 rpm.

2. Monitoring

The AD plant has been monitored for 12 months. During this period, each day, these data have been gathered: 1) feedstocks consumptions; 2) temperature inside of the two digesters; 3) organic loading rate; 4) biogas production and its composition; 5) working time of CHP, gross electricity production, electricity self-consumption, net electricity production. Each month the total solid and volatile solid content inside the two digesters has been determined by means of laboratory analysis. The laboratory tests have been carried out also to measure the specific biogas production of the different feedstocks utilized to feed the digesters.

3. Laboratory tests

The total solid and volatile solid content (for the substrate inside the digesters as well as for the different feedstocks) has been measured according to (Martillotti et al., 1987).

A laboratory device has been developed to measure the specific biogas and methane production of the different biomasses used to feed the digesters. Lab-scale unstirred fermenters were developed and placed in thermostatic baths at 40°C (Negri et al., 2013). The fermenters were made of a hermetically sealed glass jar with one metallic cover holding the valve through which the biogas produced by the tested samples reached the corresponding gasometer by flowing into one flexible nylon hose. Gasometers are made by methacrylate Torricelli pipes with 3.5 litres volume. Each gasometer has, on top, two hoses: one carrying the biogas from the fermenter and one, made of PVC, equipped with a valve for gasometer recharge. When the biogas flows from the fermenter into the gasometer, the aqueous solution is moved in a vessel equipped with one overflow device which allows to the aqueous solution to be collected in a tank. Samples of fermenting biomass from different full scale anaerobic digesters were used as inoculum. Before digestion all substrates were ground using a professional grinder (Blisxer 5 Robot coupe France).. During the experiment the temperature in each fermenter was kept at 40°C. Fermenters were kept in these conditions as long as substrate's biogas production was significantly different from the inoculum one. Biogas volumes where daily recorded: the centimeters ran by the aqueous solution in the gasometers were read and the equivalent volume in virtue of gasometer diameter was calculated.

Biogas composition was monitored by means of one “Binder Combigas GA-m3” (from Binder, D) portable gas analyzer measuring the content into methane and carbon dioxide equipped with one electrochemical cell for oxygen measurement and one infrared dispersion cell for methane and carbon dioxide percentage determination.

4. Efficiency

The global potential biogas production ($P_{BG\_GLOBAL\_POT}$; m^3_N/year) has been compared with the global biogas volume measured at the plant in order to estimate the efficiency of the AD process. The biogas produced over the year should be the most possible similar to the $P_{BG\_GLOBAL\_POT}$. When big differences are detected the AD process is ineffective and more biogas could be produced with the same amount of feedstocks. P_{BG_GLOBAL} has been calculated as the summation of the potential production of each feedstock (P_{BG_FDi}; m^3_N/year). P_{BG_FDi} is computed considering the laboratory test results and the mass of the feedstock *i* introduced into the digesters. In more details (Eq 1-2):

$$P_{BG\_GLOBAL\_POT} = \Sigma\, P_{BG\_FDi} \tag{1}$$

$$P_{BG\_FDi} = \Sigma\, m_{FDi} \cdot PS_{FDi} \tag{2}$$

where: m_{FDi} is mass of the feedstock *i* introduced in the digesters (t_{wb}/year); PS_{FDi} is specific biogas production of the feedstock *i* (m^3_N/t_{wb}); this value is the result of the laboratory tests.

Results and discussion

Table 1 shows the feedstock consumption over the year, the results about the laboratory tests and the potential biogas production for the different matrixes. Regarding the laboratory tests, as predictable, energy crops have higher specific biogas production compared to animal by-products. Food wastes show great variability although they represent suitable substrates for AD.

Energy crops are the main feedstock. In more detail, the maize silage is by the far the most important feedstock and it is the staple for digester feeding, it silage represents more than 80% of the biomass introduced into the digesters and from it stems about 85% of the potential biogas production. Slurry mass is about 6% of the global feedstock but it contribute to the biogas production is really small (0.60 %). Food wastes represent a little share of the feedstock but their contribution to the biogas production is more than proportional.

Table 1. Feedstocks consumption and potential biogas production

Feedstock	***Mass***	***Share***	***TS***	***SV***	**PS_{FDi}**	**P_{BG}**	***Share***
	t_{wb}	%	$\%_{wb}$	$\%_{ST}$	m^3_N/t_{SV}	m^3_N/year	%
Maize silage	16575	80.67	33.8	93.5	671.3	3440944	80.02
Ryegrass silage	584	2.84	28.7	90.5	553.3	323001	7.51
Triticale silage	695	3.38	30.1	92.5	589.2	113845	2.65
Corn Gluten	806	3.92	42.5	80.2	549.3	255885	5.95
Poultry manure	296	1.44	49.9	80.8	332.4	65578	1.53
Bread	47	0.23	90.0	96.8	455.3	28999	0.67
Distiller	288	1.40	28.9	90.1	931.2	46882	1.09
Caw slurry	870	4.23	8.1	84.4	712.7	19519	0.45
Pig slurry	387	1.88	3.7	83.6	625.5	5446	0.13

About the feeding, the monitoring has highlighted deep differences not only on the feeding amounts but also on timing and way. In fact, over the years, maize is the only feedstock continuously feed in the digesters (only in 6 days it has been not utilized). The food wastes (bread) and industry by-products (corn gluten) have not been continuously used and moreover are not put into both the digesters; their use strongly depends by their prices and availability on the market.The liquid fraction (LF) – coming from the digestate separation (6272 t/year) – and water (1266 t/year) have been added in the digesters to maintain the organic load and the percentage of dry matter (DM) at optimal level (DM: 8-9%). Each day about 166 t/day of the substrate – contained in the digesters but not completely digested – has been circulated between the two digesters to balance the different biomass input described above. This also allowed the mixing. The average organic loading rate is 3.32 $kg_{SV}/m^3\cdot$day.

Over the year the temperature remains in a mesophilic regime. From October and April temperature shows little variations and it ranges from 39 °C and 40 °C. It is interesting underline that, from May and September, although the heating system was off, the temperature increased up to 43.7 °C. Regarding the content of total and volatile solids inside the digesters, the results of the laboratory tests conducted monthly are reported in Fig. 1. It can be noted that, over the year, the level of total solids shows big variations (it ranges between 6 to 9% of the fresh biomass) while the volatile solids have smaller variations: from June to March they ranges between 65 to 80% of the total solid. These variations are due to the heterogeneity of the diet. The different feedstocks and in particular the food and industry wastes, are used depending on their availability and market prices.

Considering the values reported in Table 1 the potential biogas production is equal to 4300100 m^3_N/year. The measured biogas production is 3946311 m^3_N/year (daily biogas flow is equal to 10782 m^3_N/day) and it represents about the 92% of the potential biogas production. The biogas has an average methane content of 52.51% in volume and, consequently, its Lower Heating Value is 5.13 kWh/m^3_N. During the monitoring period, the CHP unit has produced 8379 MWh of Electric Energy (EE) (on average 22.89 MWh per day). The EE daily self-consumption of the plant (for pumps, screws, mixers, biogas treatments etc.) was 653 MWh with an average value of 7.79% (1784 kWh per day). Consequently the net energy produced was 7726 MWh.

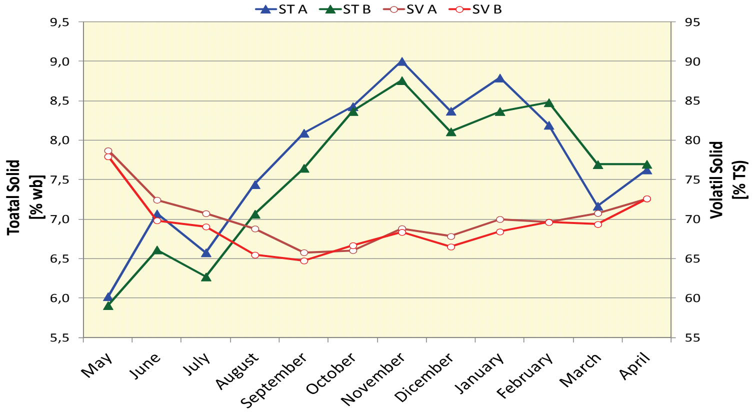

Fig. 1. Total (ST) and volatile (SV) solid variation over the year in the two digesters (A and B)

Concluding remarks

This paper reports the results of a detailed monitoring of one anaerobic digestion plant. The monitoring has highlighted that, although, over the year, several feedstocks are fed into the digesters the maize silage is, by far, the most important biomass; from it stems more than 80% of the biogas.

The comparison between the biogas production and the potential production as well as the electricity production underlines the good efficiency reached by the biogas plant. A further optimization of the plant could be achieved by means of a reduction of electric self-consumption and by the use of the heat actually wasted.

Keywords: anaerobic digestion, biogas, efficiency, energy, monitoring

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AN INTERNATIONAL NETWORK FOR DEVELOPING RESEARCH, TECHNOLOGICAL TRANSFER AND DISSEMINATION ON TREATMENT AND UPGRADING OF MEDITERRANEAN AGRO-INDUSTRIAL WASTES AND EFFLUENTS

Extended abstract

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Background

During the last years one of the most used keyword in environmental context has been "biorefinery" that is analogous to today's petroleum refinery but, differently, means use of renewable sources for production of bio-molecules and fuels (Petruccioli et al., 2011). Also the new UE FP8, the so called "Horizon 2020", considers the biorefineries' development as a strategic objective. Hence, all by-products, residues, wastes and wastewaters coming from agro-industrial activities should be increasingly regarded as potential resources that must be reused and valorized, thus minimizing the simple disposal. This approach allows to think positively to bioeconomy based on conversion of biomasses to chemicals and biofuels, thus avoiding or, at least, reducing drastically the competition on land use for food.

International Association of Mediterranean Agro-industrial Wastes (IAMAW)

In this scenario, a new scientific association dealing with the recycling and management amelioration of Mediterranean organic wastes was born in 2009. The term Mediterranean refers to climatic region and not to geographic location, so that waste problems of other areas in the world, characterized by Mediterranean climate, such as parts of Australia, South Africa North and South America, will also be addressed.

Some of the aims of the associations are: i) fostering environmental solutions for agro-food and forestry by-products, residues, wastes and effluents typical to the Mediterranean region through reduction, treatment, reuse and amelioration; ii) promoting knowledge dissemination and transfer of know-how among members, end-users, stakeholders and the scientific community; iii) improving and demonstrating techno-economical feasibility of the proposed solutions; iv) creating working links with relevant international bodies, scientific organizations and industrial partners; v) assisting policy-makers in defining more rational and uniform laws and regulations in the field of Mediterranean waste management; vi) assisting in the identification of Best Available Technologies (BAT). The members of the association are engaged in various scientific disciplines and their expertise in wastes and wastewaters valorization and treatment imply the use of various technologies (*e.g.*, composting; aerobic and anaerobic processes; bioremediation; biotechnology and physical/chemical processes for production of biofuels, fine chemicals and biomaterials).

Selected biorefinery case studies and deliverables

A selection of the main research activities and deliverables obtained by some selected IAMAW members is reported in Table 1: each row summarizes significant results on efficient wastes treatments and, mainly, on the production of biofuels, high-quality composts, feeds and biomolecules of industrial interest in food, nutrition, cosmetics and pharmaceutics. These research activities are grouped in five different topics that represent the IAMAW working groups. Various wastes and wastewaters have been characterized (Aviani et al., 2012; Diaz et al., 2011) and their valorization strategies investigated: orange peel wastes, sunflower oil cake, wheat straw and sweet sorghum biomass, winery and greenhouse wastes, dairy manure, distillery wastewater and whey are only some examples (Table 1). Several research groups have focus their attention on treatment, valorization and reuse of the residues of olive oil extraction process, namely olive mill wastes, that besides to be a serious environmental problem in relation to the incorrect disposal, can be regarded also as a possible resource containing simple and complex sugars, residual oil, proteins, minerals and phenols that could be either directly recovered by chemical extraction and purification or utilized for microbial processes (Petruccioli et al., 2011). Various case studies have dealt with upgrading of olive mill wastewater (OMWW), olive pomace or two-phase olive mill solid residue (TPOMW). The possibility to obtain high quality composts using various agro-industrial wastes and OMWs has been deeply investigated (Altieri et al., 2010) and the beneficial uses of these products have been widely tested (Raviv et al., 2011; Yogev et al., 2010). Some of the proposed treatment processes have been developed, optimized and, finally, patented (Altieri et al., 2011; Santori and Cicalini 2002).

Table 1. Main topics and selected aims of researches carried out by some IAMAW members

Topic	*Specific aims of research*	*Relevant results*	*Main Ref.*
Bioenergy from wastes	Anaerobic digestion processes of wastewaters and solid wastes from agro-industries (sunflower oil cake, OMWW, TPOMW, distillery wastewater, whey, etc.)	Optimization of anaerobic digestion and/or co-digestion processes (high-rate bioreactors, one and two-stage processes) at mesophilic and thermophilic ranges of temperature. Optimization of wastes pretreatments of: thermal, and/or chemical, mechanical, ultrasounds, microway, etc. Identification of microbiota in digestion processes through molecular biology techniques (DGGE, etc.)	Rincon et al., 2013; Siles et al., 2007; Fernández-Cegrí et al., 2012; Bertin et al., 2013
	Biohydrogen production from pretreated or mixed wastewaters	Biohydrogen and volatile fatty acids production was obtained on dephenolized OMWW. Hyperthermophilic *Thermotoga* strains were use to produce biohydrogen from molasses and cheese whey.	Scoma et al., 2013; Cappelletti et al., 2012
	Ethanol production from olive tree pruning	Optimization of steam-explosion pretreatment and consequent bioethanol production	Cara et al., 2008
	Biovalorization of biomasses (e.g., wheat straw) for energy and added-value products.	Set up of biomass pretreatments (autohydrolysis, enzymatic or acid hydrolysis) and fermentation technologies with submerged membranes for bioethanol production	Duarte et al., 2009
Waste treatment and recycling	Phyto-depuration process of OMWW	Patented process combining metabolic activity of soil microorganisms and various perennial tree species	Santori and Cicalini, 2002
	Degradation and detoxification of olive wastes and spreading on soils	Immobilized white-rot fungi inocula accelerate TPOMW detoxification and bioconversion	Sampedro et al., 2009
		Detoxification process and assessment of spreading on plants and microbial ecology in agricultural soils.	Ntougias et al., 2012
	Effect of solid olive-mill waste amendment on soil fertility and microbiota	This waste can be used as a soil amendment in olive orchards increasing the vegetative and productive activities of the trees, without long-term negative consequences on soil biochemistry and microbiota	Nasini et al., 2013
	Definition of OMWW biological process	A treatment in a Jet-Loop Reactor followed by an extensive treatment (stabilization ponds) was effective	Jail et al., 2010
	Physico-chemical treatment of OMWW	Application of lime and calcium hypochlorite led to significant dephenolisation and discolouration	Boukhoubza et al., 2009
	Optimization of dairy wastewater treatment in an industrial three-cascade-reactor plant	Assessment of the effects of aeration regimes and polluting loads on performances and on activated sludge population allowed to optimize the treatment parameters and robustness of the three-reactors plant	Tocchi et al., 2013
Ligno-cellulosic biomass	Feeds from olive pomace treated with fungi	Fungal treatment increases of protein content and digestibility and decrease of anti-nutritional compounds	Brozzoli et al., 2010
	Production of fermentable sugars and biomass fractionation	Optimization of dilute acid, hydrothermal or organosolv pretreatment of rapeseed straw, sunflower stalks and sugarcane bagasse, respectively	Diaz et al., 2011; Castro et al., 2011
		Novel direct steam-injection apparatus for sugars production by *Tamarix* biomasses grown in desert area.	Santi et al., 2012
	Activated carbons from agro-wastes	Activated carbon from olive-waste cakes was used efficiently for removal of pharmaceutical compounds	Baccar et al., 2012
Natural products from wastes	Production of enzymes from wastes and wastewaters	High production of lipases of possible industrial interest from *Candida cylindracea* grown on OMWW	Brozzoli et al., 2010
		Halotolerant fungi isolated from olive brine effluent, and grown therein, produced phenoloxidase enzymes	Crognale et al., 2012
	Fungal polysaccharides and enzymes	Production of glucans, chitin and chitosan for food and pharmaceutical industries using olive mill wastes	Di Mario et al., 2008
	Selective recovery of the polyphenolic fraction occurring on OMWW.	Antioxidants (e.g. hydroxytyrosol and tyrosol) were recovered by means of liquid-liquid solvent extraction	Kalogerakis et al., 2013
		Optimization of recovery of polyphenols, particularly hydroxytyrosol; Amberlite XAD16 allowed the higher recovery (about 60%).	Bertin et al., 2013
		Scale transfer feasibility of solid phase extraction procedure for the recovery of natural antioxidants	Scoma et al., 2013
	Biotechnological production	Anaerobic and anaerobic-aerobic integrated processes for	Beccari et al.,

	of biopolymers	polyhydroxyalkanoates production from OMWW	2009
Composting	Evaluation of thermal and static composting methods for bioconversion of olive mill waste as major ingredient and other wastes	Production of “mature” and “stable” compost rich in humus-like substances (patent MATReFO) Assessment of compost quality and its use for strawberry soilless cultivation	Altieri et al., 2011; Federici et al., 2011
		Enhancing soil nutrient status in olive orchards and short-term crops	Yogev et al., 2010
		Use of compost from olive mill residues in commercial cultivation of *Agaricus bisporus*	Parati et al., 2011
		Minimization of risks of bacterial canker spread through plant residue composting	Raviv et al., 2011
		Effective use of licorice waste compost in horticulture	Medina et al., 2011
	Vermicompsting for bioconversion of olive mill, winery and greenhouse wastes.	Development of vermicomposting processes using non-continuous and continuous feeding systems Vermicomposts as organic amendments for soil protection, soil remediation and fertility improvement	Fernandez-Bayo et al., 2009; Fernandez-Gomez et al., 2011
	Development of pilot and commercial scale composting technologies for by-products	Evaluation of resulting composts as soil conditioners, fertilizers and suppressants of soil-borne plant pathogens	Kavroulakis et al., 2010
	Compost quality amelioration by reducing polyphenols content and related toxicity	Isolation of autochthonous tannins-degrading bacterial strains from compost and their characterization for possible biotechnological applications and role in quality improvement of compost from OMWW	Pepi et al., 2013

IAMAW members have been actively involved in EU projects such as in the case of a recently ended EU project titled “Suitable Innovations and Treatment in Industrial Waste Waters Clusters (STInno)”, in which IAMAW has been a partner together with Greeks, Finnish and Swedish. The overall goal reached by the STInno project has been to map the technologies for industrial wastewater treatment, to transfer sustainable technologies to olive mill wastewater treatment. The project has led to exchange of experience and knowledge between research and business. In the context this project and parallel ones a list of 110 feasible technologies has been prepared and various criteria of searching have been identified, like patented technologies, treatment processes, etc (www.lifeoleicoplus.it).

Concluding remarks

The valorization of food processing by-products, waste and effluents is a challenging opportunity for the sustainable and competitive development of several relevant industrial sectors. However, there are several key points of technical and scientific difficulty (*i.e.* seasonality, the microbial instability and high heterogeneity of wastes and effluents) that have to be addressed and dealt with for a more effective and rational upgrading of agro-industrial wastes (Petruccioli et al., 2011). In this context, the establishment of the IAMAW is expected to play a significant role in the years.

Keywords: added-values by-products, bioconversion processes, biorefineries, IAMAW, wastes valorization.

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EARLY-WARNING SYSTEMS FOR EMERGENCIES IN WATER SUPPLY

Extended abstract

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Background

An Early Warning System (EWS) for emergency in water supply, can be defined as a system of data collection and analysis to monitor the qualitative/quantitative status of water resources, in order to provide timely notice when an emergency threatens, and thus to elicit an appropriate response in case of interruption or strong reduction of the distribution. In the framework of an agreement with the Italian Civil Protection Department, the Water Research Institute (IRSA-CNR) is developing EWS both for quantitative and qualitative emergencies concerning drinking water supply. Concerning quantitative emergencies, the goal of an EWS is to forecast on the short-medium term (from weeks to few months) the possible onset of water shortage conditions, occurring when the available resources are not sufficient to satisfy the demand, due to a significant reduction of the precipitation (drought conditions).

The development of an EWS should take into account three main aspects: a) the storage capacity of the resource, b) the meteo-hydrological conditions (recharge) expected on the short-medium term; c) the demand. In this project an indicator for water scarcity in water supply systems served by a reservoir, has been developed based on the statistical treatment of the meteo-hydrological data, and applied to the reservoir of Ridracoli (Emilia-Romagna, central Italy).

Dealing with water quality issues, the objective is to monitor the first signs of water quality variations in order to trigger early and appropriate responses, before distributed water reaches the distribution system and the consumers. For this purpose, a procedure for the emergency management of accidental spills of chemicals in groundwaters is currently being developed by IRSA. Such a procedure includes: 1) a GIS tool for the identification of the drinking water abstraction points located in the nearby of the accident, 2) mathematical methods for the quick assessment of the arrival time and concentration at the withdrawal point (e.g. fast mathematical solutions and simple numerical codes), 3) innovative monitoring strategies aiming at the early detection of contaminants. In this short note the main concepts and methods for water quality monitoring in an emergency framework are shortly described.

Methods

1. EWS for water shortage

In order to estimate the probability of occurrence of shortage conditions in a water supply system (WSS), a modeling approach to simulate different conditions of inflow, storage, demand and distribution is particularly useful. Here we present the methodology adopted to identify suitable early warning indicators for water shortage in the WSS served by the reservoir of Ridracoli (Emilia-Romagna region, central Italy, Fig. 1, left). The reservoir of Ridracoli, managed by Romagna Acque s.r.l., has been operating since 1988. It has a maximum storage of about 33 Mm^3 and the total catchment area is 88.49 km^2. The water stored in the reservoir is used to supply the administrative provinces of the Romagna region, whose total demand ranges from about 7.5 Mm^3/month in winter up to about 12 Mm^3/month in summer, totalizing almost 106 Mm^3/year. The consistent seasonal change in the demand is related to the increase of tourists from June until September.

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The methodology is grounded on the simulation of the water flow in the WSS through a mathematical model (SimBaT) (Pierleoni et al., 2007) in which users and resources are modeled by nodes connected by arcs, the latter representing pipelines and channels. The balance equation between the available resource and the water demand at each node is computed at the weekly or monthly time step. If the demand is higher than the available water, a deficit occurs. In Fig. 1 (left), the topological scheme of the Ridracoli WSS used in the simulations is shown. The identification of EW indicators is performed through the following steps: 1) An analysis of the rainfall regime (1945-2012) is carried out computing the Standardized Precipitation Indices (SPI, McKee et al., 2003) of the rainfall time series collected by all the gauges located within the area of interest, for different time aggregation scale (from 1 to 12 months, named *SPI1* to *SPI12*). 2) To seek for the relationships between the precipitation regime and the inflow to the reservoir a simple multilinear regression between the monthly inflow and the *SPI1*, *SPI3* and *SPI6* has been computed using the least-square method (Eq.1):

$$Q(m,i) = a(m) \cdot SPI1(m,i) + b(m) \cdot SPI3(m,i) + c(m) \cdot SPI6(m,i) + d(m) \tag{1}$$

where $Q(m,i)$ is the inflow for the month *m*, year *j*; $SPI1(m,i), SPI3(m,i), SPI6(m,i)$ are the means over all the available stations of the Standardized Precipitation Indices computed for the month *m,* year *j* on the cumulative precipitation over 1, 3 and 6 months and $a(m), b(m), c(m), d(m)$ are the coefficients from the multilinear regression of *SPI1*, *SPI3*, *SPI6* and the known term, respectively. It is worth to note that the coefficients have been computed for each month m.

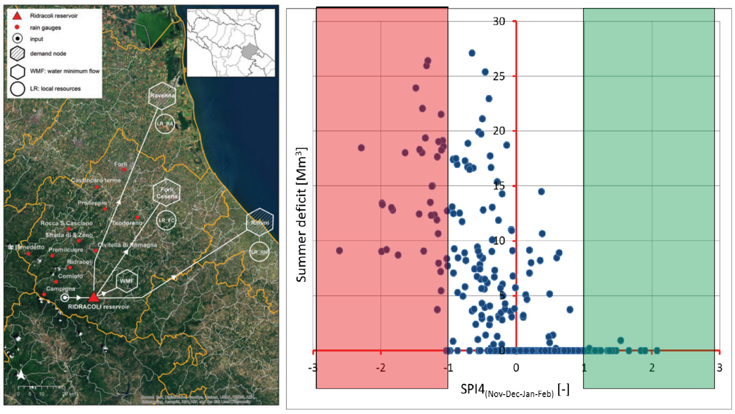

Fig. 1. Left: Location of the Ridracoli reservoir (triangle) and of the rain gauges used for the analysis of the precipitation regime of the period (1945-2010); simplified scheme of the Ridracoli Reservoir supply system. Right: Summer deficit plotted vs the winter precipitation represented by the $SPI4_{Nov-Dec-Jan-Feb}$. Green and red shaded areas represent unconditional lack of deficit and unconditional presence of deficit, respectively

The choice of the aggregation time of the *SPIs* using for the regression takes into account the different characteristic time typical of the different processes that contribute to the inflow to the reservoir (surface run-off, soil moisture content, snow melting, groundwater flow etc). 3) The mathematical model uses as an input the discharge time series of the river entering the reservoir (observed or forecast), and delivers as output the time series of the water balance at the nodes including the deficit, should a deficit occur. 4) Appropriate early-warning indicators are eventually identified from the analysis of the duration and intensity of the deficit. In particular, an effective early-warning system for the case study of Ridracoli should be able to forecast condition of water shortage during summer (when the total demand strongly increases due to the touristic season) as a function of the winter precipitation. To this goal the summer deficit has been analyzed as a function of the winter precipitation, the latter represented by the $SPI4_{Nov\text{-}Dec\text{-}Jan\text{-}Feb}$ computed over the cumulative precipitation over November through February (Fig. 1, right).

As one can see from Fig. 1 (right), when the $SPI4_{Nov\text{-}Dec\text{-}Jan\text{-}Feb} < -1$ (red box, return period approximately 6 years) the probability of occurrence of summer deficit is equal to almost 100%, whatever be the spring and summer precipitation. For $-1 < SPI4_{Nov\text{-}Dec\text{-}Jan\text{-}Feb} < 0$ (left white box) the probability to have deficit is approximately 35%, whereas for $SPI4_{Nov\text{-}Dec\text{-}Jan\text{-}Feb} > 0$ (right white box) the probability to have deficit is less than 10%, finally for $SPI4_{Nov\text{-}Dec\text{-}Jan\text{-}Feb} > 1$ the probability of deficit is nearly null. The threshold for early-warning could be further restricted, if longer term (2-3 months) weather forecast become available.

2. EWS for accidental chemical spills in groundwaters

Drinking water in Italy is mainly supplied by groundwaters (85.6% as a national average in 2008, ISTAT, 2008). Many large cities in Italy such as Rome, Milan or Naples are totally supplied by groundwaters. Therefore, in spite of the minor vulnerability in respect to surface waters, contamination of groundwater is a main concern for water managers, because it could be very severe in terms of the number of inhabitants involved. Quite often, human pressures over aquifers, especially in the alluvial plains, can be very heavy: infrastructures such as railroads, highways, airports, industrial plants are too frequently located very close to the abstraction points. In particular water suppliers seems to be frightened by possible chemical spills during road or railroad transportation of dangerous substances (Bryant and Abklowitz, 2007). For these reasons, in the framework of the afore mentioned collaboration between IRSA-CNR and the Italian Civil Protection Department, a Best Practice Protocol ("BPP") for the emergency management of accidental groundwater pollution events is being developed. The final aim of the BPP is to provide water managers as well as public water agencies and boards, with a tool to support the decision making during the different steps of the emergency: characterization of the event, identification of the water resources possibly involved, identification and alert of the institutional actors, emergency sampling and monitoring of the contamination, measures and responses both in the emergency and in the mean term (e.g. treatment, drinking water restrictions, provision with alternative resources etc.).

The main lines of the protocol are shown in Fig. 2. In previous papers other steps of the procedure have been described: a) a GIS tool which allows for the rapid identification of the water abstraction points which could be possibly reached by the contaminant (Preziosi et al., 2013); b) an analysis of different mathematical methods for the assessment of the arrival time and concentration at the withdrawal point (Di Palma et al., 2013).

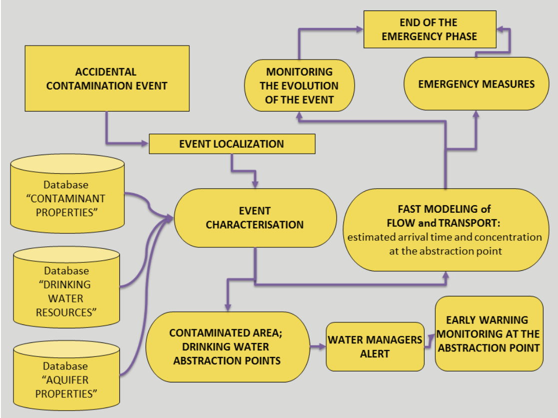

Fig. 2. Scheme of the best practice protocol for the emergency management of groundwater contamination

If an accidental spill has been reported, it is essential to early detect a sudden abnormal change in any chemical or physicochemical variable, before distributed water reaches the consumers. Should a groundwater contamination event happen in the nearby of a drinking water abstraction point, an early warning system should immediately be activated in a sampling point before the water is fed into the distribution network. There are two main issues to be faced in order to implement an effective early warning system:

a) The detection frequency (i.e. the number of analytical data collected in the unit of time) should be very high, because higher the monitoring frequency, higher the probability to find an abnormal change in the water characteristics.

b) On the other side, it is not possible to monitor all possible threatens, both chemical and biological ones. Untargeted screening methods are very expensive, very difficult to implement and cannot guarantee sampling and analysis with high frequency. It is much more effective to monitor some variables such as, for example, turbidity, which are indirect signals of unexpected modifications of the general water characteristics. This approach implies that firstly the "normal" value and its variability in a certain time-lapse is well known and documented, secondly that statistical tools to isolate the "abnormal" changes from the background conditions are implemented and continuously updated.

Currently, there is on-going research on the use of the multi-parameter water quality monitors as a part of an EWS for distribution systems. Multi-parameter water quality technology includes readily available water quality sensors that may be able to identify a physical or chemical change in water quality when analysed together (such as e.g. pH, conductivity, turbidity, temperature), which can be measured at very high frequency and used as a "proxy" for an unexpected modification of the water quality status. Such a change may suggest that a contaminant has been accidentally or intentionally added. Standard water quality parameters include chloride, specific conductance, turbidity, free chlorine, oxidation-reduction potential (ORP), pH, dissolved oxygen (DO), temperature, and sometimes total organic carbon (TOC) or UV adsorption at 254 nm.

In laboratories of IRSA-CNR we developed a protocol for unknown screening by gaschromatography-mass spectrometry (GC-MS) and assembled and optimised two possible devices based on automation of HPLC-MS systems for on-line monitoring. Two different settings have been developed, one for fixed monitoring station on an abstraction point, the second for fast automated analysis of very small volume sample (few ml) collected manually in a survey of a large area. The GC-MS protocol developed in the IRSA laboratory has been applied to follow an intentional oil spill in the river Lambro on 23rd February, 2010. The GC-MS analysis in Total Ion Current (TIC) mode showed the fingerprinting of oil pollution in the surface waters samples in the months following the spill accident (Fig. 3). From the chromatographic analysis it is evident that from February to April the more volatile fraction of hydrocarbons (represented by the alkylnaphtalene group) decreased, while chemicals (such as unsaturated olefins evidenced by the circle in Fig. 3) with higher molecular weight increased.

The developed protocol showed to be able to follow the evolution of an oil spill episode also after some months, making possible an estimate of the connected risks.

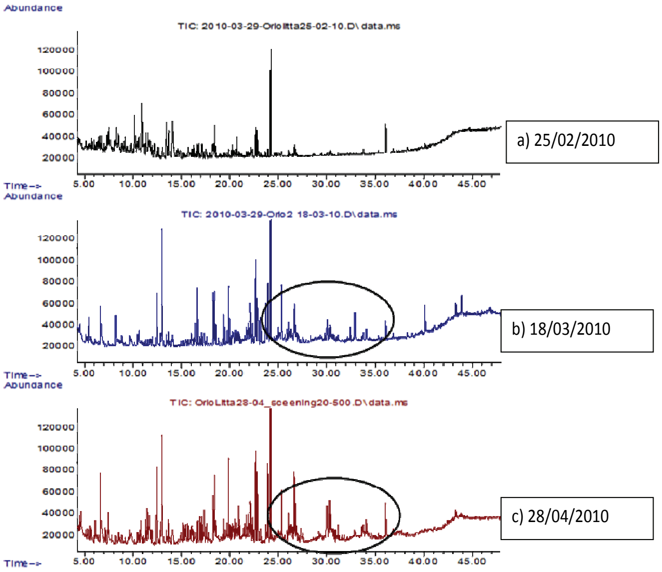

Fig. 3. TIC Chromatograms of the surface water of river Lambro after the oil spill (23/02/2010): the different chromatograms showed the evolution of the chemical fingerprinting in the months following the accident

Concluding remarks

The described activities are currently ongoing, and effective EWSs are still not operative. The ultimate aim of the project is to provide local administrators, as well as water managers, with guidelines and examples on how to deal with emergencies in water supply systems, concerning the lack of drinking water for qualitative or quantitative issues.

Keywords: contamination, early warning, unknown screening, water shortage, water supply system

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NUMERICAL MODELING OF THE SEWER SYSTEM OF RIMINI (ITALY) AND STRATEGIES FOR THE CSOs REDUCTION ON THE ADRIATIC SEA

Extended abstract

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Background

Combined sewer systems are designed to collect rainwater runoff, domestic sewage, and industrial wastewater in the same conduit. Combined sewer systems send wastewater to a wastewater treatment plant (WWTP), where it is treated and then discharged to a water body. During rainfall periods, however, the wastewater in a combined sewer system can exceed the capacity of the conduits and of the treatment plant. For this reason, combined sewer systems are designed to overflow occasionally and discharge excess wastewater to nearby channels, rivers, or other water bodies. These overflows, called combined sewer overflows (CSOs), although diluted contain stormwater and also untreated human and industrial waste, toxic materials and debris. In the last years new sewer systems are designed separated and with the introduction of LID (Low Impact Development) strategies (Gambi et al., 2011), but we have also to cope with old combined sewer systems and it is important define strategies for their best management.

The environmental impact of CSOs are considered, although indirectly, in several EU Directives and the wastewater Utilities must face the challenge to contribute to the Good Ecological Status of the water bodies that are influenced by their infrastructure. Historic data sets of registered pollutants discharged by CSOs proved the relevance of CSOs spills (Marinelli et al., 1997). Although conclusions depend on the pollutant under consideration, in general CSOs impact cannot be ignored (Dirckx et al., 2011). The first evidence of CSOs impacts on the receiving water bodies came to light in the 1960s but it was not until the 1990s that reducing the CSOs became a concern, because the most visible dry-weather pollution had been reduced by a systematic construction of WWTPs. Among the major effects caused by the CSOs is the acute short-term impact due to dissolved contaminants, bacteria and viruses, causing fish death, health risks and making water body unsuitable for the intended use (drinking water, bathing, etc.).

Objectives

The main objective of this work was to analyze the behavior of the sewer system of the city of Rimini, located in the Northern part of Italy. Is is characterized by a sewer system with a total length of about 736 km (56% is combined). Sewage flows into two WWTPs, which are designed for dry weather period and can't cope with discharges exceeding two- three times the dry weather flow. Thus, during rainfall events, in order to protect the city and the WWTPs, CSOs are activated and great part of the flows is diverted out of the sewerage. In particular 11 CSOs spill to the Adriatic Sea and this is great problem for the city, in fact Rimini has an economy based on tourism, the activations of the CSOs along the coast, especially during the summer, determines great problems both environmentally and economically.

Rimini sewer system is very complex. It consist in 52 pumping stations, 6 detention ponds with a total volume of about 114'000 m3, and 4 first foul flush tanks with a total volume of about 17'000 m3. In order to manage the discharge, during rainfall events, and to control the resulting CSOs spills, 28 movable gates are controlled in real time through water level gauges.

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Outline of the work

This work is divided in two main parts: development of the mathematical model of the sewer system and its calibration; analysis of different strategies for the mitigation of the CSOs impact on the Adriatic Sea.

The mathematical hydraulic model was developed using InfoWorks CS developed by Innovyze Ltd, integrated urban sewage drainage software with the functions of rainfall-runoff, water quality, and sediment transportation simulations. In this kind of sewer, very complex, the support of a mathematical model is fundamental in order to know, in the best way: water levels, discharges, pollutants, etc. (Calabrò and Maglionico, 2002; Freni et al., 2008).

Methods

The number of total nodes of the numerical model of the sewer system of Rimini is about 11'000. The model was calibrated using measured water level every 15 minutes in several pipes, tanks, pumps and movable gates functionality. The water level derives from a sophisticated system of real time control (RTC) and it is essential for monitoring the state of sewer storage or to convert levels to flow rate where backwater effects are not dominant.

The calibration process followed two steps. Firstly the system was analyzed in dry weather conditions. Collected measures of water level for the period 21- 25 May 2009, were compared to water levels, simulated by the model. The daily trend of the water level in dry conditions depends on the on/off of the pumping stations and on the user behaviour. In particular the sewage flows were obtained from the insertion of the annual water consumption. Two types of coefficients were used in the mathematical model for simulating the variability of wastewater flow. The first one is the hourly coefficient that allows the average flow to adapt to the real consumption. The average flow is multiplied by a coefficient less than 1 during the night to simulate the minimum consumption, while peaks are during the day. The second is the monthly coefficient used to simulate variation in water consumptions due to touristic fluxes. Rimini is indeed characterized by a high number of tourists during the summer. This coefficient based on data provided by the Statistical Office from the Province of Rimini, which contain, for every day of the year, tourist arrivals and overnight stays for the entire Province.

In the second calibration step measured and simulated water levels in wet weather conditions were compared. Different rainfall events, recorded with time step of 5 minutes, during 2008 and 2009 were used to calibrate the model. Rain data were collected by three tipping bucket rain gauges. The process was done manually, while a trial and error parameter adjustment was made. In this case, the goodness-of-fit of the calibrated model is basically based on a visual judgment by comparing the simulated and the observed hydrographs. The mathematical modeling of the network allowed the evaluation the volumes of water spilled from each CSO, as well as TSS masses, BOD_5 or COD, thus allowing estimating the environmental impact.

During rainfall events the greater part of stormwater spilled by the whole CSOs system, is send to the Adriatic Sea by 11 CSOs. The rain series used for the simulations was one year long, from 01/01/2009 to 31/12/2009. The adoption of real rainfall time series allows also to take into account the dry weather periods among rain events which are of fundamental importance to estimate the buildup of pollutants and therefore the quality of the waters that flow into the sewer system during rain events.

Results and discussion

The mathematical modelling of the network has been used to evaluate: the volumes of water spilled from each CSOs, the mass of TSS, BOD_5 or COD. It allowed estimating the environmental impact of the CSOs, the frequency of discharge, and the degree of dilution including those with more complex geometry.

Real-time control (RTC) is a custom-designed computer-assisted management system for a specific urban sewerage network that is activated during a wet-weather event. Uses and benefits of RTC are multiple (Newman et al., 2004), particularly the advanced types, can perform a variety of management functions in a given sewerage system:

- control flooding, overflows or surcharges;
- maximize storage volume;
- optimize treatment plant capacity;
- prevent operational problems and protect receiving waters.

This paper focuses on storage optimization to protect receiving waters, in fact RTC uses in-network storage (that is much less expensive than constructing conventional storage facilities) and enables more effective use of conventional storage facilities. Increasing the capacity for temporary storage of the network is essential to reduce overflow discharges into the Adriatic Sea.

The first part of this study analyzes the benefits resulting by the use of RTC techniques applied to two sewer basins of the whole sewer system: Colonnella 1 and Colonnella 2 (Fig. 1). For the simulations were considered 107 rainfall events obtained combining the events with an inter event time of at least 12 hours and a minimum depth of 0,2 mm, collected on yearly base (2009).

At the basin closing section of Colonnella 2, the flow is diverted by a pumping station to the Colonnella 1 basin. During rainfall events, if the flow exceeds the Colonnella 2 pumps maximum capacity (340 l/s), a spill occurs. Colonnella 1 pumping stations has a similar behaviour: if the flow exceeds pumping station maximum capacity (690 l/s), a spill occurs to the Adriatic Sea.

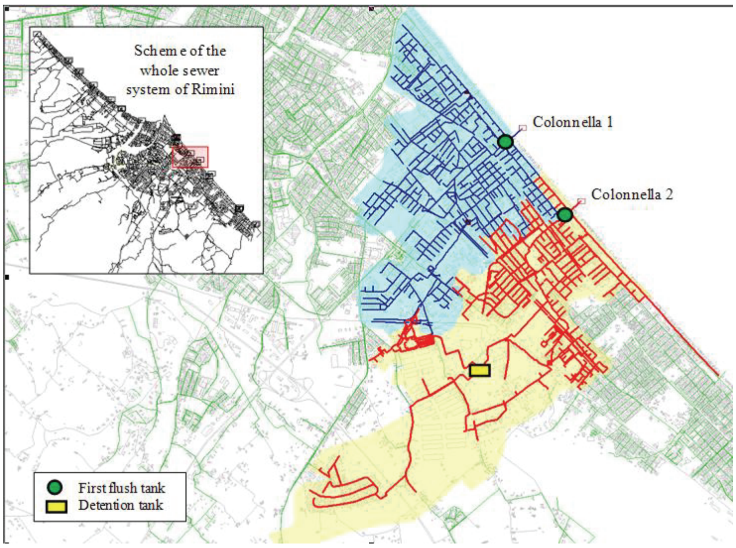

Fig. 1. Subcathments drained by Colonnella 1 and Colonnella 2

Table 1. Differences between measured and predicted L_{A10} at different floor levels

	Colonnella 1	*Colonnella 2*
Shape	Rectangular	Rectangular
Width, mm	3.900	3.100
Height, mm	1.800	1.500
Slope, %	0.117	0.017
Area, ha	225	415
Impervious area, %	76	64

The primary focus in terms of control of the system is reducing CSOs volume spilled from Colonnella 1 and Colonella 2, for this purpose three scenarios were studied:

I. CSOs with fixed weir;

II. CSOs with sluice gate and RTC based on water level;

III. CSOs with sluice gate and RTC based on water level and tanks.

The first scenario involves the insertion of two fixed weir for the regulation of overflow. The considered weirs have a fixed height equal to 25 cm for the Colonnella 1 and 48 cm for the Colonnella 2. They have been dimensioned in such a way in order to ensure the overflow only when the flow is equal to 5 times the average sewage flow in dry weather conditions.

The second scenario involves the insertion into the sewer system of sluices gate with RTC that was designed to optimize the sewer storage, by controlling the combined sewer overflows. The RTC sets the opening or closing of sluice gates by measuring the water levels upstream.

In the third scenario three reservoirs were included, actually present in the sewer system of Rimini. The first tank, located upstream of the Colonnella 2, has been inserted to solve the hydraulic criticalities of this zone, it has a volume of 30'000 m^3 corresponding of about 300 m^3/ha_{imp}. The empting of the tank is obtained with a pumping system that diverts the water to the artificial channel Deviatore Ausa, (that flows to the Marecchia River and thus out of the sewer network), in order to reduce the flow downstream. The second tank is a first flush tank that capture the first part of rainfall in order to ensure water quality It's near the pumping station Colonnella 2 and it has a volume of 4'600 m^3 (corresponding to 17.4 m^3/ha_{imp}). Downstream of the two previous tanks described, near the Colonnella 1, there is the third tank. It is a first flush tank with a volume of 3'000 m^3 (corresponding to 17.2 m^3/ha_{imp}). Both first flush tanks are emptied 24 hours after the rainfall event by a pumping station that sends the flow to the WWTP.

The three considered scenarios provide increasing benefits in terms of reductions of the number of overflows. In particular the introduction of fixed weir (Scenario I), for the CSO Colonnella 1, brings a reduction in the number of overflows of 39% (respect total rainfall events), this value rises up to 68% with the introduction of the sluice gate and of the RTC system on the water levels (Scenario II). In the third scenario the overflows are 27 that correspond to a reduction of 75% in the number of overflows respect to the total number of rainfall events. For the CSO Colonnella 2 the percentages of spill reduction for the three scenarios are respectively the 43% (fixed weir), 49% (sluice gate and RTC) and 73% (sluice gate and RTC and tanks)

In the Fig. 2 is possible to observe the characteristics of rainfall events, in terms of total depth and intensity, which can activate the two CSOs for the last two scenarios analyzed. For instance the activation of CSO Colonnella 1 in Scenario II requires rainfall with intensity and depth that are greater respect the rainfall that can activate the CSO Colonnella 2. This kind of analysis allows to characterize each CSO in terms of sensitivity to the rainfall characteristics and its environmental impact on the receiving water in terms of number of spills.

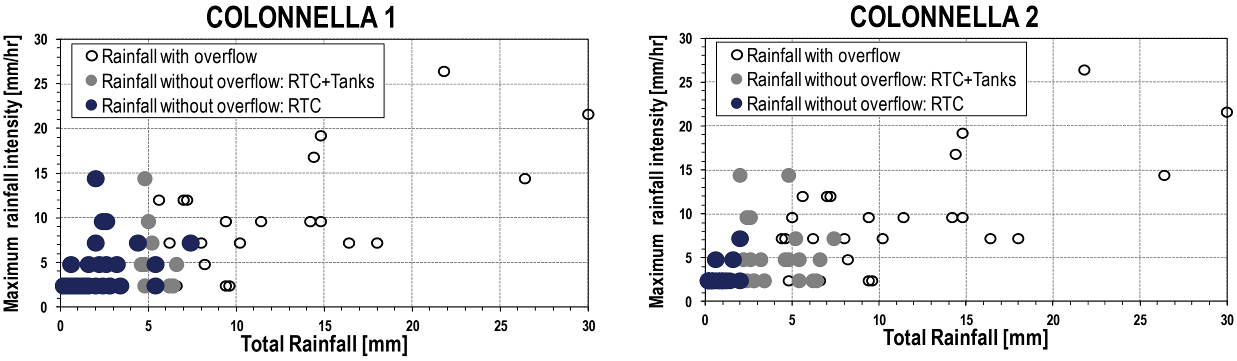

Fig. 2. Effect due to RTC and Tanks on CSOs for the 107 rainfall events simulated

Concluding remarks

This work analyzes two important CSOs present on the sewer system of Rimini: Colonnella 1 and Colonnella 2. In particular it was evaluated the efficiency, in terms of number of spills during rainfall periods, with different configurations. The simulation of the three different scenarios shows the benefit due to RTC and to the tanks located in the sewer system in terms of spill reduction on the Adriatic Sea. The RTC, respects the fixed weir, increase the efficiency of about the 17%, and the adoption of small tanks allow to increase the efficiency of about the 15% respect the only RTC.

Keywords: Combined Sewer Overflow, Numerical modelling, Rimini, RTC, Sewer System

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A DSS FOR RISK MANAGEMENT ON DRINKING WATER INFRASTRUCTURES DURING EXTREME EVENTS

Extended abstract

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Background

The safety of drinking water infrastructures is fundamental for economic, social and sanitary reasons, and should be guaranteed both during ordinary service and in case of emergencies. Besides verifying and preventing deterioration and ageing, the response of the system to extreme events should be also carefully analyzed. As a matter of fact, depending on the level of preparedness that water system authorities have adopted, the restoration of system functionality may require days, weeks, or even months.

Water supply systems are vulnerable towards several hazardous events, which can be mainly classified as natural (such as earthquakes, hurricanes, volcanic eruptions, landslides, fires…) or anthropic (both intentional and accidental, such as pollution, operational mistakes, black-outs etc.). Referring to the potential consequences of such events on the system, physical damages consisting in breakage or malfunctioning of one or more elements of the network, should be distinguished from water contamination.

A research activity is being developed by the *Water Research Institute of the National Research Council* (Istituto di Ricerca sulle Acque del Consiglio Nazionale delle Ricerche IRSA-CNR), supported by the *Italian Department of Civil Protection* (Dipartimento della Protezione Civile - DPC), with the aim of defining a strategic Decision Support System (DSS) for efficient and coherent decision-making in case of threats involving drinking water infrastructures. The DSS is based on Bayesian Belief Networks (BBNs), a semi-quantitative probabilistic tool particularly useful for managing emergency situations, characterized by time shortness and information uncertainty. It should be mainly used for detecting potential shortcomings of the system during emergencies, but also for helping water authorities in defining priorities of action, even with reference to ordinary management procedures.

In the following, the methodological approach adopted is firstly presented, with specific reference to the main features of BBNs. Then, the structure of the methodology is described in synthesis. At last, the applicability of the tool is discussed, referring to a couple of real case studies developed with the cooperation of Acquedotto Pugliese S.p.A., an Italian water authority.

Materials and methods

Several risk-vulnerability assessment methods were proposed to investigate the behavior of water supply systems (see for example Rosén et al, 2007; Beuken et al., 2008; Hokstad et al., 2009), although there is a certain lack of operative procedures (Ezell, 2007). Within the framework of available risk management methods, BBNs are identified as effective tools, useful to build a DSS to help in decision processes and in supporting analysis of the consequences of operative choices (Cain, 2001).

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A Bayesian network is a DAG (Directed Acyclic Graph) mainly consisting of three elements, namely "Nodes", "Links" and "Conditional Probability Tables". Nodes are basically the system variables, each one characterized by a set of possible states. Links define causal connections between nodes. When a node has no links from any other variable it is named "parent" and defines an input variable; the destination node of two or more links is termed "child" node. Conditional probability tables (CPTs), quantify the strength of a link through Bayes' theory, and represent the probability of a child node being in a particular state, given the states of its parents.

The most relevant technical features that make BBNs particularly useful for risk-vulnerability analysis (Aguilera et al., 2011) are the combination of qualitative and quantitative aspects, the possibility of reversal inference (from results to causes) and the easiness in getting the ranking of influencing factors, the strong learning ability, the combination of data with domain knowledge; the prediction accuracy even with rather small sample sizes. However, one of the main advantages in adopting BBNs in the water management field is the possibility of integrating different kinds of variables, and several categories of data, information and sources of knowledge.

In the present activity, the knowledge of a group of local experts, both hydraulic structures designers and academics/researchers working in the field of water management, was collected, and represented a basis for model building. Semi-structured interviews were held individually, and aimed at eliciting a broad range of knowledge with a minimum number of interviews.

Model description

The proposed model is based on the definition of different BBNs for each subsystem of a typical drinking water infrastructure, with respect to the occurrences that may potentially affect its functionality. Structural, operational and environmental information are required for compiling the BBNs, and input data can be attributed through GIS functions, or directly inserted by the user. For this purpose, geographical databases as well as data provided by water authorities should be joined and integrated.

Considering the typical structure of a drinking water infrastructure, the following subsystems were included in the vulnerability assessment procedure: a) Water source; b) Intake structures (Wells; Wellspring intake; Dams; River intake); c) Treatment plants; d) Water mains; e) Tanks and storages; f) Pumping stations; g) Control systems; h) Urban distribution networks.

Two hazard classes were considered: a) Physical hazards, associated to the potential damage of infrastructural elements determining limitations on water quantity; b) Chemical, Biological, Radiological (CBR) hazards, connected with the possible contamination of the resource and consequent quality problems.

The most influential variables for each sub-system, with respect to the hazard classes considered, were then detected, and their nature (continuous/discrete, deterministic/probabilistic) also determined at this point. Possible 'states' of these variables were also identified. The graphical conceptual structure was developed at this stage, and the specific role of the variables as well as their reciprocal influence expressed through causal links. A qualitative judgment on the strength of correlations and dependencies between variables was proposed by experts and, when available, integrated with literature results.

The structure of the model is mainly based on expert knowledge, and is therefore affected by a certain subjectivity. The procedures of formal network validation, as well as its calibration, mainly involving the values in CPTs, are fundamental for providing the system with an effective predictive capability. As a matter of fact, once outlined the structure of the model, feedback sessions were also held, involving experts, to ensure that the system had been correctly modeled. The development of real case studies also helped in verifying the applicability of the tool in case of specific occurrences, and the correctness of results. Sensitivity analysis helped in quantifying the specific role attributed to each input variable with respect to the target variable too.

Basically, two BBNs (for physical and for CBR hazards respectively) were developed for each subsystem of a drinking water infrastructure, in order to define a complex probabilistic vulnerability assessment tool from source to tap. An integration between Netica™ software (used for developing BBNs) and GIS tools, for optimizing data transfer and management, was performed and a user-friendly interface is currently being developed. Such integration is particularly helpful with the aim of developing a dynamic vulnerability mapping tool, able to update information from regional databases and to provide a graphical localization of criticalities and weak points in the water supply system.

Model application

The model validation and calibration is being carried out, with the support of Italian DPC and the co-operation of local water authorities. Particularly, there is a scientific agreement between IRSA-CNR and Acquedotto Pugliese S.p.A. (AQP S.p.A.), the local water authority in Puglia region. Different case studies were selected and are being analyzed in order to verify the efficiency of the proposed methodology. In the following, the results of two case studies are summarized.

The first one refers to the Ofanto Aqueduct, one of the most important water mains in Puglia, highly conditioned by landslide phenomena. It has an overall length of approximately 100 km, and is designed for a maximum discharge of 6.5 mc/s. It is made of steel pipes having 2400 and 2000 mm diameter, 20 mm thickness and

16 m long bars. Several damages exist, mainly induced by landslides, and therefore maintenance activities are scheduled and real time monitoring procedures have been already introduced.

The second case study refers to another fundamental drinking water infrastructure in Puglia, namely the ‘Canale principale’. It is a gravity water main made of brick laid with cement mortar and designed for a discharge of 6.5 mc/s. Its overall length is approximately 245 km with several segments in tunnels. Designed and built starting from the early 1900s, it is currently the most important drinking water infrastructure in Puglia, although several hazards (mainly a severe earthquake in 1980s) have threatened its functioning in different sections.

Structural information provided by AQP S.p.A. as well as geographical and environmental data available through regional databases, were used to insert input variables. Infrastructural information were provided partially in digital form and partially as hard copy. Regional data were instead available in digital form, mainly through online Web GIS platforms, from local authorities and institutions.

The main results of the case studies are summarized in the following Fig. 1, showing the probabilistic value associated with the state ‘high’ of the ‘breaking vulnerability’ variable.

Conclusions were discussed with AQP S.p.A. technicians and model predictions were found to be coherent with the real damage situation. Furthermore, other ‘high vulnerability’ areas were detected through the model, and thus areas where further analyses should be addressed were identified. The situation of such areas was investigated in details and it was found that several of these sections experienced severe corrosion damages, and that the local influence of environmental conditions has been never carefully taken into account.

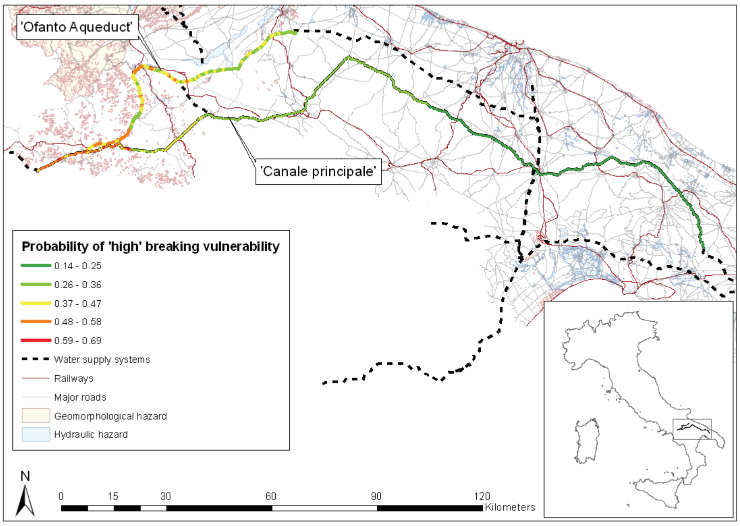

Fig. 1. Results of the case studies

Discussion

The probabilistic vulnerability model briefly described in the present work, was developed in order to support decision-makers during emergencies associated with drinking water networks. Its implementation in real case studies revealed its usefulness and operative simplicity, as well as satisfactory predictive capabilities, although some practical difficulties and approximations emerged too.

The first issue is connected to knowledge acquisition and information reliability. It is worth to remind that the adoption of a probabilistic tool such as BBNs is particularly helpful in order to avoid weighty detailed computations, that may reveal difficult in emergency conditions. Furthermore BBNs allow the integration of different sources of knowledge such as scientific and experiential, revealing particularly useful when fragmented or uncertain data are available. Nevertheless, such feature also constitutes a significant modeling challenge, since knowledge collection and structuring is quite difficult. The phase of data processing may reveal also complex, since data from different sources, available in different form (digital or hard copy), having different nature (numeric or linguistic) and different reliability should be combined and manipulated. It could be therefore useful to develop a preliminary phase of data collection and structuring, especially by local water authorities.

The second issue to be considered is connected with the integration of the vulnerability analysis tool with an hydraulic model, able to support in the investigation of the effects of changes of water quality or quantity on the hydraulic regime of a network. An hydraulic modeling software, EPANET, was used accordingly. The introduction of such tool could reveal fundamental to model the potential effects of hazardous occurrences on hydraulic functionality, thus selecting the most suitable operative strategies. Feedback sessions held with both AQP S.p.A. and DPC technicians underlined the importance of developing a comprehensive DSS, integrating vulnerability, environmental and hydraulic considerations. A user-friendly interface is currently being developed, in order to simplify data transfer and processing through GIS, Netica™ and EPANET.

At last it is worth to notice that, despite the model was primarily developed as a DSS for emergency management, the interaction with technicians of local water authorities revealed another possible field of application. As a matter of fact the tool may be also used for optimizing repair/replace procedures and supporting technicians in scheduling ordinary maintenance, through the mapping of vulnerability and the definition of a hierarchy in operations and interventions needed.

Concluding remarks

The present work summarizes the first results of a research activity oriented to the definition of a probabilistic methodology for the vulnerability assessment of drinking water infrastructures under extreme events. The vulnerability model was developed through the adoption of BBNs. Such vulnerability model was integrated in a more comprehensive framework, including GIS tools and an hydraulic modeling software, in order to provide decision makers with and effective DSS.

In case of extreme events determining a physical damage of the infrastructure or a water contamination, the model should be able to identify the elements of a water supply system that are most likely to fail or being damaged, thus originating limitations in drinking water quantity and/or dangerous quality changes. Hydraulic scenarios should be also modeled, in order to help in correctly selecting operative strategies. Actually, the methodology is being still tested through the co-operation of both researchers and water authorities.

Keywords: Bayesian Belief Networks, Decision Support System, Drinking water infrastructure, Emergency management, vulnerability assessment

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WATER UTILITIES AND THE PROMOTION OF SUSTAINABLE WATER USE: AN INTERNATIONAL INSIGHT

Extended abstract

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Background

In the European Union (EU), the Water Framework Directive (2000/60/EC) is based on the idea that water management needs to take account of economic, ecological and social issues and that its prime objective is the sustainable use and management of water resources. Throughout the EU there is growing concern regarding drought events and water scarcity. Policymakers therefore face the challenge of balancing the increasing human demand for water and the protection of the ecosystems' sustainability. Residential customers account for the majority of water demand in urban areas, mainly through household appliances, such as baths and washing machines. Implementing actions aimed at reducing water demand can deliver potential benefits not only at economic and financial levels, but also considering environmental and social purposes. Water conservation generally refers to the technical water savings that can be achieved through a particular technology or policy intervention. Sustainable use of water resources may be defined as a "pattern of use which ensures satisfaction of needs for both the present and future generations" (Bithas, 2008). Water conservation policies can have different characteristics and use a variety of instruments, all of which should encourage the efficient use of resources (Bithas, 2008). These instruments include supply restriction, water pricing, incentives for the implementation of high-efficiency household appliances and information campaigns to improve the knowledge of activities useful in reducing water consumption.

Since a number of environmental problems, including water scarcity, are caused by consumer lifestyles, it is necessary to raise water conservation awareness and the knowledge of daily life activities that are useful in reducing water consumption. Information campaigns motivate households to attempt to implement more water-efficient behaviors, and provide information on how to reduce usage. Nieswiadomy (1992) and Renwick and Green (2000) found that public education campaigns have reduced water usage. Furthermore, as argued by Barrett (2004), although it is true that higher prices will encourage better water use, without the assistance of non-price measures, price increases may become only a means of raising water-utility revenues rather than reducing water consumption.

Objectives

This paper aims to contribute to the existing literature on sustainable water use by analyzing whether Italian and Portuguese water utility companies pursue the objective of encouraging the reduction of household water consumption through web information campaigns, and by identifying which factors affect the water utility companies' willingness to promote these campaigns. To achieve this target we use a new methodology based on M-quantile regression to build a performance measure for 161 water utility companies. In this work the variable studied is a count for a construct of performance measurement, in which we use an extended version of the M-quantile regression model developed by Tzavidis et al. (2013) for count data.

Cross-national comparisons give the possibility of having a larger database to identify international best practices and provide guidance to utility managers and policy makers. Portugal and Italy are two Mediterranean countries that have similar characteristics such as climate, legislation, institutional framework and room for improvement in the efficiency (Cruz et al., 2012). Nevertheless, there are also some differences such as the scale and

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model of management, the actual role of local government and the reforms experienced (Cruz et al., 2012). To the best of our knowledge, this is the first study to address these relevant issues and, therefore, it can provide potential guidance to policy makers in defining the water management framework and in selecting firms to manage water services that are more inclined to promote sustainable water use and the reduction of household water consumption.

Outline of the work

This work is divided in four main parts:

- The first part offers a review of the literature. It focuses on water conservation policies, which can have different characteristics and use a variety of instruments, all of which should encourage the efficient use of resources.
- The second part offers a brief overview of the Italian and Portuguese water industries, showing the main features of this two Mediterranean countries, their similarities and differences.
- The third part describes the process of data collection and analysis and offers an outline of the methodology used.
- The fourth part provides the key findings of our empirical research and the resulting policy implications.

Methods

Using the latest available Report from Co.N.Vi.Ri. (Italy's National Supervisory Board on Water Resources) (2011), AIDA database of Bureau Van Dijk, Istat (the Italian National Institute of Statistics) website, the Annual Report from ERSAR (the Portuguese National Authority for Water and Waste) (2011), APDA (the Portuguese association for water distribution and wastewater collection) database, corporate annual reports and websites, and other documents available, we listed 114 Italian and 47 Portuguese water utilities for which there is information about all the variables analyzed: country (Italy-Portugal), ownership (public or mixed-private firms), diversification strategies (mono-utilities or multi-utilities), size (specified by annual sales and the population served), the expenditure for the consumption of 100 (Italian utilities) or 120 (Portuguese utilities) cubic meters of water (tariff), and the average annual rainfall during the period from 2000 to 2009 in the Italian provinces and from 2005 to 2010 in the Portuguese districts where the water utility companies' main business was located.

For each company we hand-collected data about suggestions for reducing household water consumption and regarding the sustainable reporting information had given through the corporate websites. Using dummy variables, we reported the following 14 items: 1. Existence of a corporate website, 2. Presence on the home page of a link or notice regarding household water conservation best practices; 3. Presence on the websites of information regarding household water conservation best practices; 4. Promotion of the practice of turning off the tap while washing; 5. Promotion of the practice of taking a shower instead of a bath; 6. Promotion of the practice of using a high efficiency toilet or flushing the toilet less; 7. Promotion of the practice of washing fruit and vegetables by soaking in a container; 8. Promotion of the practice of using the washing machine and dishwasher with a full load; 9. Promotion of the practice of periodically checking the tightness of taps and valves; 10 Promotion of the practice of applying flow reducers to taps; 11. Promotion of the practice of washing the car using a bucket; 12. Promotion of the practice of closing the main water tap in the case of long absences; 13. Promotion of the practice of watering plants and flowers in the evening; 14. Presence of a sustainability report on the websites. Regression analysis is a standard tool for modelling the relationship between a response variable y and some covariates x. It summarises the average behavior of y given x and has been one of the most important statistical methods in applied research for many decades. However, in some circumstances, the mean does not give a complete picture of a distribution. It does not consider, for example, the extreme behavior of y conditional on x. Quantile regression summarises the behavior of different parts (e.g. quantiles) of the conditional distribution of y at each point in the set of the x's. In the linear case, quantile regression leads to a family of hyper-planes indexed by a real number q € (0,1). Given a set of covariates x and a response variable y for each value of q, the corresponding model $Q_y(\mathrm{q}|\mathrm{x}) = x\beta_{\mathrm{q}}$ shows how the q-th quantile of the conditional distribution of y given x varies with x. The set of regression quantile parameter estimates satisfies the criterion of the minimum sum of absolute asymmetrically weighted residuals and estimates of β_{q} are obtained using linear programming methods. M-quantile regression further extends this idea by a 'quantile-like' generalisation of regression based on influence functions. The relationship between sample M-quantiles and standard M-estimates of a regression function is shown by sample quantiles and the sample median. In fact, the M-quantile regression line of order q is defined as the solution (Eqs. 1-2)

$$Q_y(\mathrm{q}|\mathrm{x}, \psi_{\mathrm{q}}) = x\beta_{\psi\mathrm{q}} \tag{1}$$

$$\int \psi_{\mathrm{q}}\big(y - Q_y(\mathrm{q}|\mathrm{x}, \psi_{\mathrm{q}})\big) dF(y|x) = 0 \tag{2}$$

where: F denotes the distribution of y given x underlying the data and Ψ_q denotes the influence function associated to the q-th M-quantile. Being a robust regression model, it can be fitted using an IRLS algorithm, which guarantees the convergence to a unique solution. M-quantiles are somehow less intuitively interpretable than quantiles. However, M-quantile regression also shares other advantages of robust regression connected to the great flexibility in modelling that comes from using different influence functions such as the Hubers or the Hampel function.

The use of M-quantile regression with discrete outcomes is challenging, since in this case there is no agreed definition of an M-quantile regression function (Tzavidis et al., 2013). A popular approach for modelling the mean of a discrete outcome as a function of predictors is through the use of generalised linear models, by assuming that the response variable follows a Poisson distribution and using the logarithm as link function. (Tzavidis et al., 2013) consider extending the robust version of the estimating equations for generalized linear models. In particular, for M-quantile regression the estimating (Eq. 2) can be re-written as (Eq. 3-4):

$$\sum_{j=1}^{n}\left\{\psi_{\mathrm{q}}\left(r_{j_{\mathrm{q}}}\right)\frac{1}{\sigma\left(Q_{yj}\left(\mathrm{q}\left|x_j,\psi_{\mathrm{q}}\right.\right)\right)}\cdot\frac{\partial Q_{yj}\left(\mathrm{q}\left|x_j,\psi_{\mathrm{q}}\right.\right)}{\partial\beta_{\psi_{\mathrm{q}}}}\cdot w(x_j)-a\left(\beta_{\psi_{\mathrm{q}}}\right)\right\}=0 \tag{3}$$

$$r_{j_{\mathrm{q}}}=\frac{y_j-Q_{yj}\left(\mathrm{q}\left|x_j,\psi_{\mathrm{q}}\right.\right)}{\sigma\left(Q_{yj}\left(\mathrm{q}\left|x_j,\psi_{\mathrm{q}}\right.\right)\right)} \tag{4}$$

$$Q_{yj}\left(\mathrm{q}\left|x_j,\psi_{\mathrm{q}}\right.\right)=\exp\left\{x_j\beta_{\psi\mathrm{q}}\right\} \tag{5}$$

$$\sigma\left(Q_{yj}\left(\mathrm{q}\left|x_j,\psi_{\mathrm{q}}\right.\right)\right)=\left[\exp\left\{x_j\beta_{\psi\mathrm{q}}\right\}\right]^{\frac{1}{2}} \tag{6}$$

$$\frac{\partial Q_{yj}\left(\mathrm{q}\left|x_j,\psi_{\mathrm{q}}\right.\right)}{\partial\beta_{\psi_{\mathrm{q}}}}=\exp\left\{x_j\beta_{\psi\mathrm{q}}\right\}x_j \tag{7}$$

where Eq. 4 is the Pearson residual, Eq. 5 , Eq. 6, Eq.7 is a correction term for obtaining unbiased estimators (Tzavidis et al., 2013).

The M-quantile regression for count data can be used to construct a performance measure of the Italian and Portuguese water utility companies. A key concept in the application of M-quantile methods to data is the identification of a unique 'M-quantile coefficient' associated with each datum observed. For most values in the x-range, the fitted M-quantile surface $\hat{Q}_{yj}\left(\mathrm{q}\left|x_j,\psi_{\mathrm{q}}\right.\right)$ will increase monotonically with q, starting below all the y-data values when q=0 and finishing above all y-data values when q=1. If the q-th M-quantile surface passes through y_j, then we set the performance measure for the j-th company to $q_j = q$. In the continuous y case the M-quantile coefficient for observation j is simply defined as the unique solution q_j to the equation $y_j=Q_{yj}\left(\mathrm{q}\left|x_j,\psi_{\mathrm{q}}\right.\right)$. However, with count data and $Q_{yj}\left(\mathrm{q}\left|x_j,\psi_{\mathrm{q}}\right.\right)$defined by the Poisson M-quantile regression model, values of y_j observed can never be part of the strictly positive domain of $Q_{yj}\left(\mathrm{q}\left|x_j,\psi_{\mathrm{q}}\right.\right)$.

$$\hat{Q}_{yj}\left(\mathrm{q}\left|x_j,\psi_{\mathrm{q}}\right.\right)=\begin{cases}\min\left\{1-\varepsilon,\frac{1}{\exp\left\{x_j\hat{\beta}_{\psi 0\varsigma}\right\}}\right\}, y=0\\ y_j, y_j\rangle 0\end{cases} \tag{8}$$

For a detailed discussion see Tzavidis et al. (2013). Thus, the performance of each company is defined by q_j that solves (Eq.8). We applied the M-quantile regression for count data to the number of pieces of information given through the corporate websites (y variable) in order to study the distribution of y given the auxiliary variable: country, annual rainfall, diversification, ownership, tariff, population served, or annual sales. Then we evaluated the performance of each company by the identification of unique q_j for each company. These coefficients were then averaged from observations based on the group to define a group-level M-quantile coefficient. Table 1 reports the average values for each group defined by the auxiliary variables. Four variables (annual rainfall, tariff, population served, and sales) are continuous, so they were divided into three categories: low (the first 33% of the distribution of the variable, first tertile), medium (from 33% to 66% of the distribution, second tertile), high (the last 33% of the distribution).

Table 1. Group level M-quantile coefficients

Country		***Annual rainfall***		***Diversification***		***Ownership***		***Tariff***		***Population served***		***Annual sales***	
Italy	0.417	Low	0.496	Mono	0.435	Publicly	0.442	Low	0.437	Low	0.365	Low	0.328
Portugal	0.472	Medium	0.466	Multi	0.430	Mixed-Private	0.417	Medium	0.463	Medium	0.375	Medium	0.489
		High	0.337					High	0.399	High	0.564	High	0.481

Information campaigns on sustainable water use are mainly promoted by water companies located in Portugal. So, Portuguese water utilities seem to be more sensitive to promoting the reduction of household water consumption. Moreover, considering the data obtained regarding the amount of rainfall, as expected we find that companies located in geographical areas characterized by drought and water scarcity, such as the south of Italy (which also includes the two main Italian islands, Sicily and Sardinia) and the Alentejo and Algarve regions in Portugal, tend to pay more attention to the promotion of sustainable water use than others. The ranking referring to the average annual rainfall shows that an increase in rainfall reduces the companies' willingness to promote sustainable water use.

A second issue is the degree of diversification, used to group firms in mono- and multi-utility companies. The data show that when companies operate only in the water industry they have a slightly higher inclination to foster public information campaigns on their own websites, promoting sustainable water use and the reduction of household water consumption. So, multi-utility companies, on average, seem to be less sensitive to water sustainability issues, since they are involved in multiple and different problems which affect their multi-businesses.

Ownership also seems to have an impact on water utility companies' willingness to promote sustainable water use through the firm's website. A fully publicly owned company pays greater attention to this issue than a mixed or totally private firm. This finding could be explained by considering a public shareholder's goal of maximizing the benefits of the community through the preservation of water resources, avoiding any waste and excess consumption. In contrast, private shareholders are more oriented towards the company's profit; consequently, they have less interest in decreasing water consumption since this determines a contextual decrease of revenues and net income.

The evidence that has emerged regarding the expenditure for 100/120 cubic meters of water show that companies who apply lower tariffs (the first and second tertiles) are more interested in a reduction of water consumption, while those who apply higher tariffs pay less attention to this issue. Tariffs are frequently used as a tool for improving water savings. So, some water utilities seem to discourage higher consumption through tariffs charged to citizens than encourage more sustainable behavior through information campaigns on the web. However, if the price elasticity score is lower than -1.00, this choice improves revenues and net income of the companies and the expenditure of citizens.

The last aspect considered in this paper concerns the presence of some scale incentives for the implementation of sustainable water use campaigns. The evidence relating to the clusters defined on the basis of both revenues and population show that the incentives exist. Larger companies that provide water services to many citizens (the upper tertile) have a greater willingness to invest resources in water conservation campaigns, since their potential recipients are very numerous. Moreover, due to the higher number of people to reach and to inform, the best tool is probably a website, since it is the most efficient and the least expensive. In contrast, the same campaign is not cost-effective for a company that serves only few thousand customers.

Moreover, larger firms (second and third tertile) in terms of total annual sales (large mono-utility companies and also multi-utility companies that serve relatively few water customers and operate in other areas) have a higher incentive to promote water conservation campaigns than their smaller counterparts since they have, on average, more resources to invest in effective websites/campaigns that are able to encourage the reduction of household water consumption and the promotion of sustainable water use.

Concluding remarks

This paper applies the M-quantile regression for count data to a dataset of 161 Italian and Portuguese water utility companies for determining the factors that affect water utility companies' willingness to foster public information campaigns aimed at promoting sustainable water use and reducing household water consumption. This knowledge can provide guidance to policy makers in entrusting the service to the companies that are more inclined to fulfill the objectives of sustainability and conservation. Larger firms, companies located in drought regions and in the driest areas, companies that are publicly owned and apply lower tariffs embody the type of institutions that make greater use of web information. We find also that Portuguese utilities seem to be more sensitive than Italian companies to promoting the reduction of household water consumption through web information campaigns.

Keywords: Italy, M-quantile regression, Portugal, sustainable water use, water utilities

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LIFE CYCLE ASSESSMENT (LCA) OF POLYURETHANE SHELL FOR CHAIRS: FROM MANUFACTURING TO REUSE

Extended abstract

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Background

Extending the products service life in the plastic manufacturing industry and in the furniture field is one of the measures for reducing the environmental impact, embodied energy and global greenhouse gases (GHG) emissions. To achieve extended the product service life organizations must design products for disassembly to facilitate the new steps in the life cycle and encourage the reuse and recycling of materials and components. The expertise (on an experimental) of reuse of polyurethane shell for chairs by ILPO could be implemented to extend service life of the shell of chairs and improve environmental sustainability.

The Life Cycle Assessment (LCA) methodology is applied to calculate environmental impacts, the energy and GHG emissions avoided thanks to the regeneration process of the polyurethane shell of chairs. Life cycle thinking is one of the key issues in sustainable development. LCA methodology facilitates comparisons of environmental performance of different products on an equal basis, ensuring a level playing field; LCA helps to avoid resolving one environmental difficulty only to create others elsewhere, by taking a comprehensive approach in one consistent framework; considering the entire life cycle of a product from the extraction of resources, through production, use, and recycling, up to the disposal of waste; quantifying resources consumed as well as emissions; that can be attributed to the product; providing indicators of the product's contribution; to a wide range of environmental problems such as climate change, toxic pressures, and resource depletion (JRC, 2010).

Polyurethane (PUR) is one of the most versatile materials, and it represents an important class of thermoplastic and thermoset polymers as their mechanical, thermal, and chemical properties can be tailored by the reaction of various polyols and polyisocyanates. There are many uses range from flexible foam in upholstered furniture, to rigid foam as insulation in walls, roofs and appliances to thermoplastic polyurethane used in medical devices and footwear, to coatings, adhesives, furniture, sealants and elastomers used on floors and automotive interiors. PUR has increasingly been used in a variety of applications due to its comfort, cost benefits, energy savings. PUR durability contributes significantly to the long lifetimes of many products. More and more attention is being focused on polyurethane recycling due to on-going changes in both regulatory and environmental issues. Increasing landfill costs and decreasing landfill space are forcing consideration of alternative options for the disposal of polyurethane materials.

PUR is successfully recycled from a variety of consumer products, including: appliances, automobiles, bedding, carpet cushion, upholstered furniture (Zia et al., 2007). Despite this, in the chairs field PUR recycle/recovery is difficult. Therefore, the average useful life of a PUR chair is about 15 years (PCR, 2009). With the method of regeneration PUR shell of chairs developed by ILPO, the service life of a PUR chair could be extended to around 30 years.

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Objectives

The main objective of this work has been to evaluate and quantify the environmental impacts through LCA application of a polyurethane shell of chairs manufactured by ILPO Spa. The LCA is applied from manufacturing shell of chairs through RIM (Reaction Injection Moulding) technology, starting from supply of raw materials to the potential reuse after use by a process of its regeneration developed by ILPO. The results of this scenario have been compared with the same product sent to landfill after use without being regenerated. The purpose of the analysis and the comparison has been to estimate the "savings" in terms of environmental and energy potential impacts resulting from the extension of the average service life of the product.

Outline of the work

The results of this work are divided in three main parts: the first part covers the LCA application of the “first life” of the PUR shell of chairs with a landfill scenario as end of life; the second part covers the LCA application of the “second life” of the PUR shell of chairs with a recovery scenario thanks to regeneration process; the LCA comparison of the two case studies is third part.

Methods

The LCA methodology has been used in accordance with UNI EN ISO 14040-44 (2006) standards for the environmental impact assessment of the PUR shell of chairs and of the comparison scenario. LCA is an objective evaluation procedure to examine the energetic and environmental impacts related to a product, process or activity. This procedure is carried out by identification and quantification of energy and materials used and by the amount of waste and emissions released into the environment.

The evaluation covers the whole life cycle of the product, process or activity and includes the extraction and treatment of raw materials, manufacturing, transport, re-use, recycling, and waste treatment. The main characteristic of LCA is a new analysis of the industrial system.

Traditional methods prefer to study single elements of the production processes while LCA considers the whole system (‘from cradle to grave’), in which all phases of transformation are considered because they participate in the realization of the production process.

Organizations are more and more interested in pro-active strategies which consider environmental problems during the design phase of the product rather than in ‘end of pipe’ strategies (based on technological operations at the end of the product design). The European environmental legislation measures and the introduction of ISO rules, in particular 14040 series related to LCA, have induced organizations to apply control procedures, energetic-environmental verification, environmental management systems and ecological labels (Ecolabels, EPD-Environmental Product Declaration- Carbon footprint) to their own processes.

Consequently, organizations now direct research to new technological solutions that satisfy such requirements. By improving the environmental characteristics of a product, process or activity, organizations contribute to develop a strategic market in which eco-efficiency becomes an element of quality. The LCA phases are: 1) Goal and scope definition; 2) Life Cycle Inventory Analysis (LCI); 3) Life Cycle Impact Assessment (LCIA); 4) Life Cycle Interpretation (ISO 14040-44, 2006). The LCIA phase is carried out using international indicators which quantify the impacts. For LCIA phase of this work the CML 2000 method (CML, 2007) has been applied and Simapro 7.3 software has been used (Prè, 2012). The laboratory tests in ILPO R&D department (UNI EN 1728) are applied to a PUR shell of chairs already in use for 5 years by subjecting it to a treatment of accelerated aging of sun/rain/cold/warm, thanks to which it appears feasible the way of systematic reuse of ILPO PUR shell of chairs.

Results and discussion

This paper presents the LCA results of ILPO PUR shell of chairs “second life” (regenerated) and their comparison with ILPO PUR shell of chairs “first life” produced twice. The LCA system boundaries include the manufacturing shell of chairs through RIM (Reaction Injection Moulding) technology, starting from supply of raw materials to the potential reuse after use by a process of their regeneration developed by ILPO (Fig.1). The mass of shell of chairs equal 2.6 kg during 30 years (experimental scenario) has been chosen as functional unit (FU). The use phase has been excluded because of the trade is B2B (Business to Business).

The distribution phase has been considered equal to 1000km by lorry 20-28t fleet average. The Ecoinvent 2.0 database (Frischknecht and Jungbluth, 2007) has been used for secondary data. The primary data are ILPO plant during 2011-2012 manufacturing period. Table 1 and Fig.2 describe the environmental potential impacts divided in 4 life cycle phases: shell of chairs manufacturing; B2B distribution; regeneration process (after use); end of life scenario (landfill). Table 2 presents the LCA results of comparison scenario.

In AD, AD, GWP, ODP, TE and PO impact categories, the manufacturing product phase affected 60%-70%, mainly due to raw material and paints inputs. In EU, HT, FEW and MAE the end of life product phase affected about

70%, mainly due to emissions to water of landfill. The Cumulative Energy Demand (CED) measured is 319 MJ and the measured water consumption direct and indirect is 16.9 ton.

Table 1. The environmental impact potential of LCA ILPO PUR shell of chairs life (FU: 30 year)

Impact Category	*UM*	*Total*	*Manufacturing*	*B2B Distribution*	*Regeneration Process*	*End of Life*
Abiotic depletion (AD)	kg Sb eq	0.131	0.110	0.004	0.015	0.001
Acidification (A)	kg SO_2 eq	0.057	0.046	0.003	0.007	0.001
Eutrophication (EU)	kg PO_4^{---} eq	0.052	0.014	0.001	0.003	0.034
Global warming (GWP100)	kg CO_2 eq	14.41	11.06	0.60	1.88	0.88
Ozone layer depletion (ODP)	kg CFC-11 eq	7.1E-07	4.4E-07	9.7E-08	1.5E-07	2.7E-08
Human toxicity (HT)	kg 1,4-DB eq	4.6	1.7	0.1	0.9	1.8
Fresh water aquatic ecotox. (FWE)	kg 1,4-DB eq	6.2	1.0	0.0	0.6	4.5
Marine aquatic ecotoxicity (MAE)	kg 1,4-DB eq	7094	1587	106	964	4436
Terrestrial ecotoxicity (TE)	kg 1,4-DB eq	0.033	0.023	0.001	0.006	0.003
Photochemical oxidation (PO)	kg C_2H_4 eq	2.9E-03	2.4E-03	1.1E-04	3.5E-04	7.6E-05

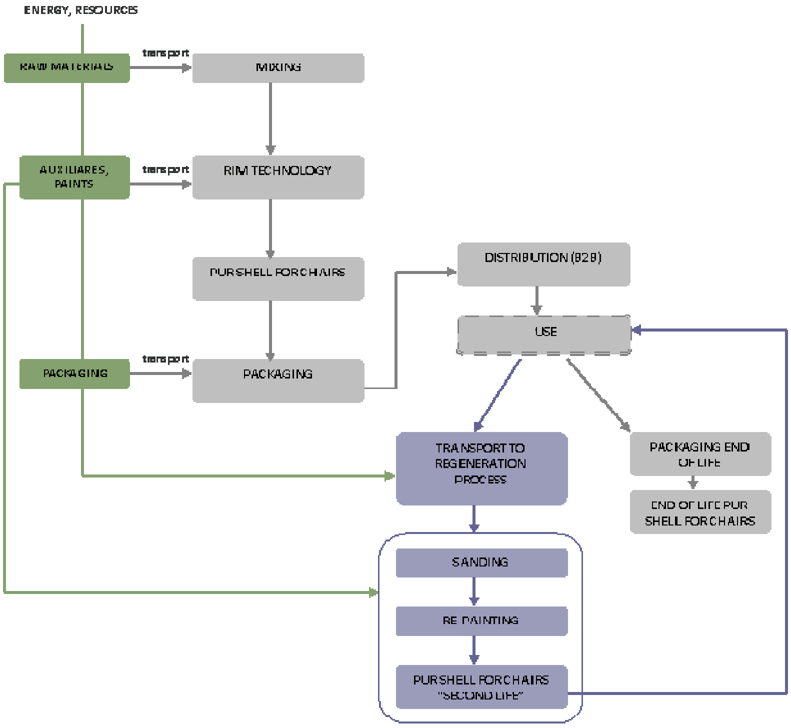

Fig. 1. System boundaries of LCA study

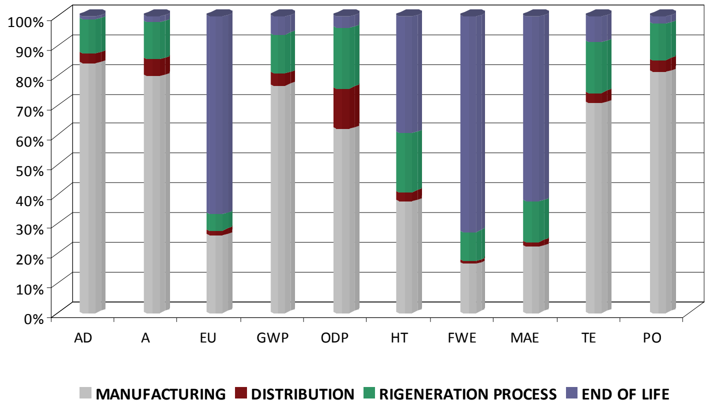

Fig. 2. The environmental impact potential (%) of LCA ILPO PUR shell of chairs life

Table 2. The environmental impact potential compare of LCAs ILPO PUR shell of chairs life (FU: 30 years)

Impact Category	*UM*	*Shell of Chairs Not Regenerated*	*Shell of Chairs Regenerated*	*Difference %*
Abiotic depletion (AD)	kg Sb eq	0.23	0.13	-77
Acidification (A)	kg SO_2 eq	0.10	0.06	-74
Eutrophication (EU)	kg PO_4^{---} eq	0.10	0.05	-88
Global warming (GWP100)	kg CO_2 eq	24.53	14.41	-70
Ozone layer depletion (ODP)	kg CFC-11 eq	1.13E-06	7.12E-07	-59
Human toxicity (HT)	kg 1,4-DB eq	7.09	4.59	-54
Fresh water aquatic ecotox. (FWE)	kg 1,4-DB eq	10.83	6.17	-75
Marine aquatic ecotoxicity (MAE)	kg 1,4-DB eq	11752.08	7093.59	-66
Terrestrial ecotoxicity (TE)	kg 1,4-DB eq	0.05	0.03	-65
Photochemical oxidation (PO)	kg C_2H_4 eq	0.005	0.003	-75

Concluding remarks

The extensions of product life cycle and resource conservation are important environmental issues. The comparison between the LCA scenario of the PUR shell of chairs with service life without regeneration and LCA scenario regenerated PUR shell of chairs with a service life estimated of 30 years (experimental scenario), it was found that the estimated impact of the life cycle of the regenerated PUR shell of chairs is less than about 50% compared to the shell of chairs not regenerated. Regeneration of a PUR shell of chairs rather than producing it twice it allows to avoid about 10.12 kg CO_2 eq. emissions, 235 MJ of energy and 5.8 t of water consumptions.

Therefore the possibility to extend the life cycle of a PUR shell of chairs can solve two problems: the end of life management and the energy saving for manufacturing a new product. Reusing is an important action to reduce wastes and contain the environmental impacts.

Keywords: environmental impact, extended service life, Life Cycle Assessment, polyurethane shell, resource conservation,

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BARILLA SUSTAINABLE PACKAGING DESIGN AND ITS INTEGRATION IN THE EPD® PROCESS

Extended abstract

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Background

Barilla, in February 2011, was the first food company to perform environmental impact calculation in an easy, quick and reliable way and to provide certified and published results according to the Process Certification Clarifications guidelines for International EPD® System. Since 2004 packaging of Barilla products are designed with the support of the tool "LCA packaging Design" that performs streamlined Life Cycle Assessment (LCA) of different packaging solutions and evaluate environmental burden in terms of CF (Carbon Footprint) WF (Water Footprint) and EF (Ecological Footprint) at the first designing phases. This tool is linked to the EPD system LCA Database, which stores the most updated and verified data available coming from Barilla's suppliers and international LCA databases. Particular attention is made in the analysis of the Italian waste management system, aiming at reducing the impact of production as well as increasing the overall recyclability of packaging at disposal stage.

The overall recyclability of Barilla's packaging is increased from 85% in 2008 to 96% in 2012, and the 41% of recycled materials. Within 2014 the 98% of the packaging will be recyclable.

Introduction

The approach developed for the evaluation of packaging design is strictly linked to the EPD® process system (Ruini et al., 2012) and it is based on the Life Cycle Assessment methodology; using the following three main elements:

1. The packaging specific data;
2. The LCA database;
3. The packaging system.

The packaging specific data are elaborated by the packaging system using the LCA database. The packaging specific data are collected in specific LCA spreadsheet, called "LCA packaging Design" tool, that is able to elaborate LCA indicators of several packaging alternatives. The aim of the tool is to allow packaging designer to evaluate different packaging alternatives and to support decision making with environmental data.

1. Packaging specific data

Represents all the information related to the description of the packaging of the product that are: packaging component typology (e.g. bottles, trays, etc); material (e.g. glass, polypropylene, etc); percentage of recycled content; shaping process (e.g. thermoforming, etc); component mass; input transport carriers; distance of supplier.

These information shall be detailed for each component of the packaging (bill of material) and split per CU (Consumer Unit), HU (Handle Unit) and PU (Pallet Unit). Moreover further information shall be defined to the whole packaging system, which are: transport efficiency, as ratio of CU per PU; country of disposal.

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Components information are required to elaborate environmental burden of material production and transport, while packaging system information are essential to elaborate the end of life scenario (the share of the packaging mass delivered to different disposal treatment i.e. landfill, recycling and incineration).

2. LCA Database

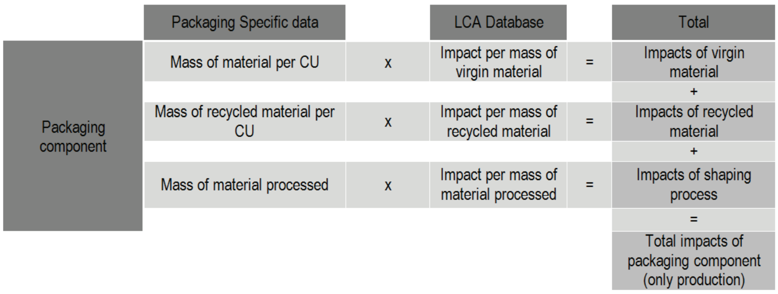
The database is organized among different data modules groups linked to the packaging specific data. Raw materials: includes information about packaging materials (e.g. cardboard manufacturing for American box production);

- *Shaping process*: environmental performances related to the shaping of raw material to obtain packaging components (e.g. Thermoforming for the plastic trays)
- *End of life scenario*: includes data about the disposal of packaging materials. Information are detailed per country and material (e.g. The Italian recycling of PET plastic is about 62%). The module is updated yearly when new information is available. Sources of information are national consortium for the packaging waste management and available country statistics.
- *Packaging waste disposal treatment*: contains information about environmental burden due to the disposal of the packaging material.
- *Transports*: data on the main means of transport used for the Barilla's purposes

Each data module stores the environmental aspects related to material and process, main hypothesis applied, as requested by the ISO 14040 series (functional unit, system boundaries, data quality, data collection and treatment, allocation and cut-off rules) (ISO 14040, 2006; ISO 14044, 2006). All data modules are internally verified and are ready to be used for both EPD and packaging R&D purposes.

3. Packaging system

The packaging system is the elaboration architecture that allows to link packaging specific data to LCA database in order to elaborate packaging environmental impact in a cradle to cradle perspective. An example of packaging process system is reported in Fig.1.



	Packaging Specific data		LCA Database		Total
Packaging component	Mass of material per CU	x	Impact per mass of virgin material	=	Impacts of virgin material
					+
	Mass of recycled material per CU	x	Impact per mass of recycled material	=	Impacts of recycled material
					+
	Mass of material processed	x	Impact per mass of material processed	=	Impacts of shaping process
					=
					Total impacts of packaging component (only production)

Fig. 1. Example of packaging component impacts calculation

Thanks to the elaboration architecture every specific data is related to the LCA database by means of specific algorithms. The spreadsheet tool developed for Barilla's designers contains also automatic check to avoid basic input data errors, e.g. the respect of mass balance, uniformity of comparison among alternatives. The tool allow packaging designer to input only data about packaging and perform LCA without being experts.

4. Relation between sustainable packaging design and EPD Process

The relation between the "LCA Packaging Design" and the EPD system is essentially the database, both processes are supplied by the same data sources, therefore results reliability could be considered the same. The EPD process aims at evaluating impacts of the whole Barilla's product while the "LCA Packaging Design" is focused on packaging analysis, especially for benchmarking different packaging solutions of the same product.

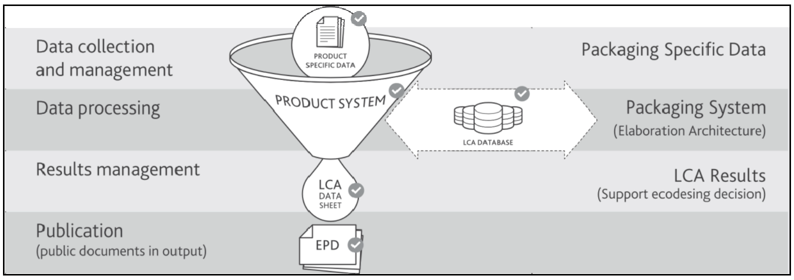


Fig. 2. Scheme of the Barilla EPD Process System ("funnel process") and the packaging ecodesign process

Case studies

The case studies presented in this paper are about bakery products, the first is about the analysis of a new component for Ringo snack, while the second is about the analysis of two alternative solutions of multilayer flow pack. Both case studies report the analysis of former and new packaging version of the same product. New solutions analyzed are currently available on the market and the environmental analysis supported the decision about their substitution.

1. Ringo Snack Case study

The case study is about the change of materials of the Ringo Snack flow pack. The substitution realized is from a multilayer of PP (polypropylene) and metalized PET (polyethylene terephthalate) to a new metalized PP film. Since the new packaging is made by single material it has been recognized recyclable by the COREPLA (the Italian consortium for the recycling of packaging plastic waste) (COREPLA, 2012). Moreover the mass of the new solution is lower than the former of about a 13%.

Table 1. Bill of material per Consumer Unit

Bill of material per CU	*Former version*	*New version*
Mass per CU [g]	1.21	1.05
OPPcoex film [%]	41%	35%
OPPcoex Met film [%]	-	48%
PET Met film [%]	38%	-
Adesive + Ink [%]	21%	17%

The benefits elaborated by the system are -17% Carbon Footprint, -13% Water Footprint and - 26% Ecological Footprint. The benefits come mainly from the change of material, nevertheless the recyclability is increased from a 0% to a 8%. In fact as single material the flow pack is considered as plastic film by the COREPLA system, therefore the potential recycling is assumed as 8% according to their data (COREPLA 2012).

In order to clearly explain to customer the change of material, a specific label highlighting the recyclability of the new component was added in the packaging graphics (see figure 3).

Fig. 3. Icon to communicate recyclability of packaging component (Italian version)

2. Flow pack of Mulino Bianco biscuits

The second case study, as the first, it is about the biscuits packaging of Mulino Bianco. Here the changes of material aimed at improving the recyclability of the packaging. In this case the bakery pack is made of heterogeneous multilayer composed of paper and metalized plastic film. The two solutions have the following variables: Percentage composition of the two materials; Packaging mass.

All the other components of the packaging system are considered out of the scope of the analysis (e.g. HU and PU). It is important to underline that COMIECO (Italian consortium for the recycling of paper packaging) was involved in the project and recognized the new packaging solution as fully recyclable because of the lower presence of plastic. In order to keep the same performance of the former the mass of the new solution was increased, as shown in Table 2. The reported figures are elaborated as weighted mass of three different references of sales. The weighting factor is based on 2011 sales volume.

Table 2. Bill of material per Consumer Unit

	Former version	*New version*
Average packaging mass [g]	14.8	15.7
Coated paper for flexible packaging [%]	79%	85%
OPP coex met film [%]	21%	15%

In this case the *cradle to grave* comparison of the two solutions does not discover remarkable environmental impact differences. Results highlight indicators in reverse trend. The higher mass of the new packaging increases the impact of WF and EF, mainly influenced by paper production, while the CF decreases because of the less quantity of plastic. Moreover the recyclability of the new solution increases saving GHG emissions from landfill and incineration. The recycling scenario of the new packaging is significantly influenced by the change of material, because packaging paper are characterized by high recycling rates (e.g. about the 80% of packaging paper is actually recycled in the Italian territory) (COMIECO 2012). The new packaging is able to save about 12 grams of paper per CU. Widening the boundaries of the analysis from a *cradle to grave* to *cradle to cradle analysis*, the benefits of the new design becomes evident. Elaborating the potential benefit of the recycling, by evaluating the potential recycling as avoided impacts of substitution of virgin paper, the benefit are about -40% CF and WF, -25% for EF.

Despite the former case the benefit are highlighted only if benefits of the end of life are included. This kind of assessment increases the uncertainty of the analysis because the actual use of the recycled paper coming from recycling process is actually unknown. In this case the benefits are elaborated by assuming the substitution of paper with the same quality of the packaging itself.

Results and discussion

The results of the case studies showed how it is possible to perform LCA to assess the potential environmental benefits of new packaging solution at the first design step. This solutions were elaborated using data comes from verified and certified database, that increased the reliability of results, and support decision making. Moreover for the second case study the results obtained by the spreadsheet tool started detailed LCA study on packaging scenario to confirm results. In both case studies data about waste scenario were critical, and the real benefits of new design solution come from the detailed analysis of the recycling system of packaging waste.

Concluding remarks

The two case studies shown how the EPD process and packaging design approach are related by means of the environmental database that contains the entire life cycle inventory required for the elaboration of the environmental burdens. Packaging suppliers are continuously asked to provide their own data in order to keep updated the DB module The methods developed allow designers to ease LCA analysis by input only data about packaging, while all the information about production and disposal are available in the tool.

Keywords: EPD System, packaging, streamlined LCA, sustainability tool

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LIFE CYCLE ASSESSMENT (LCA) AS A MEANS OF COMPARISON BETWEEN ACTIVE AND PASSIVE REMEDIATION TECHNOLOGIES FOR WASTEWATER AND CONTAMINATED SOILS

Extended abstract

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Background

Life Cycle Assessment is a powerful and widespread tool to evaluate the environmental efficiency of products and processes. An application is reported of the Life Cycle Assessment tool in an unusual field for this method such as the evaluation of remediation techniques for contaminated soils and water in order to understand the environmental impacts related with clean-up interventions.

The initial goal of the study was to assess technology-specific impacts of two different remediation systems, but soon the lack of appropriate tools to address the use of natural resources such as groundwater became self evident. The difficulty to address similar issues (i.e. land use) through the LCA methodology appeared in other fields of application too, suggesting the need to find new methodological tools to fill this methodological gap (Bayer and Finkel, 2006).

Objectives

In this case study it has been used to investigate the behavior of two different technologies for the remediation of polluted groundwater on a Life Cycle perspective (Lemming et al., 2010). The main focus of the LCA study was to address the environmental benefit deriving from the in-situ remediation operated by the PRB, which leaves groundwater in the aquifer instead of discharging it as surface water as the PTS does, thus allowing the conservation of a natural resource which cannot be restored in short periods.

Outline of the work

A first stage of the work has been dedicated to the Life Cycle Assessment of the two remediation technologies: a Permeable Reactive Barrier (PRB) built with the funnel-and-gate design (in-situ remediation technology) and a Pump and Treat System (PTS) using Activated Carbon (active remediation technology). The sizing and design of the PRB was based on an actual working plant while the sizing and design of the PTS is based on literature data.

The comparison of the environmental performance shown by the different technologies in the preliminary phase has lead to define critical impact categories for both and to tune the model and related assumptions according to observation and analysis of preliminary results.

A new implementation of the model has been set after an extensive evaluation of the influence of the groundwater resource depletion as a potentially-leading element and further development of this kind of analysis are planned for the research group.

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Methods

The passive nature of Permeable Reactive Barrier systems (PRB) implies greater material production requirements in the installation phase and significant reduction in energy related impacts (Higgins and Olson, 2009).

The barrier has been modeled according to the "funnel and gate" method. In a funnel-and-gate configuration, low permeability funnels direct ground water towards a permeable treatment zone or gate. The "funnel" typically consists of sheet pilings, slurry walls, or some other material and is preferably "keyed" into an impermeable layer (clay, bedrock) to prevent contaminant underflow. This funnel is emplaced to encompass and direct the flow of contaminated water to a "gate" or "gates" containing a permeable zone of granular Fe(0) or other reactive material (USEPA, 1998). In this case, zero valent iron (ZVI) was used as dechlorinating agent.

To allow comparison, assumptions have been made as follows: the functional unit has been identified as 1 m3 of treated groundwater; the expected lifespan of the technology has been set to 10 years; treatment efficiency has been supposed to match legal pollutant concentration requirements; the only contaminant taken into account is TCE; the special cement mixture used in the construction of the funnel (see inventory table) has been modeled according to standard bentonitic cement; the initial installed amount of ZVI is expected to be used for the whole plant lifespan.

The main impact categories affected by this technology are related to water, both directly as for the Ecotoxicity to water aspects and indirectly through human toxicity (Diamond et al., 1999; Zaitsev et al., 2010). The recycled cast iron production process accounts for the best part of the main impact categories, followed by the production of the bitumen mix for the funnel. The Italian electricity mix implemented affects the nuclear waste aspect, as previously stated. The Pump-and- Treat System has been modeled assuming the same treatment efficiency and volume of treated groundwater as the PRB. The contaminated groundwater is extracted through two wells, each one 17 meters deep, and pumped to the GAC vessels through two conduits for a total length of 20 meters. Each well is expected to pump out of the aquifer 1.8 L/s of contaminated groundwater. The daily flow (311 m^3) through the GAC vessels is approximately 8 times higher than the groundwater flow taken into account for the LCA of the Permeable reactive barrier. It has to be noted that the pump and treat system works extracting groundwater and discharging it as surface water after treatment, thus consuming a non renewable (in the short-medium term) resource. The groundwater removal which is necessary for PTS remediation has been modeled in SimaPro including among the components of the process the use of a groundwater volume corresponding to the treated groundwater volume, and as a component of the waste scenario an equivalent volume of slightly polluted wastewater.

The main impacts related to the PTS system are ecotoxicity (both chronic and acute), for which the main contributors are the GAC production, human toxicity, mainly due to the construction processes, global warming and bulk waste, whose main contributor is the wastewater.

Results and discussion

Impacts related to the different technologies and sub-processes have been calculated through the implementation of the SimaPro model, with the EDIP97 method, which returns weighted results on 16 impact categories. The Pump-and-Treat System shows a poorer overall environmental performance compared to the PRB system, mainly due to the large contributions of the GAC production and wastewater disposal: in particular, human toxicity, bulk waste and global warming potential are the most unfavourable impact categories for the PTS. It has to be noted though that the PTS accomplishes its remediation objectives in a much shorter time than PRB (approximately 1.4 years against 10 years): it can be thus assumed that assessing its performance on a longer operation might show significant improvements, as the operation related processes are minor contributors to environmental impacts. As shown in Figs. 1-3 (values expressed in EDIP Points), the main impacts related to the PTS are attributed to the GAC production process and digging of the boreholes, while the ecotoxicity on water and toxicity on soil appears to be the most affected impacts categories.

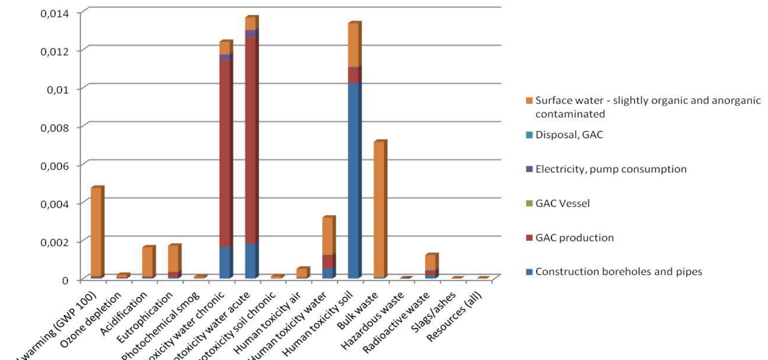

Fig. 1. Impacts of the Pump & Treat System, operation and disposal processes in the different impact categories (including long-term impacts) [Pt]

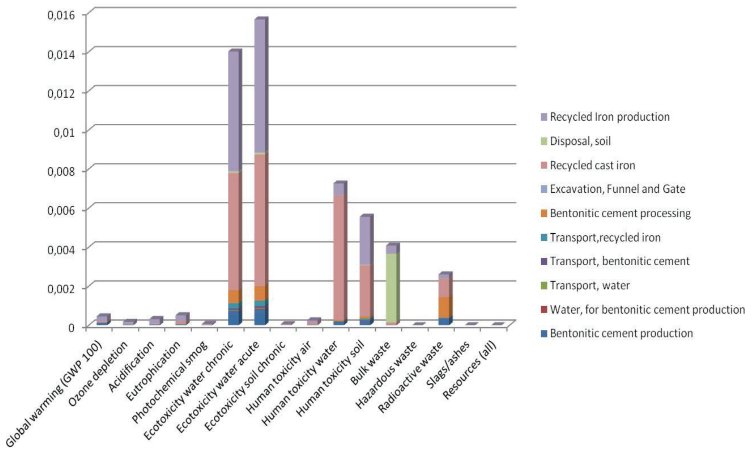

Fig. 2. Impacts of the Permeable Reactive Barrier, operation and disposal processes in the different impact categories (including long-term impacts) [Pt]

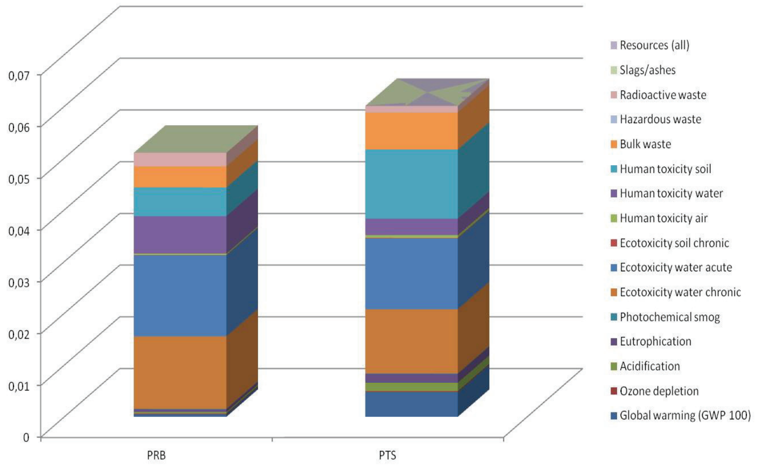

Fig. 3. Comparison between overall impact of PTS and PRB [Pt]

The Permeable Reactive Barrier shows worst environmental performance on ecotoxicity on water and toxicity to human health on water and soil, but, if compared with PTS technology on the same premises (i.e. same pollution conditions and same water volume to be treated), the overall impact remains 15% lower.

Concluding remarks

The designed case study of Life Cycle Assessment applied, on the same premises, on two different remediation technologies underlined the different environmental performance they provide, both in absolute value and relative distribution among the impact categories, but, most of all, it has given the opportunity to experiment a possible solution for a gap of the LCA model. In absence of an appropriate consideration of the negative impact deriving from the active remediation approach, which extracts groundwater from boreholes, changing the nature of the resource into surface water, the comparative study could not be complete. In this case, the readiness of the active technology in the remediation process is counterbalanced by this aspect, resulting in a positive comparative performance of the passive one, which preserves the groundwater resource's (non - renewable in long - medium term) quantity while restoring its quality in observance of the contamination values established by law, which are stricter than the values established for surface water.

The opportunity to provide a correct and comprehensive account of the environmental costs and impacts of the groundwater resource depletion, caused by contamination and remediation technology to be applied, proved to be a key element in a decision support approach to Life Cycle Assessment and this study offers a first attempt to fill a gap into LCA modeling.

Keywords: active remediation technology, LCA, PRB, PTS, remediation technology

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ENVIRONMENTAL ASSESSMENT OF INTRODUCING A PUBLIC DRINKING FOUNTAIN WITHIN SAN LEO TOWN

Extended abstract

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Background

A vast majority of the European population lives and works in cities, consuming an estimated 80% of the energy used in the EU. Local administrations, as the closest government level to citizens, are ideally placed to address climate issues in a comprehensive manner. In this field a most promising initiative is the Covenant of Mayors (EUMayors, 2013), a voluntary European movement involving local and regional committed to reduce CO_2 emissions through increased energy efficiency and development of renewable energy sources. The reference document is EU 2020 (COM, 2010), the European strategy for smart, sustainable and inclusive growth aimed at achieve substantial objectives by 2020, such as the reduction of greenhouse gas emissions by at least 20% compared to 1990 level; the increase to 20% of the share of renewable energy sources in the final energy consumption and a 20% increase in energy efficiency. As in general way, also for the accomplishment of the EU 2020 emission and energy targets, local authorities play a key role and Covenant of Mayor endorses and supports remarkably the efforts deployed by local authorities in the implementation of sustainable energy policies.

Currently, about 5000 signatories cities (EUMayors, 2013), with different size from small villages to major metropolitan areas are involved in the Covenant of Mayor. All the signatories are committed to implement sustainable energy policies to meet and exceed the EU 20% CO_2 reduction objective through increased energy efficiency and development of renewable energy sources. These actions serve as examples for others to follow and an increasing number of municipalities are showing the political will to sign up to the Covenant. Finally, movements such as Covenant of Mayors endorse local authorities to respond several sustainability issues such as the strong social demand for better health, softer modes of transport, more natural areas in the cities, shorter circuits for food supply, shorter distances between working, living and leisure areas, reduced vulnerability to global economic shocks, especially for the poorest populations, and the creation of local and sustainable jobs. In other words, the endorsement of local authorities is crucial to improve the quality of life of their citizens and to face the challenge of sustainability.

Another critical issue observed at urban level concerns the development of integrated solutions for drinking water usage and for water management. In fact, the 60% of all water is allocated to domestic human use (Toppeta, 2010) and by 2025 the water demand in municipal areas will increase by almost 80 billions cubic metres (Doobs, 2012). Worldwide, 44% of people are living in water stressed areas, and this number (o this rate) is expected to grow dramatically in the next future (Dirks and Keeling, 2009). Particularly, freshwater consumption is expected to rise of 25% by 2030, due largely to the increase in urban population (Washburn et al., 2010). There is the need to implement innovative solutions and at the same time to increase awareness among users, with the aim to locate distribution and to optimize usage of municipal drinking water.

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Objectives

Through a case study this paper investigates a successful story implemented in an Italian small-town, San Leo concerning the introduction of an innovative system: public drinking fountain. The main objective of this study is to evaluate the environmental benefits of the fountain introduction. For this reason an environmental assessment was carried out with a life cycle approach, performing a comparative analysis with bottle water. Definitely, the experience of San Leo public fountain aims to demonstrate that cities offer good opportunities for decisive local action and also local authorities can facilitate the address of sustainability challenges and real behavioral changes.

Outline of the work

In the first section the paper presents the successful experience implemented in the Italian small-town of San Leo. The paper describes the project launched in 2012 by the local administration and in particular by the Mayor who has favored the introduction of the public fountain in San Leo.

Section two illustrates the analysis performed with the aim to quantify the environmental advantages of this novel initiative. A cradle-to-cradle (McDonough and Braungart, 2002) approach was adopted and an environmental life-cycle analysis of the fountain system was carried out.

The last section shows the comparison of water fountain versus bottled water environmental performances. In this section several general remarks from the analysis of the fountain system of San Leo are highlighted. Finally an overview of the main results and the benefits useful to reach Covenant of Mayor commitment is provided.

Methods

This paper describes the local initiative promoted by the Municipality of the small town in Province of Rimini (Italy) San Leo, consisting in the installation of a public fountain in the fraction of San Leo, called Pietracuta. The village of Pietracuta has 993 residents and is located on a road with heavy traffic. Such as to be visible from the roadway, the public fountain is located in a strategic position, equipped with parking that facilitate the up and downloading of the bundles, and thus favors the access to people not resident in Pietracuta. This particular location is provided with the presence of an adjacent dispenser of fresh milk, two cafeterias and comfortable footpath that allows for a more safe accessibility by several kind of users. The choice of the location is certainly behind the success of the initiative that has dispensed 445.000 liters of drinking water during only the first year.

Fig. 1. Water fountain launch in 2012, San Leo, Rimini, Italy

The public drinking fountain of San Leo is branded Fonte Alma and produced by Celli spa. Celli is a leading Italian company in the field of systems and equipment for the beverage dispensing and one of the main landmarks in the world. Celli S.p.A. has always committed in innovation, technology and the company's product quality. Since the availability of safe drinking water has been becoming an increasingly heartfelt and urgent request, Celli S.p.A. has strengthened its Water Division, autonomously developing new solutions and products with the “Alma” brand name (Celli, 2010). The mission for Alma is to make water available directly from the water supply in a safe manner, and ensuring optimum quality standards. With this in mind, Alma water dispensers were the first to obtain TIFQ certification, guaranteeing the health and safety of the water dispensers for public use, also in outdoor environments. The growing awareness of pollution-related problems, and of the environmental damage caused by the transportation of water in glass or plastic containers, is leading to a swift revolution in consumers’ habits, now more closely focused on safer, eco-friendly solutions. Accordingly, Fonte Alma drinking fountains are designed to make water readily available, always pure, at ambient temperature or even cooled, either still or sparkling.

In order to better understand the whole benefits in terms of sustainability from the installation of this kind of system, an assessment that evaluates the environmental advantages of the public fountain system in San Leo was carried out (Moschi, 2013). The environmental analysis has been performed adopting a life-cycle approach, in compliance with the standards ISO (ISO 14040, 2006; 14044, 2006). The analysis has compared the consumption of drinking water from public fountains, refined at the municipal level instead of bottled water. The assessment has adopted a "from cradle to grave" approach, considering as functional unit the Italian pro capita water consumption per year (196 litres) referring to the 2011 data (IANOMI, 2012).

The life cycle of the service provided by the water public fountain has been divided in 5 different phases:

1. material consumption
2. maintenance operations
3. energy consumption
4. transports
5. end of life of materials substituted during the maintenance operations.

The materials consumption phase comprises the glass production for the packaging and the water consumption to fill in the bottle, i.e. pro capita water needed per year plus the losses in the distribution net (235,2 litres). The maintenance operation includes energy and water consumptions, the filters, the UV lamp, the pipes and the cleaning agents. The maintenance comprises also the end of life phase that consist landfilling or recycling in compliance with the current end of life scenarios for the Italian wastes. The energy consumption phase includes the overall energy request to run the machine (pumps, UV lamp, coolers).

Transports have been modeled with several mobility scenarios, in order to take into account all the effects of the distance modifications. Particularly, the analysis accounts 4 different scenarios:

- km 0 scenario: citizens have been supposed to reach the fountain on foot or by bike
- km 1-5 scenario: citizens reach the fountain by car covering an average distance of 6 km (including the return)
- km 5-15 scenario: citizens reach the fountain by car considering an average distance of 20 km (including the return)
- "real" scenario: citizens reach the fountain in compliance with the results of the interview analysis (walking, by bike, by car based on the declarations in the questionnaire).

The analysis of the travel to the water provision covers the average supply for each provision in order to establish the number of travel done to get the pro capita water amount. Allocation factors have also been applied in order to consider the real car fleet in compliance with the interview answers (51% diesel, 33% gasoline, 8% natural gas, 8% LPG). These percentages are consistent with the Italian national framework.

Results and discussion

With the aim to make a comparison between San Leo public fountain and the current scenario where citizens use bottled water, a study of Environmental Product Declaration (EPD) of an Italian bottled water brand has been considered as data source (Breedveld, 2009). The environmental profile outlined by the EPD has been adapted to make real the comparison, specifically the transport phase has been ri-calculated in order to be consistent with the fountain water scenario previous described. The impacts related to the infrastructure construction (both for the public fountain and for the bottling plant) has not been included in the analysis. Table 1 shows the results of the characterization phase for the fountain water *real scenario*.

Table 1. Life Cycle Impact Assessment of fountain water *real scenario*

Impact category	*Unit*	*Material+Mainten.*	*Transport*	*Energy*	*EOL*
Global warming (GWP100)	kg CO_2 eq	0.451465481	4.69194542	1.362837983	3.11191E-06
Ozone layer depletion (ODP)	kg CFC-11 eq	4.66932E-08	6.31003E-07	1.61566E-07	3.59309E-13
Photochemical oxidation	kg C_2H_4 eq	0.000233837	0.004930262	0.000603086	3.24955E-09
Acidification	kg SO_2 eq	0.001686663	0.008218353	0.00545548	1.50778E-08
Eutrophication	kg PO_4^{3-} eq	0.000622215	0.001536452	0.001168138	5.08521E-09
Non renewable, fossil	MJ eq	7.530028049	67.8764107	18.88197333	5.74009E-05

Focusing on global warming potential, the transport phase accounts for more than 70% of the total impact and the energy phase contributes for a 20%. Starting from the previous results, the comparison of the fountain water and the bottled water environmental profile shows a clear reduction (>70%) for all the impact categories. This result is confirmed for all the assumed transport scenarios. Another important results concerns the plastic and waste reduction. The water fountain service allows to reduce the amount of plastic utilized for the water bottles (0.019 kg/L), for a total amount of 5748 kg of packaging waste per year and 4200 kg of PET per year. As listed below, succeeding the waste management system of San Leo Municipality, a consequent reduction in waste derived from the avoided use of plastic bottles for one year is achieved:

- 765 kg separate collection
- 861 kg incinerator
- 2583 kg landfill

The assessment carried out with a life cycle approach has identified the transport as the most critical phase. Starting from these results, it is possible to set the best transport scenario for the water provision area able to satisfy the CO_2 reduction (20%) that is one of the principal Covenant of Mayor targets. As final results, Fig. 2 shows two transport scenarios where the distances are connected to the accomplishment of two CO_2 reduction targets. A 20% of CO_2 reduction would be achieved, if all the users came from Area B (15 km radius). Then Area B (9 km) attains the most ambitious target of 50% of CO_2 reduction.

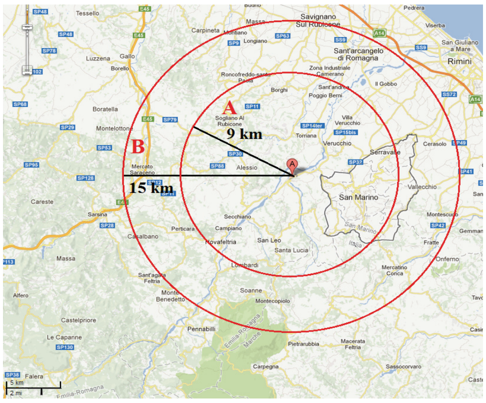

Fig. 2. Extension of water provision areas for CO_2 reduction targets

Concludig remarks

The water fountain in San Leo is a valid experience to address the impacts of climate change. As the analysis has demonstrated, the public fountain system meets the growing need for the consumption of drinking water from the mains, with ready-to-use dispensers for fresh water. It also offers considerable benefits for the environment: a reduction in waste disposal (bottles in PET or other materials) and in urban pollution from transport, deliveries, etc. As a result, the environmental benefits provided by the fountain system help to respond to environmental issues, such as CO_2 emission and waste reduction. Finally the experience of San Leo contributes to establish a new role of local authorities, away from a regulatory role towards a new one that enables others to act. The result is the facilitation to realize a behavioral change and to put in practice sustainable society.

Keywords: climate change, drinking water, life cycle assessment, urban sustainability, waste reduction.

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CONTRIBUTION OF THE ACCOUNTANT FOR ECONOMY DEVELOPMENT THROUGH ENVIRONMENTAL ANALYSIS, REPORTING AND COMMUNICATION SERVICES

Extended abstract

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Background

There are many evidences that the current environmental and economic problems are linked, and that they rise from the limits in the current patterns of development. Therefore it becomes necessary an integrated management approach, as stated also in the Rio + 20 United Nations Conference in 2012.

At the EU level, the need of an integration and update of the GDP concept is already emerged, in order to include also qualitative variables such as quality of life, externalities of the current economic system, and the objective limits imposed from a context of finite resources in opposition to an ideal of continuous growth.

To this regard, the EU Regulation 691 / 2011 requires to reorganize and transmit data relating to air pollution, green taxes, accounts of goods / waste flows, defining in this way a common framework for the collection, compilation, transmission and evaluation of European environmental economic accounts, making them satellite accounts of the European System of Accounts (ESA) which is the main tool behind the Union's economic statistics as well as many other economic indicators, including GDP, and this would supplement existing indicators with data that incorporate environmental and social aspects for a more coherent and comprehensive assessment.

The recent 09/04/2013 recommendation of the EU suggests methods to determine the environmental footprint of organizations (OEF) and the environmental footprint of products (PEF) by measuring performance over of the life cycle (van Wensen et al., 2011). This is to decouple economic growth from resource use and environmental impacts, and overcome fragmentation in the different methods of measuring and communicating environmental performance.

At the Italian national level, during the recent 11th National Conference of Statistics organized in Rome in February 2013, the National Statistics Institute has taken the concept of "equitable and sustainable well - being" - (BES) as a reference model for the development of the period 2013 - 2020. This comes, along with the European programming, to redefine the concept of growth by focusing on the concept of well - being or quality of life, based on criteria of sustainability, understood as the vulnerability of the country or individual or company with respect to levels of well - being achieved, and criteria of equity, to highlight the correlation between inequality and risk factors. Links between BES and GRI indicators were then proposed to tie the macro and micro scales of the reporting system.

At the microeconomic level, a recent survey carried out by United Nations Global Compact has shown that international companies are already aware of the environmental and climate problems, and are planning for the coming decade a strong integration of sustainability issues to internal elements of business, even with provision of specific investments and developing new solutions to production and consumption characterized by respect for the environment variable, defined as "green economy".

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Objectives

Integrated reporting makes it possible to view and manage elements that, despite being external to the firm, contribute to create value for it. This comes from the availability, accessibility, and quality of various resources used (or "capitals"), such as the financial capital (i.e. funds), industrial capital (i.e. fixed assets), human capital (e.g., the ability of employees), intellectual capital (e.g. intangible assets), natural capital (e.g. environmental goods) and finally the social capital (e.g. relations with stakeholders). For optimal operation of a business each of these "capitals" will have to find adequate consideration individually and in relation to possible conflicts with other types of capital. The convergence of consensus in favor of "integrated reporting" makes clear that the involvement of accountants is necessary. Their involvement has been already formalized in the Italian regulatory framework for the services of sustainability reporting.

To this end, we realize conferences from several years, in collaboration with the Ordine Dottori Commercialisti of Bologna and with the participation of local authorities and other professional bodies, to promote the launch of sustainability and integrated reporting practices since the aspects / impacts of energy management of enterprises, in view of the substantial connections that occur with environmental, social, and economic aspects: the accountants may collect data relating to the energy and environmental performance of enterprise customers, use them to check the consistency of the costs in relation to the types of consumption and make appropriate assessments on the occasion of the financial statements, and put the local authorities aware of reference, so that they can use for their own planning and monitoring processes. The launch and development of this initiative may be of interest to individuals of various types, and in particular for those most directly involved:

- local authorities can be facilitated in enhancing the local production, create the conditions for the growth of wealth, welfare and employment, to recognize and limit discharges of "externalities," and in making planning processes and energy monitoring, with particular reference the constraints requested by the EU with the 20-20-20 directive;
- companies can gradually closer and better manage the increasing number of environmental requirements, initiate cost reduction, improve the supply of information to their stakeholders. So finding new and different competitive opportunities, improving their image, diversifying production according to the new characteristics of market demand (green economy), and equipping themselves to better manage the process of internationalization, given the already developed attention to sustainability and integrated reporting in many parts of the world. Through the intermediation of accountants then one should be able to involve SMEs, constituting almost all of the Italian entrepreneurial system, which usually do not have the economic and organizational resources to independently initiating such processes;
- accountants, preferably in collaboration with professionals from other disciplines, can play an important role in fostering the initiatives outlined above with the offer of innovative services, including interdisciplinary in nature, such as connector and interface between institutions and local authorities on one side and civil society, business and territory on the other side, to facilitate a two-way flow of information.

To this purpose, accountants have to acquire basic tools and basic knowledge of energy audits for production units. The energy management of a production unit is based on examining of energy flows and consumptions. Industrial audits are essentials tools for the correct management of energy and environment especially in the very high consumption sectors (Segreto et al., 2013). The energy audits allow to optimize the plants and their management and to keep under control consumptions and costs. The basic instrument for energy management is the energy accounting, which is integrated with the industry accounting, and it is based on the availability of information on energy consumption (thermal and electrical) and production.

A working group of ENEA (Italian National Agency for New Technologies, Energy and Sustainable Economic Development), in collaboration with the Association of Certified Accountants, has developed a web application that allows doing an industrial pre - audit defining the class of consumption.

The aim of the collaboration is developing a useful free web tool for fiscal experts that help them in energy accounting. Figs 1 and 2 show two sample pages of such tool. A form is presented to the user to enter the relevant data about the production unit and then send them to the server for data collection and analysis.

The server keeps a set of reference data, taken from the EU Best Available Techniques Reference Documents (IPPC Bureau, 2013), and compares them with the user entries. At the end of the process, the user gets a quick answer about compliance and performance of his production unit.

Methods

The information tool that can improve the current model of economic development, taking into consideration the factors outlined above, is the "sustainability accounting and reporting". This procedure (Schaltegger et al., 2006) is, unfortunately, a practice that still lacks an unique definition for businesses, but it is already a subject of the Recommendation 2001/453/CE, of numerous scientific contributions, and it has been transposed into Italian regulations for medium and large enterprises as a result of DL 32/2007, requiring directors and managers to assess whether it is necessary to include in the financial statements information on environment and employment (as a result of the provisions at European level by the EU Directive 2003/51/CE).

Dati nuovo stabilimento

Nome Azienda: Prova	Provincia: Bologna	Comune: Bologna
Categoria: Acciaio	Dimensione: 300 m³	Produzione annua: 20000 Kg

Consumi processo

☑ Elettrico	500 MJ	138.9 kWh	31.67 Nm^3CH_4	0.02597 tep
☑ Termico	5000 MJ	1389 kWh	316.7 Nm^3CH_4	0.1139 tep

Consumi climatizzazione

☑ Elettrico	2000 MJ	555.6 kWh	126.7 Nm^3CH_4	0.1039 tep
☑ Termico	50000 MJ	13890 kWh	3167 Nm^3CH_4	1.139 tep

Consumi riscaldamento

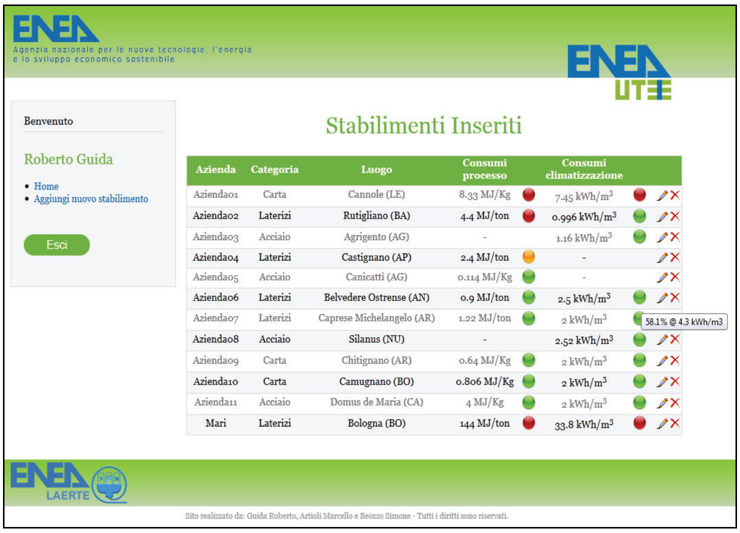
☑ Elettrico	2000 MJ	555.6 kWh	126.7 Nm^3CH_4	0.1039 tep
☑ Termico	50000 MJ	13890 kWh	3167 Nm^3CH_4	1.139 tep

Consumi raffrescamento

Consumi acqua calda

Consumi illuminazione

Fig. 1. Sample page (data entry) of the web tool for energy pre-audits



Stabilimenti Inseriti

Azienda	Categoria	Luogo	Consumi processo		Consumi climatizzazione		
Azienda01	Carta	Cannole (LE)	8.33 MJ/Kg	🔴	7.45 kWh/m³	🔴	✎ ✕
Azienda02	Laterizi	Rutigliano (BA)	4.4 MJ/ton	🔴	0.996 kWh/m³	🟢	✎ ✕
Azienda03	Acciaio	Agrigento (AG)	-		1.16 kWh/m³	🟢	✎ ✕
Azienda04	Laterizi	Castignano (AP)	2.4 MJ/ton	🟠	-		✎ ✕
Azienda05	Acciaio	Canicattì (AG)	0.114 MJ/Kg	🟢	-		✎ ✕
Azienda06	Laterizi	Belvedere Ostrense (AN)	0.9 MJ/ton	🟢	2.5 kWh/m³	🟢	✎ ✕
Azienda07	Laterizi	Caprese Michelangelo (AR)	1.22 MJ/ton	🟢	2 kWh/m³	🟢 58.1% @ 4.3 kWh/m3	
Azienda08	Acciaio	Silanus (NU)	-		2.52 kWh/m³	🟢	✎ ✕
Azienda09	Carta	Chitignano (AR)	0.64 MJ/Kg	🟢	2 kWh/m³	🟢	✎ ✕
Azienda10	Carta	Camugnano (BO)	0.806 MJ/Kg	🟢	2 kWh/m³	🟢	✎ ✕
Azienda11	Acciaio	Domus de Maria (CA)	4 MJ/Kg	🟢	2 kWh/m³	🟢	✎ ✕
Mari	Laterizi	Bologna (BO)	144 MJ/ton	🔴	33.8 kWh/m³	🔴	✎ ✕

Sito realizzato da: Guida Roberto, Artioli Marcello e Beozzo Simone - Tutti i diritti sono riservati.

Fig. 2. Sample page (compliance check) of the web tool for energy pre-audits

Sustainability reports will then be integrated into traditional financial reports to overcome the current limitations and produce a tool ("integrated reporting") with better features and information management (Herzig and Schaltegger, 2006). The translation of environmental and social impacts of economic activities in terms of financial and accounting aspects makes possible to better manage these impacts, and to see the effects on the overall economic and financial situation of the company, highlighting risks and intangible assets in particular, the latter resulting from elements such as reputation and brand value, which currently represents a large percentage of the market value of a company in many cases.

To reduce the gap between the debate, now rich, and corporate practice, still poor, the Environmental Commission of Ordine Dottori Commercialisti (Certified Accountants Association) of Bologna has recently signed agreements with some local authorities in the region, and in particular with the Municipality of Bologna (with which the Accountants Association of Bologna has recently signed the Protocol on the Implementation of the "PAES" - Action Plan for Sustainable Energy), and the Italian National Agency for New Technologies, Energy and Economic Development (ENEA, which has developed specific software for environmental and energy data collection) to encourage the adoption of integrated reporting tools.

Concluding remarks

The collaboration between accountants and energy management experts can ensure the starting of sustainability accounting and integrated reporting, even with simplified modalities easy to use by SMEs. It will allow even further collaborations with other environmental technicians and local authorities, to provide to businesses and to the general economic system the needed information to manage the challenges of competitiveness and adaptation linked to the increasing constraints in order to the growing relevance of environmental issues.

Keywords: energy management, information management, integrated reporting, sustainability, sustainability accounting and reporting.

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GREEN ROOFS FOR SUSTAINABLE WATER MANAGEMENT IN URBAN AREAS

Extended abstract

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Background

New housing developments and city infrastructures have led to a predominance of impervious areas in the urban environment and rainwater can no longer percolate naturally in the soil, leading to changes in the ground-water balance. Green roofs, green streets, and vegetated walls are increasingly addressed and studied as elements that help cities to adapt and mitigate the effects of climate change, achieve environmental benefits, enrich architecture and life quality. At the same time the principle of green corridors, till nowadays an element of the suburban territory, is reaching the urban environment because of its benefits in improving the microclimate and the urban quality of life.

Although many urban green technologies require availability of land space which is usually not available in densely built downtown urban areas (Berndtsson, 2010; Gambi et al., 2011), in every city, however, there is an abundance of roof area.

Moreover turning the roofs green through covering them with soil and vegetation is widely believed to contribute to achieving numerous hydrological benefits: studies show that, compared to traditional hard roofs, green roofs decrease runoff peak discharge, delay peak runoff and reduce runoff volume. Furthermore, green roofs and vegetated walls are beneficial for buildings, reducing noise levels, energy consumption and providing a better indoor comfort for their inhabitants (Berghage et al., 2010; Carter and Rasmussen, 2006; VanWoert et. al., 2005).

Green roofs are therefore being more and more installed by constructors and designers, but often it is just an aesthetical matter, and their scientific performance is still not known in detail.

In fact their performance is site specific, and taking other project as references is fine, but especially in different climatic areas it could lead to mistakes.

This is why it is very important the monitoring of pilot projects for an effective design and correct building codes for green roofs in a specific climatic area.

Objectives

This paper presents the description of a pilot green roof on the engineering laboratories of University of Bologna, Italy. The first results of the monitoring and simulation phase of the green roofs project that has been carried out by University of Bologna in collaboration with the Columbia University of New York aim at providing more evidence on green roof stormwater performance.

This project is the first green roof in the city of Bologna as no green roofs have been monitored for annual stormwater retention in this area.

Only one green roof in City of Genova, belonging to north Italian climate (the specific climatic context of the Mediterranean region: areas with this climate receive almost all of their precipitation during their winter season, and may go anywhere from 4 to 6 months during the summer without having any significant precipitation.) has been monitored and gave a 70 percent result in retention of the annual runoff (Palla et al., 2009).

The main objective was to compare this result to the Bologna pilot green roof and see how it differs from the other climatic area results.

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Outline of the work

This work is divided in two main parts:

- the first part describes a literature review on green roofs and the characteristics of the green roof built in Bologna;
- the second part presents the experimental data collected on the pilot green roof project

Methods

We have many different design choices in realizing a green roof on flat or tilted roofs, garages, basement parkings. Green roofs are made of different overlapping layers: essentially a waterproofing layer is right above the structural roof part. Then a root protection sheet, a drainage panel and a fabric filter go next, and at the end the growing medium and the plants. The growing medium thickness determines the type of roof, and if it's moderate, we can talk about an extensive green roof. There is still ambiguity in literature about the exact thickness borderline between extensive and intensive green roofs, but usually we can say that extensive ones are 8-15 cm high, above that range we have an intensive green roof. Extensive roof means low build-up height (80-150 mm), low load (from 80 kg/m^2) and low-growing plant, thus we usually have low care and maintenance. On the other hand an intensive roof means higher build-up (250-500 mm), heavier load (300-600 kg/m^2), larger plant selection but also more care and maintenance. The advantage is that it can be utilizable and walkable, so it can constitute a green garden within the city. In both cases the growing medium can host a variety of plants.

For the Engineering School of Bologna University the choice was driven by the structural constraints on site: the existing roofs had a load capacity that was able to host only an extensive roof, without the costly need of being reinforced.

In the extensive roof type the vegetation is usually very drought resistant and plants can adapt to difficult environmental conditions. Therefore sedum was chosen for the pilot green roof in Bologna and the sedum shoots were scattered on the growing medium during the construction that was held in June 2013. As the construction ended in summer good watering was important after the planting, and the substrate was always kept moist during the first few weeks thanks to the sprinkler irrigation system installed. The full scale installation of the sedum extensive green roof in the city of Bologna, Italy provided an experimental green roof area of about 50 m^2.

Moreover as the starting roof had a square shape, it was divided in two equal areas by a steel median divider: in one half the experimental green roof of 50 m^2 (substrate depth 10 cm) was installed while on the other half the conventional roofing assembly with bituminous membrane was left as reference twin roof. The entire surface went under maintenance of the bituminous membrane on both parts (total of 100 m^2) (Fig. 1). Both roof sections (green and black) were instrumented to monitor runoff profiles within the roofing systems using a hydraulic device made in the DICAM-CIRI laboratory. On the perimeters of the roof there is a gravel strip: 30 cm wide – grain size 18/30 mm.

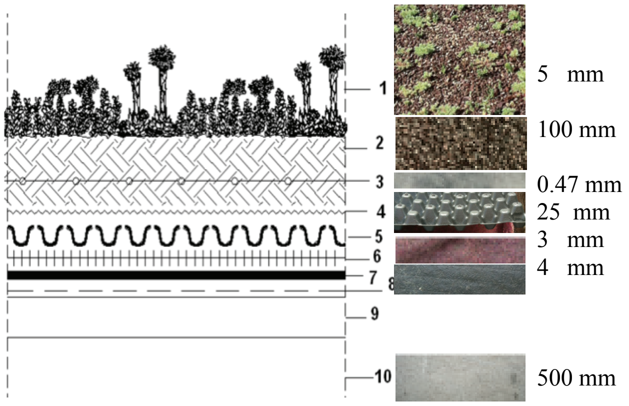

Fig 1. Extensive green roof with sedum plants and twin reference roof; Layers for green roof (* Elements constituting the SEIC green roof system): 1.Extensive vegetation – Sedum; 2.SEIC extensive substrate - growing medium; 3.Optional anchoring system for tilted roofs; 4.MediFilter MF1 - filtering mat; 5.MediDrain MD 25 – drainage element; 6.MediPro MP300 - root protection fabric; 7.Waterproofing root barrier membrane; 8-9-10.Structural elements

The hydraulic device for the water flow monitoring consists of a transparent low-density polyethylene (LDPE) rectangular channel equipped with a 90º V-notch weir and an ultrasonic level measurer placed above the instrument. The dimension of the V - notch orifice has been designed to be able to calculate the flow rates with a conversion formula from the water level.

The equation (Eq. 1) adopted for the conversion from the water level measured and the flow is the following one:

$$Q = 1.42 \cdot h^{2.5} \tag{1}$$

where: Q is the flow in m^3/s, h the water depth in m.

This is measured on both twin roofs: this set-up allows direct comparison of the performance and benefits of the green roof and the impervious reference roof.

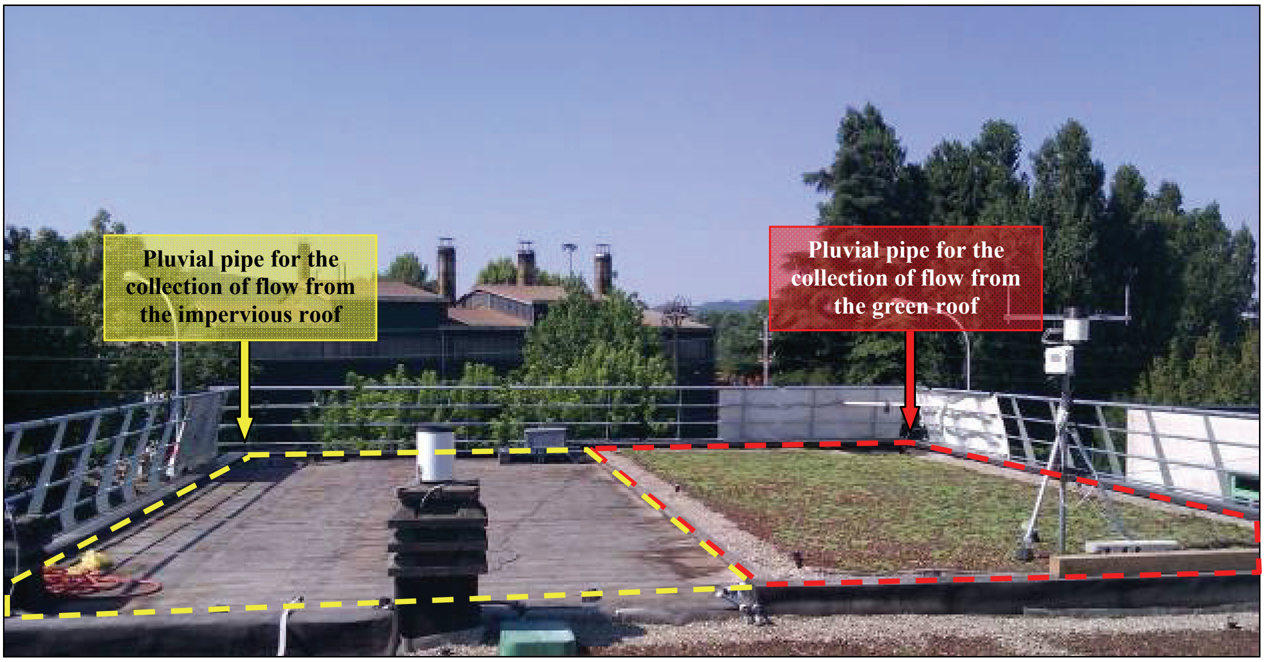

Fig. 2. Representation of the green roof and the impervious roof with the bituminous membrane

Results and discussion

Green roof stormwater performance is affected by regional climatic conditions, storm size, rain intensity, frequency, and duration, antecedent moisture in the soil, transmissivity of drainage layer, vegetation species and diversity, length of flow path, roof size, growing medium composition and depth, and roof age.

In this paper the following factors affecting runoff dynamics from green roofs were considered: type of green roof and its geometrical properties; soil depth and moisture characteristics; season, weather and rainfall characteristics; vegetation.

All these aspects were controlled and monitored thorough the design and construction process and then through specific environmental sensors which were installed on the prototyped extensive green roof located in Bologna, Italy, on the roof of the DICAM Department laboratory.

Given the fact that an irrigation system was installed, it was possible to run rain simulations at specific external conditions. Therefore a compared study of the delay in time between the simulated rain event and the real rain event registered in a period of a month was studied.

For example the time delay for the green roof for the last week of July, after the 2 daily irrigation sessions, at 5:00 am and at 9:00 pm, was recorded with the instrumentation put in place. The duration of one irrigation is 20 minutes and the total flow is about 360 liters. The results showed a different behaviour of the roof for the irrigation at 5:00 am (substrate still wet) and the 9:00 pm one (soil dried during the hot day). For the irrigation at 5 am the flow to the pluvial vertical pipe started after about 18 minutes from the start of the irrigation, while for the irrigation that started at 9:00 pm there is flow to the vertical pluvial pipe after about 34 minutes.

During rainfall events it is possible to study the behaviour of the impervious roof compared to the green roof. For example the rainfall event recorded on August 20th, 2013 (Fig. 3) is characterized by 2 rainfall peaks, the first with a maximum intensity of about 54 mm/hour, and, after one hour, the second peak of a maximum intensity of about 18 mm/hour and the total rainfall is about 9.7 mm. It is interesting to observe that the first peak generates a peak flow of about 0.24 L/s for the impervious roof and about 0.02 L/s for the green roof while the second rainfall peak generates a maximum flow of about 0.14 L/s for the impervious roof and about 0.05 L/s for the green roof, greater than the first peak due to the saturation of the soil. It is possible also to observe that the delay between the rainfall peak and the maximum flow is about 2 minutes for the impervious roof and 13 minutes for the green roof.

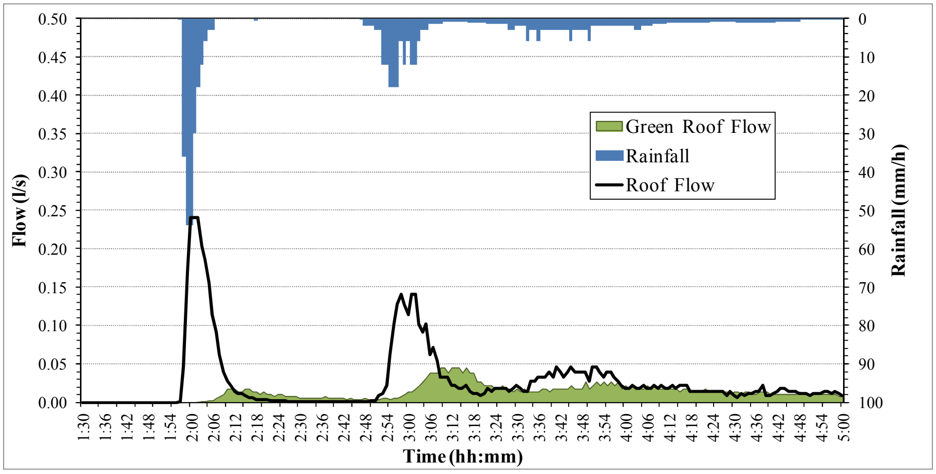

Fig. 3. Monitoring results for the rainfall event collected on 20/08/2013; comparison between impervious roof and green roof flows

Concluding remarks

In this paper the green roof installed in the University of Bologna and the first results of the monitoring activity were described.

The research is still at its first phase, as the roof has been completed at the beginning of July 2013, but the first results show the effectiveness of the green roof in delaying and reducing peak flows compared to a traditional impervious roof.

In the next months the monitoring activity will allow to collect other rainfall events and it will be possible to analyze the behavior of the green roof also through numerical models.

Keywords: green roof, monitoring, rainwater discharge delay, stormwater

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ENVIRONMENTAL QUALITY CRITERIA IN ANIMAL FOOD PRODUCING SYSTEMS: A MATTER OF FOOD SAFETY AND FOOD SECURITY

Extended abstract

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Background

The quality of the rural environment is a key factor in the determination of dietary intake of contaminants of priority interest, such as polychlorinated biphenyls (PCBs), especially in farmed animals kept outside (Brambilla et al., 2004; EFSA, 2010). On average, the assumption of soil, sediments, air depositions, can represent from 50% (in the case of free-range chickens) to 20% (pigs, cattle, buffaloes) of the amount of feed/fodder daily intaken, on dry matter basis, This would result that a 20 kg dry matter forages fed cattle, could ingest up to 4 kg dry matter coming from the above quoted environmental matrices. The monitoring activities on animal products from rural/extensive farming systems are highlighting some emerging problems: local environmental background concentrations of bio-accumulating contaminants in soil, sediment, water, where extensive farming is carried out, are not able to guarantee the compliance with the maximum limits in foods, thus, managing dietary human exposure under the toxicological guidance values, such as the Tolerable Daily Intake (TDI). Currently, the food safety legislation does not provide specifically environmental requirements that would support quality/compliance of rural food products; there is only one general statement about the quality of the pasture in Annex III of Regulation 183/2005/EC: grazing on pasture should be managed in such a way able to reduce the contamination of foods of animal origin by chemical, physical and biological agents (COM, 2005). The mismatches still existing between environment and food legislations on "dioxins and dioxin-like compounds" (PCDD/F and DL-PCBs) may be taken as an example of the difficulty to adopt measures for risk management based on the quality of the environment as a critical part of HACCP plans along a specific food production chain. This work aims to propose environmental quality criteria able to support the quality and safety of Buffalo Mozzarella cheese production in a geo-referenced area, accounting for the experience gained during the 2008 Dioxin crisis in the Campania Region (Borrello et al., 2008).

Objectives

Evaluate the scenario when six indicator NDL-PCBs (# 28, 52, 101, 138, 153, and 180) of strict environmental origin may affect the contamination levels in buffalo milk, stating a EURL maximum level of 40 ng/g fat basis, accounting for the PCBs contamination in top soil, sediments, air deposition at farm level, and their intake from hays, drinking water, and high stem forages, respectively (CR 1259, 2011).

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Outline of the work

Seven different buffalo farms located in not impacted area of Campania Region (Salerno district) were considered for this study, accounting for results from monitoring plans in dairy products implemented after the 2008

Dioxin crisis" in Campania region. Buffalo milk samples (N = 49) drawn from this background area showed NDL-PCBs levels lower than 6 ng/g fat (uppebound) with 80% of congeners reported below the corresponding LOQ (0.5 – 1 ng/g fat). Farming system (alimentary regimen, drinking water included, milk yields and fat percentages), NDL-PCB contamination in top soil, in water sediments, and on Zea mais leaves intended for silage were considered for the modelling. The overall PCB intake was then transposed into milk contamination predicted values, accounting for reported carry-over rates for NDL-PCBs. From such data, it was then possible to state background contamination in milk, and those environmental conditions able to raise PCB levels in milk close to maximum limits.

Methods

Top soil samples were drawn at farm level and analysed during the investigations carried out in Campania Region under the Dioxin Emergency plan (ISPRA, 2012). Buffaloes drinking water was sampled and particulate matter originating from the mud washed out from from buffalo hair estimated by gravity. Top soil contamination in hays (5 cm height cut from soil level) was measured similarly (Pecoraro et al., 2008). Leaves from Zea mais intended for farm silage production were sampled to evaluate bulk deposition. PCB (six indicators) analysis were carried out on dry weight matrices. Briefly, matrices were spiked with extraction Internal Standards, extracted with a mixture of n-Hexane: Acetone (2:1). After acidic attack on Extrelut columns impregnated with sulfuric acid, eluates were reduced to 0.2 mL, and after the addition of clean-up standards, applicated on activated alumina columns for the clean-up. NDL–PCB fraction was then collected, brought to 0.1 mL with the addition of the injection standards and analyzed. Extracts were assayed by HRGC coupled with low resolution MS/MS (TSQ Thermofisher on a HP 5 MS 60m ultra-inert column, as already reported (Miniero et al., 2011). All results were computed with the upper bound approach, as stated in the food safety legislation. Contaminations associated to hay, water, silage, and other feeds were then computed on the feeding regimen, to estimate the overall intake. Carry-over of selected PCBs to milk was estimated using a 36% factor, accounting for the overall PCB intake and the amount of fat excreted with buffalo milk (Feidt et al., 2013). The PCB (six indicator) contamination of commercial feeds was derived from a recent EFSA opinion (EFSA, 2010). Critical environmental concentrations in top soil, water and air deposition were then computed taking as benchmark the P95 value of the PCB distribution in dairy products (20 ng/g fat basis) (EFSA, 2010). Critical air deposition parameters for PCBs on mais leaves (ng/m^2/day) have been recovered from the measured planar surfaces, accounting for a vegetative cycle of 90 days and an air deposition efficiency of 30%.

Results and discussion

The feeding regimen, on average, in the seven buffalo farms was based on the following daily intakes, per head: 6.6 kg silage, 5.4 kg hay, 6.0 kg soya beans plus other commercial feeds. Water intake was estimated in 50 L/head/day. Top soil associated to hay resulted on average 20% of the dry matter content (min-max 6–30%), while soil/sediments associated to drinking water resulted in 4 g/L. Farms average milk production was at 10 kg /head/day, with a fat percentage of 10%. This would result in a 1000g fat excretion/head per day.

PCB contamination in farm top soil ranged from 0.2 to 84 ng/g, with a mean value of 5 ng/g dry matters. This value was also applied to drinking water, as far solids dispersed in drinking water originated from the mud sticked on the buffalo hair. Mais leaves coming from different fields resulted contaminated in the range of 0.2–2.9 ng/g (mean 0.5; N=9). In Table 1, the detailed data of the PCBs contamination on Zea mais leaves is reported expressed both on dry weight and on square meter basis. In Table 2, the contribution of top soil, water (sediments) and air deposition on mais leaves to Σ PCB (6) intake in dairy buffalo is illustrated, under the different scenarios (minimum, average, maximum PCB contamination).

The computed critical environmental parameters able to rise the milk contamination of Σ PCB (6) around the P95 percentile of occurrence in dairy products and around the ML, accounting for the background contribution from commercial feeds are illustrated in Table 3. Considering a 90-day full vegetation cycle of Zea mais harvested for mais silage production, and a 30% efficiency of bulk deposition on leaves, the critical value of 2 ng/g (dry matter) on leaves corresponding to around 200 ng/m^2, would lead to an environmental air quality parameter of 6.5 ng/m^2/day for bulk depositions of the Σ PCB (6).

Concluding remarks

Accounting for the outcomes of environmental, feed and food investigations as follow-up of the dioxins crisis in buffalo mozzarella from Campania Region, Italy, grazing food producing animals are more exposed to the intake of micropollutants than intensive farmed ones. To this respect, the very recent ranking of PCBs among IARC group 1 substances (Lauby-Secretan et al., 2013), clearly indicates as priority the reduction of the human exposure to the aforesaid POPs. On the basis of the reported measured concentration of PCBs indicators in air deposition on forages, is then possible to model their carry-over to food of animal origin and predict potential uncompliances with respect to regulatory Maximum Residue Limits (Food Safety), thus reducing human exposure. Both the Food Safety and Food Security aspects are strongly linked to the environmental requirements, and indirectly impact on human health and welfare, also in terms of the safe, social, and economic access to the food resources. On the other side, extensive farmed food producing animals may act as sentinel of the overall quality of the environment: a significant rise of the background contamination level in dairy products may indicate a poor environmental quality. This topic will be also proposed for the discussion within the Milan EXPO 2015 theme "Feeding the Planet, Energy for Life".

Table 1. PCB contamination (ng/g dry weight, above; ng/m^2 below) on mais leaves from not impacted farms (samples 1-7) and impacted farms (samples 8-9)

Sample	***# 28***	***# 52***	***# 101***	***#118***	***#138***	***#153***	***#180***	***Σ PCB (6)***
1	0.016	0.008	0.017	0.027	0.023	0.024	0.024	0.1
2	0.011	0.006	0.015	0.027	0.026	0.034	0.021	0.1
3	0.018	0.006	0.051	0.038	0.055	0.066	0.035	0.2
4	0.041	0.016	0.028	0.041	0.072	0.099	0.056	0.3
5	0.021	0.010	0.028	0.012	0.030	0.035	0.028	0.2
6	0.013	0.000	0.014	0.018	0.036	0.037	0.034	0.1
7	0.017	0.004	0.036	0.047	0.072	0.085	0.041	0.3
8	0.111	0.092	0.475	0.382	0.457	0.538	0.215	1.9
9	0.140	0.103	0.619	0.750	0.750	0.787	0.364	2.9
Sample	# 28	# 52	# 101	#118	#138	#153	#180	Σ PCB (6)
1	0.95	0.49	1.0	1.6	1.4	1.5	1.4	7
2	0.80	0.39	1.1	1.9	1.8	2.4	1.5	8
3	1.3	0.42	3.7	2.8	4.0	4.9	2.6	17
4	2.5	0.97	1.7	2.5	4.3	6.0	3.4	19
5	1.4	0.64	1.8	0.79	2.0	2.3	1.8	10
6	0.66	0.02	0.69	0.90	1.8	1.9	1.7	7
7	0.85	0.22	1.8	2.4	3.7	4.3	2.1	13
8	11.6	9.6	49.3	39.6	47.4	55.8	22.3	196
9	14.0	10.3	51.7	64.7	64.7	68.4	36.2	245

Table 2. Results of the modeled intake of PCBs from air deposition, top soil, and mud associated to mais leaves hay, drinking water. Contribution from commercial feeds also included.

Matrix	***Amount (g)***	***Σ PCB (6) (ng/g dw)***			***Σ PCB (6) Intake (ng/head/day)***		
		min	mean	max	min	mean	max
Top soil in hay	1.080	0.02	5.0	86	22	5.400	92.880
Sediments in water	2.000	0.02	5.0	86	40	10,000	17.200
Mais leaves	6.600	0.1	0.5	2.9	660	3.300	19.140
Feeds	6.000	0.5	0.5	0.5	3.000	3.000	3.000
Total intake					3.722	21700	287.020
Carry- Over Rate 36%					1.340	7.812	103.727
Milk contamination (ng/g fat basis)					1.34	7.81	104

Table 3. Critical environmental parameters able to rise the milk contamination around the P95 percentile of PCB (6 indicators) occurrence (20 ng/g fat basis) (**S1**) and around the ML (40 ng/g fat basis) (**S2**) in dairy products

Matrix	***Amount (g)***	***Σ PCB (6) (ng/g dw)***		***Σ PCB (6) Intake (ng/head/day)***	
		S1	S2	S1	S2
Top soil in hay	1.080	17.5	25	13.500	27.000
Sediments in water	2.000	17.5	25	25.000	50.000
Mais leaves	6.600	2	4	13.200	26.400
Feeds	6.000	0.5	0.5	3.000	3.000
Total intake				54.700	106.40
Carry- Over Rate 36%				19.690	38.30
Milk contamination (ng/g fat basis)				**19.7**	**38.3**

Keywords: contaminants, dietary exposure, environment, extensive farming, food security

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BACTERIAL COMMUNITY STRUCTURE AND THEIR CHANGES IN CONTAMINATED ECOSYSTEMS

Extended abstract

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Background

Within the different ecosystem compartments, bacterial diversity reflects the natural and stressed environmental conditions to which they are subject. The presence of contaminants can lead to the disappearance of key species and/or to the selection of microbial groups able to partially or completely remove such molecules.

Environmental contamination may result in changes in the microbial ecology, possibly changing the types of bacteria that carry out important ecosystem processes such as nutrient transformation and biomass decomposition. Microbial biodiversity in fact has a functional importance in the maintenance of soil and water biological processes, because most of the transformation involved in biogeochemical cycles is mediated exclusively by microorganisms. It has been reported that shifts in bacterial community structure, associated with a reduction in microbial biodiversity, lead to losses of functional stability (Girvan et al., 2005). Owing to their small size, large numbers and ubiquitous distribution in the environment, microorganisms are valuable indicators of the occurrence of disturbances due to exogenous physical-chemical stressors. The assessment of variations in microbial community structure is of basic importance in making it possible to evaluate the impact of an environmental stressor. The presence of toxic chemicals in microbial ecosystems induces the synthesis of detoxifying or degradative enzymes and certain stress proteins. Effects due to chemical toxicity tend to narrow the spectrum of microbial diversity because organisms that are not capable of resisting the toxic effects either die or enter a static metabolic phase, leaving those that have evolved resistance mechanisms and are thus capable of utilizing the excess chemicals as nutrients, to proliferate and become dominant members of the impacted ecosystems (Ogunseitan, 2000).

In recent years, it has been recognized that biodegradation and/or mineralization of some contaminant molecules is only possible through the presence of microorganisms able to transform them (Topp et al., 2013). Consequently some relationships between microbial communities and pollutants have been established. Among pollutants, pharmaceuticals including antibiotics, for both human and veterinary use, are frequently found as microcontaminants both in water and in soil ecosystems. Pharmaceuticals are molecules designed to produce a therapeutic effect on the body, usually active at very low concentrations, can pass through biological membranes and persist in the body long enough to avoid being inactivated before having an effect. These compounds are excreted through feces and urine as a mixture of metabolites and substances which are often unchanged. The primary sources of pharmaceutical contamination are represented by domestic, urban, hospital, and industrial wastewater, as well as by effluents from sewage treatment plants (STPs), aquaculture, and intensive livestock farming. Moreover, re-use of solid and liquid livestock manure and sewage sludge in agriculture, in order to recycle nitrogen compounds as fertilizers, can contribute to the dispersion of pharmaceuticals into soil and, under certain conditions, into water bodies. At present, the presence of antibiotics, steroids, blood lipid regulators, estrogens, painkillers, anti-inflammatories, antiseptics, antihypertensive drugs, antiepileptics, antineoplastic agents and other substances in surface water bodies and in soils receiving livestock manure or sewage sludge, even at very low concentration (ng-µg/L or Kg), is well-documented (Boxall, 2004). Percolation of pharmaceuticals into groundwater and their presence in sea coastal water have been detected as well. The environmental occurrence of these intrinsically and biologically active molecules may cause direct (toxicological effects on non-target organisms) and indirect effects such as

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antibiotic resistance (Bottoni et al., 2010). People can be exposed to pharmaceuticals through polluted water or by consumption of contaminated food.

Non-PCR-based methods commonly used in environmental studies are epifluorescence microscopy techniques, such as Fluorescence *In Situ* Hybridization (FISH) (Barra Caracciolo et al., 2013; Barra Caracciolo et al., 2010). They make it possible to characterize *in situ* bacterial populations in their natural ecosystems. In particular FISH investigates the overall taxonomic composition of bacterial communities by using rRNA-targeted fluorescent probes. This technique is also used for testing the efficient remediation of xenobiotic pollutants by microbial communities (Whiteley and Bailey, 2000). In fact the ability to monitor diversity structuring, stability and long-term resilience during process management are key requirements for monitoring and predicting bioremediation efficiency.

Objectives

In this work, through the sensitive Fluorescence *In Situ* Hybridization molecular method, we analyze the bacterial community of two different contaminated ecosystems, water and soil, and changes in their structure related to the presence of two different group of pharmaceuticals (anti-inflammatory drug and veterinarian antibiotics) in order to better investigate the effect of the selected compounds on the natural microbial community and to assess the microbial populations involved in their degradation. A description of Fluorescence *In Situ* Hybridization (FISH) technique, used in the two study cases, is reported; it was able to assess the phylogenetic characterization of active microbial communities in their natural environments (water and soil). The sensitivity of the FISH method in determining changes in microbial community structure related to the presence of contaminants is presented.

Outline of the work

This work reports two study cases:

- First, we considered a freshwater bacterial community in the presence of a non-steroidal anti-inflammatory drug, naproxen, in the Tiber River, Rome, Italy. Experiments with Naproxen, considered a high priority pharmaceutical, were conducted on water samples collected in the North of Rome. An experimental set consisting of 32 destructive closed microcosms each (100 mL capacity) was set up. Aliquots from the drug working standard solution were spiked to treated microcosms to a final concentration of 100 µg/L of naproxen. Spiking and all operations were conducted under sterile conditions and, once the solvent (acetonitrile) had completely evaporated at room temperature in order to eliminate any additional carbon source, 50 mL of the river water (natural or previously sterilized) was added to each microcosm. All microcosms were incubated at 20°C on an orbital shaker (125 rpm) in the dark. FISH analyses were conducted on the natural initial condition and at the end of the experiment, when chemical analyses confirmed the biodegradation of the naproxen.
- The second case deals with experimental plots chronically contaminated by some veterinarian antibiotics (mixture of Sulfamethazine, Tylosin and Chlortetracycline), located in the Agriculture and Agri-Food Canada experimental farm in London, Canada. These antibiotics are commonly used as livestock production for growth promotion, prophylaxis and treatment of illness. This experiment was conducted on twelve 2 m^2 plots that received annually for 11 years a mixture of the three selected antibiotics to achieve concentrations for each drug of 0.01, 0.1 and 1 mg/kg soil to a depth of 15 cm. Drugs were applied each June by mixing in aqueous mixtures of the antibiotics to 1 kg of soil from each plot. Three plots were left untreated as controls. Before the experiment the soil had not been treated with materials that could have carried drugs. Plots were cropped continuously to soybeans during each growing season, and received no further management. The control plots were otherwise managed exactly as described for the treated. Starting in 2005, the annual applications were increased 10-fold to achieve concentrations of 0.1, 1 and 10 mg/kg. Each microplot was sampled for FISH analysis 5 months after the last antibiotic application in order to evaluate the long term effect of the antibiotics on the bacterial community.

Methods

The evaluation of bacterial biodiversity is mainly limited by their small size, by the absence of distinguishing phenotypic characters, and by the fact that most of these organisms cannot be cultivated. The number of techniques for studying microbial communities has increased exponentially over the last 20 years and the advent of culture-independent methods, such as molecular biological techniques, has changed the view of microbial diversity. Fluorescence *in situ* hybridization (FISH) method makes it possible to identify microorganisms *in situ* using fluorescently labeled ribosomal RNA targeted oligonucleotide probes. FISH combines the precision of molecular genetics with the visual information from microscopy, allowing visualization and identification of individual cells in their natural microhabitat, so that nucleic acid sequences can be examined inside cells without altering their morphology or the integrity of their various compartments.

The FISH technique for detecting RNAs has been introduced into living cells using probes that fluoresce only when hybridized. *In situ* identification of individual microbial cells with fluorescently labeled rRNA-targeted oligonucleotide probes (phylogenetic stains), is based on the high cellular content of ribosomes, which can be found in living organisms and, consequently, like many 16S or 23S rRNA molecules. rRNAs are the main target molecules because they are relatively stable and include both variable and highly conserved sequence domains. The selection of particular regions of the rRNA molecule then enables phylogenetic specificity to be varied from the universal to the subspecies level. Under appropriate reaction conditions, complementary sequences in the probe and target cell anneal, and the site of probe hybridization is detected by fluorescence microscopy. The most common target sequences are in bacterial 16S rRNA, but other ribosome subunit sequences have also been used. In the FISH approach it is assumed that actively growing microbes have many ribosomes and should theoretically yield brighter fluorescence signals owing to higher rRNA-targeted probe hybridizations. Probes hybridize to whole bacterial cells, resulting in the selective staining of target cells. Fluorescent probes suitable for use in FISH have been developed at a variety of taxonomic levels (e.g., universal, or domain-, family-, or species-specific) and they can be designed based on phylogenetic trees. The FISH protocol includes four steps: fixation and permeabilization of the sample, hybridization, washing to remove un-bound probe and detection of labeled cells by microscopy. Prior to hybridization, bacteria must be fixed and permeabilized in order to allow penetration of the fluorescent probes into the cell and protect the RNA from degradation by endogenous RNAs. Hybridization must be carried out under stringent conditions for proper annealing of the probe to the target sequence. For this crucial step of the FISH procedure, a pre-heated hybridization buffer is applied to the sample containing fluorescently labeled probes complementary to the target RNA. The hybridization takes place in a dark humid chamber, usually at temperatures between 37 and 50°C. Stringency can be adjusted by varying either the formamide concentration or the hybridization temperature. The oligonucleotide probes typically consist of 18 to 30 nucleotide bases conjugated to a fluorescent marker on the 5' end which allows detection of probes bound to cellular rRNA by fluorescence microscopy. Multiple group-specific rRNA probes targeting microbial taxa can be used in a FISH experiment for simultaneous phylogenetic classification as well as quantification of physiologically active microbial populations in an environmental sample.The phylogenetic composition of the bacterial communities of the two ecosystems we considered was analyzed. At the domain level, EUB338 probes (EUBI, II and III) targeting *Bacteria* were used. Inside this domain various Cy3-labelled commercially synthesized oligonucleotide probes were applied (Table 1). Each surface water or soil subsample was filtered through a 0.2 µm polycarbonate membrane using a gentle vacuum (soil subsamples were pre-treated in order to eliminate particulate loads that interfere with probe fluorescence, Barra Caracciolo et al., 2005). FISH of the harvested cells, counterstained with DAPI, was performed according to published protocols (Barra Caracciolo et al., 2005). The average number of cells binding each of the probes was calculated as a proportion of the total DAPI positive cells from 10 to 20 randomly selected fields on each filter section (corresponding to 500-1000 stained cells). The slides were examined and counted on a Leica DM 4000B epifluorescence microscope at x1000 magnification.

Table 1. Probes and their characteristics applied in hybridization

Probes	***Corresponding Taxa***	***Sequence (5'-3')***	***rRNA position***	***%Formamide***
ALF1b	*Alpha-Proteobacteria*	CGTTCGYTCTGAGCCAG	16S(19-35)	20
BET42a	*Beta-Proteobacteria*	GCCTTCCCACTTCGTTT	23S(1027-1043)	35
GAM42a	*Gamma-Proteobacteria*	GCCTTCCCACATCGTTT	23S(1027-1043)	35
DELTA495a	*Delta- Proteobacteria*	AGTTAGCCGGTGCTTCCT	16S(495-512)	35
DELTA495b	*Delta- Proteobacteria*	AGTTAGCCGGCGCTTCCT	16S(495-512)	35
DELTA495c	*Delta- Proteobacteria*	AATTAGCCGGTGCTTCCT	16S(495-512)	35
DELTA495b	*Delta- Proteobacteria*	AGTTAGCCGGCGCTTCCT	16S(495-512)	35
EPS710	*Epsilon- Proteobacteria*	CAGTATCATCCCAGCAGA	16S(710-727)	30
PLA46	*Planctomycetes*	GACTTGCATGCCTAATCC	16S(46-63)	30
PLA886	*Planctomycetes*	GCCTTGCGACCATACTCCC	16S(886-904)	35
CF319a	*Bacteroidetes*	TGGTCCGTGTCTCAGTAC	16S(319-336)	35
LGC354a	*Firmicutes*	TGGAAGATTCCCTACTGC	16S(354-371)	35
LGC354b	*Firmicutes*	CGGAAGATTCCCTACTGC	16S(354-371)	35
LGC354c	*Firmicutes*	CCGAAGATTCCCTACTGC	16S(354-371)	35
HGC69a	*Actinobacteria*	TATAGTTACCACCGCCGT	23S(1901-1918)	25

Results and discussion

In natural river water samples the Bacteria dominant group was the *Beta-Proteobacteria* (data not shown). The comparison of the autochthonous bacterial community analyzed 20 days after the naproxen-treatment in the microcosms shows changes in the abundance and shifts in the dominance of several groups. In fact at day 20, close to the naproxen halving (Grenni et al., 2013), a significant increase in *Alpha-* and *Gamma-Proteobacteria* groups was observed Fig. 1). Natural bacterial populations respond differently to contaminant occurrence; the increase in number of these groups can be presumably related to naproxen degradation, while the decrease of *Beta-Proteobacteria* to a toxic effect of the pharmaceutical. Although naproxen was degraded in this experiment (Grenni et al., 2013), we cannot exclude the possibility that some key ecosystem functions, performed by the bacterial populations who suffered the toxic effect, were negatively affected. This hypothesis was found in a recent study that showed how the activity of nitrifying *Beta-Proteobacteria* (*Nitrosomonas europea*) was inhibited in the presence of the drug naproxen. In Fig. 2 the FISH results of the antibiotic mixture (Tylosin, Sulfamethazine and Chlortetracycline) treatment are reported. As it is possible to see in the graph, most of bacterial groups were unaffected 5 months after the treatment, except *Planctomycetes* (Pla) and *Bacteroidetes* (CF). *Planctomycetes* displayed a significant decrease in number (t test, $p < 0.01$) in soils treated with low and medium concentrations (0.1 and 1 mg/kg) of antibiotics; in fact their values were more than 10 times lower than those in the control soil. This effect at low concentrations may be due to a suppressive combination in which multiple antibiotics were used, associated with an acquired resistance to one antibiotic used and enhanced susceptibility to the others (suppressive combination). The decrease in their number may also have been due to a competitive advantage of populations belonging to other bacterial groups that did not undergo inhibitory effects from the presence of the antibiotics, such as the *Alpha-*, *Beta-* and *Gamma-Proteobacteria* groups. However, the *Planctomycetes* in soil treated at a high concentration (10 mg/kg) had abundance values comparable to those of the control soil, showing no long-term effects at that concentration. *Planctomycetes* is a microbial population with intrinsic resistance to many antibiotics due to the absence of the peptidoglycan layer in their cell wall and they are naturally resistant, for example, to penicillins, which interfere with the synthesis of peptidoglycan.

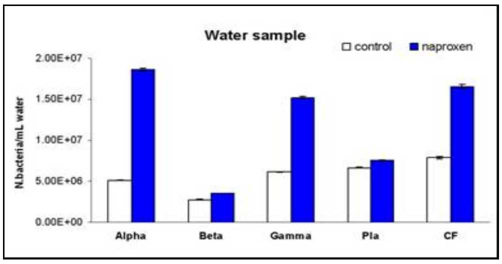

Fig. 1. Bacterial community structure detected by FISH in freshwater samples 20 days after the naproxen treatment. Alpha = *Alpha-Proteobacteria*; Beta = *Beta-Proteocateria*; Gamma = *Gamma-Proteobacteria*; Pla = *Planctomycetes*; CF = *Bacteroidetes*. The verticals bars represent the SE.

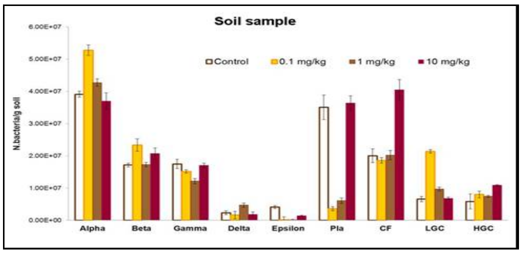

Fig. 2. Bacterial community structure detected by FISH in soil samples 5 months after the antibiotic treatment. Alpha = *Alpha-Proteobacteria*; Beta = *Beta-Proteocateria*; Gamma = *Gamma-Proteobacteria*; Delta = *Delta-Proteobacteria*; Epsilon = *Epsilon-Proteobacteria*; Pla = *Planctomycetes*; CF = *Bacteroidetes*; LGC = *Firmicutes*; HGC = *Actinobacteria.*

Bacteroidetes phylum (CF) increases in number at the highest concentration (10 mg/kg) and this could be due to a resistance mechanism. The overall results show not only that antibiotic occurrence can affect bacterial population dynamics, but they also can induce resistance mechanisms via bacterial conjugation among different soil populations. The impacts of antibiotics on microbial soil populations are therefore surprisingly complex and further studies are necessary to better investigate induction of antibiotic resistance. The latter cause particular concern because can be acquired by pathogenic microorganisms, reducing the effectiveness of antibiotics.

Concluding remarks

In this work we report, as example, the effects of selected contaminants on bacterial communities of two different ecosystems, soil or surface water. Contaminants affect natural bacterial communities causing directly or indirectly changing in community structure like dominance and/or disappearance of some bacterial groups with potential loss of important ecosystem functions. The overall results suggest the usefulness of bacterial structure and functioning studies as microbiological indicators for assessing freshwater and soil quality states.

Keywords: antibiotics, contaminants, FISH, microbial community structure, pharmaceutical

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INTEGRATED APPROACH FOR THE ANALYSIS OF ECOSYSTEMS AT RISK: A CASE STUDY IN A WASTE LANDFILL

Extended abstract

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Background

Waste landfills are currently the most widely used method to dispose municipal waste, mainly in highly populated cities. Landfills can be a source of a large number of toxicant elements and compounds diffuse through air fallout or leachate release. Some research has been shown that landfills spreads a large number of compounds that, since industrial revolution, are increasingly accumulated in the soil and in the litter and that in some situations, may be available for the species even at considerable distances from the source (Gagnon and Saulnier, 2003).

There are many studies on the chemical characterization of leachate and air but they represent only the first step for a meaningful environmental impact evaluation. For these reasons one of the most important activities concerning the management of a municipal waste landfill regards the control and environmental monitoring aimed to safeguard both of the structural aspects of the plant (i.e., efficiency) both the environmental quality of the site.

Quantification of heavy elements levels in soil and air cannot generate sufficient information on impact because the absolute metal concentration alone does not reflect the degree to which these compounds affect the environment (Cheung et al., 1993). Data on the bioaccumulation and effects of leachate on wild populations are essential to assess the environmental impact of these disposal sites.

In this paper we propose an evaluation method that brings together biomonitoring techniques, morphometric measurements (fluctuating asymmetry), cytometric tests on cells of the hepatopancreas of Armadillidium vulgare (*Isopoda, Crustacea, Latreille*, 1804) and quantitative analysis of lichens; an integrated approach that can provide information about the state of health of the ecosystem before it gets evident alterations

Objectives

- Enlarge the field of study of the monitoring compartment by inserting the "organic".
- Detect contamination so early before if their effects occur through the use of soil macro-invertebrates and lichens.

Outline of the work

This work is divided into four parts:

- Analysis of heavy element contents in terrestrial isopods (*Armadillidium vulgare*)
- Analysis of heavy element contents in lichen transplants
- Ratings of fluctuating asymmetry in Armadillidium vulgare

Flow cytometric analysis of hepatopancreatic cells of Armadillidium vulgare

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Methods

The primary study area is centered on the municipal solid waste landfill of Ginestreto and extends on a surface of about 25 km^2 in the municipality of Sogliano al Rubicone (Emilia-Romagna, Italy). In order to evaluate the impact of the landfill fallout on the surface environment, epiphytic lichens and terrestrial isopods were used as bioindicators of air and soil contamination. Leachate employed in cytometric laboratory tests has been collect from the same site. Only for asymmetry study isopods were collected isopods in other two sites as control/comparison. The first is located at the campus of Urbino University (Marche, Italy), a protected woodland called "Fosso del tasso" in which there are no significant human activities. The second is in the area of Pantiera (Urbino, Italy in an agricultural context.

Lichens

Lichens are organisms commonly used in air monitoring studies as they are highly efficient accumulators of many chemicals such as heavy elements. Due to this ability, it has been assumed that the heavy element concentrations in lichens reflect their atmospheric levels. Consequently, these organisms are considered important biomonitors of air quality and are extensively employed to assess the impact of several human activities (e.g., vehicular traffic, industrial and power plants, incinerators and smelters) on atmospheric contamination. Lichen transplants are frequently employed in air monitoring surveys (e.g., Ayrault et al., 2007). The advantages of lichen transplants are: uniformity of species, entrapment surface and exposure period, flexibility in selection and number of monitoring sites, knowledge of the original concentrations of contaminants in lichens before exposure, opportunity to carry out biomonitoring studies in areas where native lichens are absent.

In this study the transplanted lichens were collected in an uncontaminated area of central Italy. Before exposure, thalli were washed to remove the particles trapped on the surface and acclimated for 24 h in a cell conditioned at a temperature of 15±2° C. The lichen transplants were exposed for 4 months (October 2012 – January 2013) in 31 sites located: i) close to the municipal solid waste landfill; ii) close to the main roads of the study area; iii) in zones far away from the potential anthropogenic sources of contamination. After exposure, the lichens were frozen at -20° C and pulverized with liquid nitrogen. The pulverized lichen samples were solubilized by acid digestion. The digestion was performed in a microwave lab station using a mixture of ultrapure reagents (HF, HNO_3 and H_2O_2). The solution was analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) to determine the concentrations of As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Tl and Zn.

Isopods

The terrestrial isopods are considered bioindicators of soil quality and suitable for studies on environmental contamination. For their important role in decomposition processes in surface soil, these invertebrates are in close contact with soil contaminants and are able to accumulate heavy elements. Adult individuals of *Armadillidium vulgare* isopod were collected by hand-sorting in June 2012. The isopods were sampled in 13 sites placed at different distances from the waste landfill (up to 8 km) along a transect aligned to the main wind direction. In each sampling site 10 isopod individuals were collected within a range of about 100 m.

Heavy element analysis

In laboratory isopods were rinsed with deionized water to clean them of adhering soil particles; then they were kept for 72 h in plastic Petri dishes at a constant temperature of 18° C with a photoperiod of 12 hours, to allow emptying of the intestinal tract. The isopod specimens were killed by freezing at -80° C and freeze-dried for 48 h. The freeze-dried isopods were digested with a mixture of ultrapure reagents (HNO_3 and H_2O_2) in a microwave lab station. The solution was analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) to determine the concentrations of As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Tl and Zn.

Fluctuating Asymmetry

Fluctuating asymmetry (FA) is the random and non-systematic deviation from the normal condition of symmetry, occurring without stressing factors, be they environmental or genetic. Our hypothesis is that the FA will be greater in the presence of environmental stresses such as pollution.

We compared the morphological alterations of three pools of isopods sampled in rich habitats with different land use and in general with a different anthropogenic pressure. In particular an optical microscope associated with a camera was used to capture photographs of seven symmetrical traits: number of composite ommatidia of the eye, length of the first flagellum, second and the third segment of the antenna, merus, carpus and propodus of the seventh pareiopods. The captured images of nearly 100 specimens were processed by the image analysis software Image J. The asymmetry index used is defined as (Godet et al., 2012)(Eq.1):

$$FA = \frac{|R-L|}{\frac{R+L}{2}} \qquad (1)$$

where: FA is fluctuating asymmetry; R is right size; L is left size.

Flow cytometry of hepatocytes

The hepatopancreas of the terrestrial isopod *Armadillidium vulgare* takes an important role in bioaccumulation of contaminants, such as heavy elements. To evaluate the effects of landfill leachate treatment Flow Cytomteric tecniques were, for the first time, applied to the hepatopancreatic cells of isopods.

This organ (*Armadillidium vulgare*) has been thoroughly investigated by many authors, due to both their morphologic characteristics, which are related to the physiological condition, and their role in bioaccumulation of contaminants. The terrestrial isopods hepatopancreas is composed of four blind-ending tubes. The hepatopancreatic epithelium contains two cell types: the large B cells and the wedge-shaped S cells that lie between the B cell. The main features of B cells are the presence of well developed microvilli, active Golgi complexes, extensive arrays of rough endoplasmic reticulum, numerous mitochondria and a lot of lipid droplets. This ultra-structural features suggest the role of the B-cells in secretion of digestive enzymes and absorption of nutrients. The S-cells accumulate large amounts of elements such as calcium, and uric acid salts. Experiments of contamination of isopods with landfill leachate were conducted in order to verify the different behaviour of hepatopancreatic cells during 30 days of exposition (Manti et al., 2013).

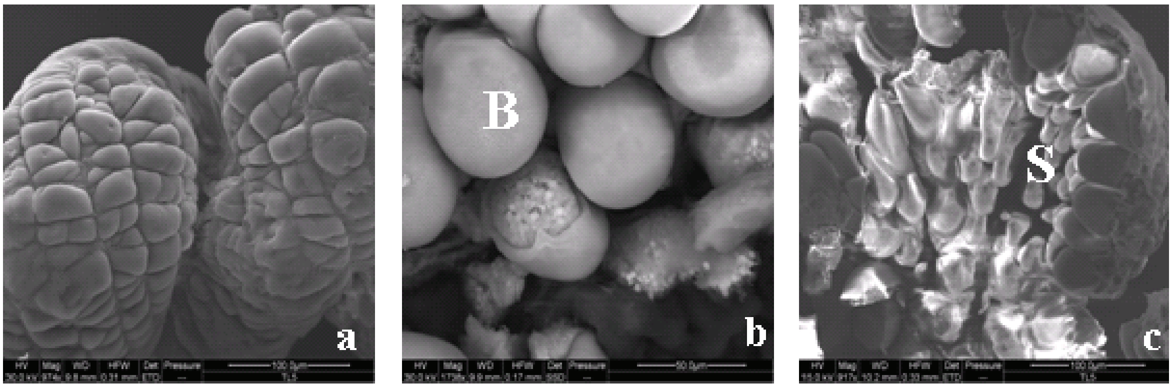

Fig. 1. Normal appearance of digestive epithelium of external gland (a); normal appearance of digestive epithelium of internal gland showing B and S cells (b, c). Electron microscopic analyses (ESEM) show the morphologic characteristics in hepatopancreas of Armadillidium vulgare, in particular the images underline the different size of cells (ranging from 20-30 µm and 50-70 µm Ø respectively).

Results and discussion

Lichens

The analytical data indicated that in the monitoring sites of the study area the heavy element concentrations in transplants are usually higher than their levels in non-exposed lichens. According to the *Exposed to Control ratio* (EC ratio = element concentration in lichen transplant / element concentration in non-exposed lichen) Cd, Cr, Pb, Sb and Zn are in severe accumulation in the transplants placed close to the municipal waste landfill of Ginestreto as well as in some sites close to the main roads. In the landfill sites these heavy elements reached the highest enrichments with EC ratio average values of 4.7 for Sb and about 2 for Cr, Pb, Sb and Zn. As, Co, Cu, Ni and Tl are accumulated by lichens with EC ratios usually within 1.25 and 1.75. No accumulation process was found for Hg.

Heavy element accumulation in Isopods

The heavy element concentrations in isopods were rather uniform. Cd, Pb and Sb showed the highest contents in individuals collected in the traffic-influenced sites. Among the analyzed heavy elements, Cd, Cu and Zn were bio-accumulated by isopods with average values of the Bio Accumulation Factor (BAF = element concentration in isopod / element content in soil) of 1.1, 6.1 and 1.3, respectively. These results are in agreement with data reported by other authors (Blanusa et al., 2002) as well as in our research realized in a similar environmental setting.

Fluctuating Asymmetry

Performing a test of the effects between subjects and a comparison in pairs on the three sampling sites, we obtained that the most significant differences are for the traits metric unlike those meristic (number of ommatidia) that are not significantly different. We also verified that the index of F.A. shows the most significant differences between the landfill site and the control group.

FCM analysis

In this study, we correlated the presence of Big and Small cells, in terms of cell count and viability, with the presence of some elements. Our findings were underlining Small SYBR Green I (a fluorochrome able to labelled nucleic acids) Bright cells correlate with specific chemicals (Ca, Cu, Co) confirming their resistance to stress stimuli.

Furthermore, we also investigated **B** cell trends that highlight a general 2 fold increase in Propidium Iodide positive frequency in respect of **S** cells, confirming their more pronounced sensitivity to environmental stress. In samples observed the S cells are more abundant than B cells. Substantial differences in metal accumulation are known between the isopod species *Porcellio scaber.* Considering that B cells seem to play a role in metal excretion and S cells in metal storage we may assume in *Armadillidium* a clear prevalence of S cells.

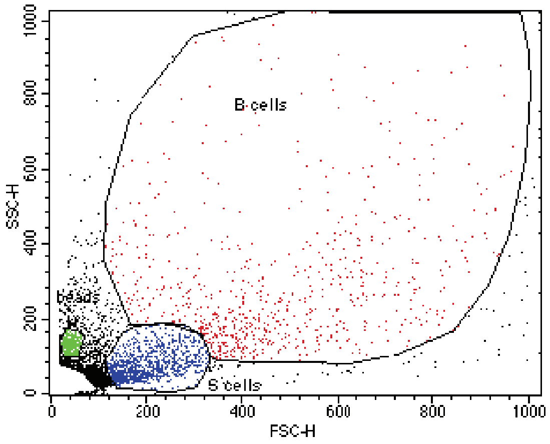

Fig. 2. Cytometric dot plot FSC vs. SSC of hepatopancreatic cells

Concluding remarks

Soil is a dynamic system and it is subject to dilution phenomena, erosion and transport of materials and pollutants. Air and soil chemicals analysis can determine an underestimation of the environmental impact, because this last can manifest itself as ecological debt. The use of biological indicators can be integrated to traditional monitoring to give a qualitative and quantitative evaluation of the impact on biological systems. We can conclude that isopods and lichens are efficient bioindicators also for landfill fallout, and their response to the pollutant effects can be consider as a good marker to evaluate the real ecological damage of a contaminated environment.

Keywords: flow cytometry, isopods, leachate, lichen transplants, waste landfill

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BIOGAS IMPACT MITIGATION THROUGH BIOCOVERS: LAB TESTS AND ANALYSIS IN SITU FOR THE CHARACTERIZATION OF FILTERING MEDIA

Extended abstract

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Background

Among the several technologies for mitigation of landfill gas emission, this research deals with interim systems which can be used as daily cover.

Aiming to identify the parameters that can help to define the quality of filtering material suitable for daily biocovers, several research were carried out, both lab tests that field trials. It is estimated that in 2010 more than 2 million tons of Stabilized Humid Fraction (SHF) from mechanical-biological treatment were produced in Italy, and that more than the 80% of this fraction is disposed in landfill and the remaining parts is used to realized the final covers. Furthermore, the legislation allows the use of this material for the daily covers, but in landfills where this is done, problems of odor nuisance perceived by the neighbor population are very common.

Objectives

The objective of this research is therefore to define quality parameters that suggest that the SHF analyzed is suitable for daily biocovers for gas emission mitigation. In particular, Biochemical Methane Potential (BMP) and Dynamic Respiration Index (DRI) tests have been performed as well as specific test to determine the mitigation efficiency of the daily biocover (emission measurement).

Our paper will show the main results of three work steps:

1. determination of stabilization parameters (BMP, DRI, SV, Water content);
2. study of the possible reactivation of aerobic or anaerobic processes in the SHF sample through a specific lab test;
3. monitoring campaign on the daily cover to assess the mitigation effect of the SHF.

Methods

At the beginning, in order to characterise the different filtering materials many parameters were carried out, in particular for every SHF analysed it was determined: BMP, DRI, SV, Water content and pH.

Moreover, to measure the emission flux on daily covers the accumulation chamber was used in field tests. Finally, during the pilot tests, two batch reactors were used in order to create aerobic or anaerobic conditions and to simulate the emissions naturally present in a landfill cover. Both determination parameters and lab test were carried out on different sample of SHF. The flux of biogas form the cover was measured according with the Static Accumulation Chamber method (Corti et al., 2009; Huber-Humer et al., 2011).

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An infrared concentration level detector, Ecoporbe , was used for the first time used with the accumulation chamber method. Ecoprobe 5, produced and calibrated by RS Dynamics Ltd. (Prague, Czech Republic) is a tool for a fast and cost-effective in-situ mapping of hydrocarbons and other organic contaminants in the subsurface environment.

For every measurement point, the following procedure was repeated:

- Location of sampling point by means of a GPS (Global Position System) instrument following a regular grid;
- Preparation of the sampling surface in order to ensure optimal adhesion of the chamber to the soil, thereby preventing gas from escaping during measurement;
- Survey and acquisition for 2-3 minutes of the concentration (ppm) of CO_2 and CH_4 inside the chamber.

To determine the possibility that in the SHF filtering materials the degradation process are reactivated, the residual biogas potential production and the residual respiration index after the mechanical-biological treatment were evaluated.

To estimate the biogas potential production of each SHF, the BMP analysis were carried out in duplicate and both the BMP21 (biogas produced at 21 days) and the BMPf (when no significant biogas production is detected) were measured. For analysis a modified manometric method has been applied (Ponsa et al., 2008; Hansen et al., 2004).

The BMP was determined using 1L stainless steel bottles, incubated in a water bath at 37.7°C, tightly closed by special cap provided with a ball valve to enable the gas sampling. To ensure anaerobic conditions, the bottles were flushed with inert gas. All the equipment, 2 bar proof pressure, was specifically design and developed.

The dynamic respiration index was determined according to Adani et al. (2008). The oxygen uptake was determined by measuring the difference in oxygen concentration between the inlet and outlet air flow, the air having passed through the biomass, as well as by using knowledge of the absolute content of starting SV in the biomass, the flow rate, and the time during which oxygen consumption was measured. The time test length depended by the material stability degree and lag-phase occurred and ranged from few hours to three days.

In order to assess the potential reactivation of aerobic or anaerobic degradation on the top of daily cover, some batch reactor tests were carried out. In particular it was tested every filtering materials during a period of 24 hours; during the test several parameters were monitored to detect possible degradations events as temperature (both internal and external), air or biogas in-let flow, atmospheric pressure, methane and CO_2 emission flux. Two adiabatic cylindrical batch reactors are used. To perform the tests specific measurement protocols were preliminarily defined.

Results and discussion

1. Lab tests results

With the aim to assess the range of emission flux on daily cover in an active landfill measurement campaigns with the accumulation chamber were carried out.

The flux measurements were performed directly on the waste and during working activity. The range of methane flux was found to be about 11.31±3.3 CH_4 mol/m^{2}day and in case of CO_2 flux is about 40.87±3.7 CO_2 mol /m^{2}day. The CH_4/CO_2 ratio was about 0,3 because in the daily cover oxygen concentration don't allow to start the anaerobic process. From the data analysis it was observed a variability of the measured data; observing the pressure values measured at the time of each flow measurement, the atmospheric pressure seems to be a forcing parameter.

The results of this preliminary field tests were useful to define the inlet flux in the following lab tests.

For each sample used in the pilot and lab test, the stabilization parameters reported in Table were determined. The SHF2 was characterized by higher values of density and lower porosity. The TS was found to be higher in the SHF2 samples while the VS were found to be the same in the tested samples. Values of pH 6 were recorded for SHF1 samples while alkaline pH was found for SHF2. Furthermore, the BMP and the DRI, parameters directly related to the material stability, resulted to be higher for the SHF1 samples. Observing the temperatures measured at the beginning of test, it can be noticed that the highest temperature were detected in the samples used for the aerobic conditions tests (SHF1_2811A and SHF2_0512A). The highest methane and CO_2 fluxes were measured for the SHF1_2811A sample while the highest H_2S concentration were measured in the SHF2_1912AN samples processes in the presence of anaerobic conditions. Thus, in the following only the results obtained in the aerobic conditions tests are showed. Regarding the first sample of SHF, the temperature inside the reactor reached a maximum of 71 ° C after 60 hours of flushing and both flux of CO_2 and methane increase during the test while the concentrations of H_2S were maintained constant and equal to about 1 ppm.

Even in the case of the SHF2, the internal and the surface temperatures showed an increase in the early hours of flushing until a maximum peak equal to 52 °C (lower than the beginning temperature) after about 21 hours of blowing. The flow of methane was found to be always lower than the instrumental detection limit (0.03 molCH_4/m^2 * day) with the exception of the first measurement made after 4 hours of flushing in which it was found to be equal to 2.38 molCH_4/m^2*day. The flow of carbon dioxide increased progressively with a maximum of about 33.47 molCO_2/m^2*day after 22 hours of flushing (hours in which the temperature inside the reactor resulted to be maximum). The concentration of hydrogen sulphide, equal to 1.78 ppm before the test, generally decreased.

The results of the laboratory tests had proved the absence of reactivation of the biological stabilization

Fig. 1 compares the reactor temperature measured in the lab tests. The internal temperatures of the reactor, both in the case of aerobic than anaerobic conditions, measured on the sample of SHF1 were found to be greater than those recorded for the SHF2, up to a maximum difference 23 ° C with reference to the first 24 hours, and 49 °C when considering the entire duration of the aerobic conditions test. It should be noted that in both cases the samples SHF1 in phase transfer were characterized by higher temperatures.

Table 1. Stabilization parameters

	Density	***Porosity***	***TS***	***VS***	***pH***	***BMP21***	***DRI, potential***	***DRI, real***	***Initial Temp.***	***Initial CH_4 Flux***	***Initial CO_2 flux***	***Initial H_2S conc.***
	kg/m^3	%	%	%		Nl/kgTVS	mgO$_2$/h*kgSV	mgO$_2$/h*kgSV	°C	moliCH$_4$/ m^2*day	moliCO$_2$/ m^2*day	ppm
SHF1 2811A	575	49	60	43	6	276	1195	1195	59	1.82	19.80	1.2
SHF2 0512A	431	56	82	42	8	180	849	427	53	0.03	3.37	1.8
SHF1 1212AN	537	46	52	46	6	344	1126	1126	34	0.03	3.31	1.2
SHF2 1912AN	428	57	89	41	9	241	993	63	12	0.03	0.66	5.3

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Moreover the temperatures recorded during the aerobic tests are much higher than those recorded during the anaerobic test in which, as said before, no reactivation phenomena were recorded.

The CO_2 fluxes measured during the tests, agrees with what is observable in the temperature graph. The flow measured testing SHF1 under aerobic condition results to be very high and higher to those measured in the other tests by about an order of magnitude.

In laboratory tests there was no evidence about reactivation of degradation processes in anaerobic conditions, and this is probably due to the fact that the kinetics are slower anaerobic with activation times longer than 24-48 hours, more so than the time intervals of interest.

Furthermore, between the two tested SHF, the SHF2 resulted to be more suitable for bio-filtration process because of the lower emissions measured; for this reason it has been used in the field test.

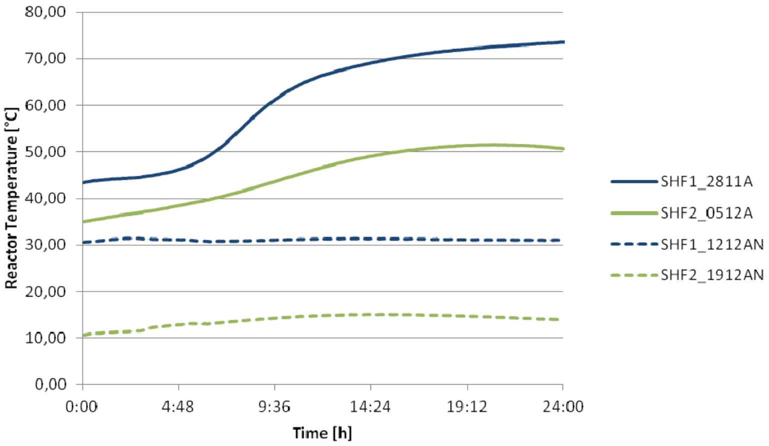

Fig. 1. Temperature, Comparison between the lab tests performed

2. Field tests results

In the field test, to assess the mitigation effect of a SHF daily cover a specific monitoring campaign was done. The measurements were done in four different times in the working period:

- before the waste deliveries;
- in the middle of the working day;
- at the end of the waste deliveries

- after the waste covering, on the experimental daily cover.

In particular, for the test, two experimental daily cover were prepared: one in SHF and one in natural soil.

The average daily flow was approximately 5 $molCH_4/m^2*day$ and about 20 $molCO_2/m^2*day$, and an average H_2S concentration of about 3 ppm is detected in the control volume in contact with the emissive surface.

With reference to the pressure trend in Fig. 2, in the monitoring day a decrease of few millibar was recorded. The emitted flux is low in the first measure when the pressure value is greater (1001 mbar), and stood on the constant values during the other measures of the day.

The flows recorded on natural soil cover show higher CH_4/CO_2 ratio than the ones measured on the SHF cover. In particular, the measured flows show an oxidative capacity of the SHF probably due to the development of methanotrophs bacteria, which usually grow in porous media rich in nutrients (such as compost), able to convert methane emissions into CO_2.

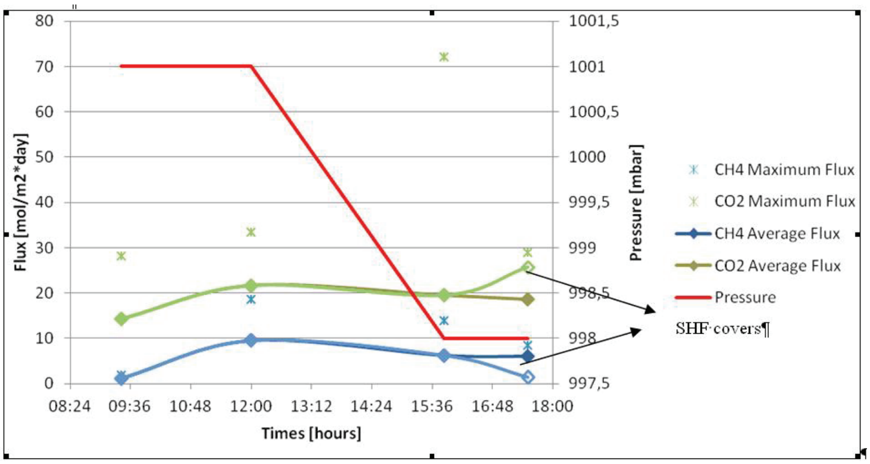

Fig. 2. Flux and pressure measured on the daily covers, field tests

Concluding remarks

The results of the study show that not all the SHF tested were suitable to be used for the daily cover but that the preliminary determination of some biological stability parameter may be helpful to assess the suitability of the material.

In fact, it was shown that, if the values of BMP and DRI are low, the reactivation of biological stabilization processes does not occur.

In the field tests on the SHF cover has instead been a reduction of methane emission almost immediately but further analysis must be done to determine the bio-filtering characteristics of this material.

In particular, to verify the presence of any osmogene substances, some analysis of the odours compound detectable in the emission will be carried out.

Keywords: biofiltration, landfill biogas, landfill emission monitoring, methane emission mitigation, odor mitigation

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MEASUREMENT OF ODOUR EMISSION CAPACITY IN WASTEWATER TREATMENT PLANTS BY MULTISENSOR ARRAY SYSTEM

Extended abstract

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Background

Odours emitted by wastewater are one of the major concern for local authorities in relation of the nuisance generate in the neighborhoods of the wastewater treatment plants (WWTPs). Odour impacts from WWTPs are generated by primary and secondary odour emissions (Zarra et al., 2008); emissions of primary odours are mainly related to the wastewater type; emissions of secondary odours are related to the treatment units that are present in the plant (Zarra et al., 2012). Control of odour emissions is very important issue to avoid impacts and therefore complaints. A characterization of the potential odours emissions of wastewater from the different treatment units could be the best approach to identify the most appropriate abatement systems and to design an efficient management plant. At present, the more recognized way in the scientific literature used to measure the potential odour emissions of liquids is the determination of Odour Emission Capacity (OEC) according to the method presented by Frechen and Köster (1998). This method defines the Odour Emission Capacity of a liquid as the total amount of odorants, expressed in OU/m^3_{Liquid}, which can be stripped from 1 m^3 of the liquid under given standardized conditions. The measure of the odour concentration, according to Frechen and Köster (1998) procedure, is performed using dynamic olfactometry technique.

Dynamic olfactometry (DO), standardised in Europe by EN 13725:2003, is a sensorial technique that uses human noses as a sensors and is able to measure odour by referring directly to their effects on a panel of qualified examiners. The most significant weaknesses of DO are related to high costs of qualified panels and their time-consuming feature, as well as the limit in the detection of low odour concentrations (Capelli et al., 2008). Odour concentrations can be also monitored by multisensor array systems often called as electronic noses (e.Noses) that can replace the use of human noses and can also work continuously (Belgiorno et al. 2013). The OEC method according Frechen and Köster (1998) procedure presents different problems due to the high costs and time related to the elevate number of DO determination (Belgiorno et al., 2013).

This paper presents a new way to detect OEC to control odour emissions in a WWTP using a innovative multisensor array system, based on combination of different specific and non specific sensors, instead of the dynamic olfactometry. The overall aim is to reduce costs and time for the determination of OEC, increasing the sensitivity of the measurements and automating the control of odour with an electronic device able to detect OEC in the WWTPs.

Methods

Sampling program

Wastewater samples were collected at the Salerno WWTP located in the industrial area of the Salerno City (Italy). The investigated WWTP is a conventional activated sludge treatment plant designed for 700.000 PE. Wastewater samples were collected at the following three different treatment units: screening channel before the grit (O1), primary sedimentation (O2) oxidation (O3).

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Sampling was carried out one time a month from January to June 2013 at each sampling treatment unit. The first 15 samples (from January to May) were used to create the odour quantitative model (training phase) for the multisensor array system (seedOA) and to characterize the OEC of all investigated treatment units according to Frechen and Köster (1998) procedure. The last 3 samples, collected in June 2013, were used to validate the use of the seedOA for the determination of the OEC, alternatively to the dynamic olfactometry. A total of 18 samples were collected over the research period, 6 from each sampling unit and a total of 90 DO analyses were carried out. All measurements were made at the SEED (Sanitary Environmental Engineering Division) Laboratory of the University of Salerno.

Odour emission capacity (OEC)

OEC was measured according to Frechen and Köster (1998) method by Eq. (1).

$$OEC = \int \frac{(C_{od} - C_{100})}{V_L} dV \tag{1}$$

where: C_{od} is the concentration of odour emission from air samples collected at suitable volume of fluxed air after beginning (V_{to}=0) to V_t (volume at time t), detected by dynamic olfactometry in accordance with EN 13725:2003; C_{100} is the concentration of odour emission established as the limit which defines the end of the test, fixed at 100 OU/m^3 (Frechen et al., 1998); V_L is the volume of liquid sample used for the analyses.

Air stripping tests were used to collect odour emissions from wastewater samples using the experimental setup schematized in Fig. 1. Air samples are collected in 7 liters Nalophan® bags respectively at 2, 10, 20, 30 and 40 min of air fluxing with a constant flux of 1.5 L/min of odourless air and a degree of turbulence of 0.5 L/min. All the collected samples have been analyzed using both the dynamic olfactometry and the seedOA.

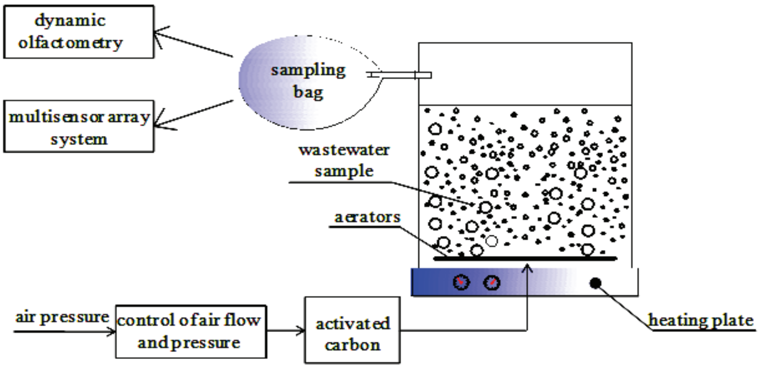

Fig. 1. Experimental setup used for odour emission sampling to OEC determination

Dynamic olfactometry

Olfactometric analyses were conducted according to EN 13725: 2003 in the Olfactometric Laboratory (SEED) of the University of Salerno, using an olfactometer model TO8 (ECOMA, D) based on the ‘‘yes/no’’ method. All the measurements were analyzed within 14 h after sampling (Belgiorno et al., 2013).

Multisensor array system (seedOA)

The novel multisensor array system (seedOA) designed by the SEED of the University of Salerno (Italy) was used in this research activity. The system consists of a set of 2 specific gas sensors (NH_3 and H_2S), 12 metal oxides non-specific gas sensors and 2 internal conditions control sensors (humidity and temperature), placed in the innovative fluid dynamics chamber (CODE®) patented by the SEED of the University of Salerno (Italy) (Viccione et al., 2012). The sensors used for the experimental research were selected on the basis of the potentially odorous substances emitted from the investigated type of plant according to previous studies (Zarra et al., 2009). A working flow rate of 300 ml/min for the sampling air analysis was used during all the analyses period. Air samples are analyzed by seedOA thought cycles of “odourless air-odour-odourless air”.

Acquired data are recorded in an external computer and processed by statistical and mathematical tools. The Partial Least Squares (PLS) pattern recognition technique was used to create quantitative model for each investigated treatment unit (Gardner, 1991).

Results and discussion

OEC characterization with odour concentration determined by dynamic olfactometry

Fig. 2 shows the odour concentrations detected by dynamic olfactometry for all collected wastewater samples at the investigated treatment units (O1, O2, O3) at different sampling time (2, 10, 20, 30, 40 min) over the OEC stripping tests. Results show that all analyzed samples of the investigated units fell below the lower limit of 100 OU/m^3 after 30 minute. The highest concentrations to the respective measurement times were detected for the oxidation unit (O3), while the lowest were determined for the wastewater influent (O1).

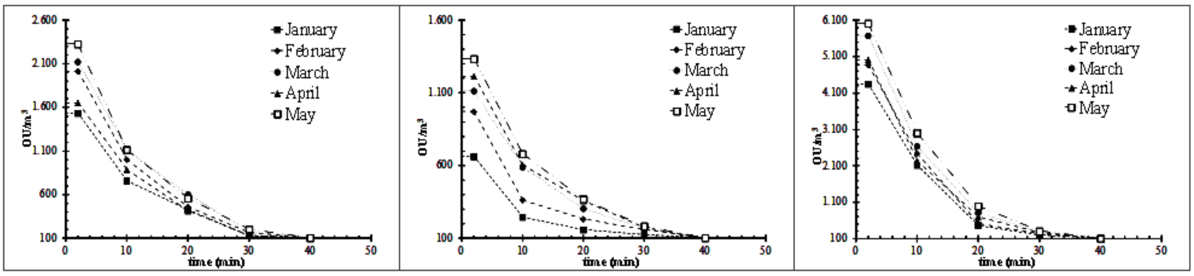

Fig. 2. Results of the odour concentration detected by dynamic olfactometry analysis of the samples collected at the investigated units (O1 (left), O2 (centre) and O3 (right)) out over the OEC stripping test

Values of odour emission capacity (OEC) measured according to Frechen and Köster (1998) method are summarized in Table 1. Results show that the higher average value of the OEC in the monitored period was detected for the unit O3 (18.324 OU/m$^3_{\text{liquid}}$), while the lowest value was determinate for the unit O2 (3.737 OU/m$^3_{\text{liquid}}$).

During the time, in May were detected the highest values of OEC for all the investigated units. The highest change in percentage, between the OEC values was recorded for the sedimentation (O2 unit), with a variation of 248% from the minimum to the maximum value.

Table 1. OEC characterization of the investigated treatment units according Frechen et al. 1998 procedure

Investigated treatment units	***Sample***				
	January	***February***	***March***	***April***	***May***
	OEC (OU/m$^3_{\text{liquid}}$)				
O1	5.759	7.573	8.884	6.376	9.034
O2	1.517	2.840	4.299	4.753	5.275
O3	14.534	16.781	20.133	17.221	22.953

Odour quantitative model creation

Fig. 3 shows the scatter plot of the odour concentrations measured during the OEC stripping tests by dynamic olfactometry according to EN13725:2003, and predicted with the seedOA applying the PLS models obtained for the each treatment unit investigated.

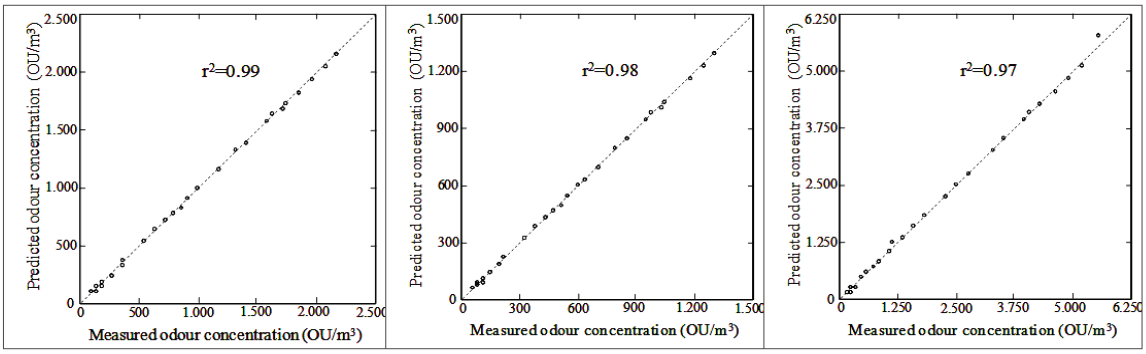

Fig. 3. Scatter plot of odour concentration for O1 (left), O2 (centre) and O3 (right)

Results show for all three calculated PLS models a good linear regression with very high level of confidence, respectively equal to 0.99, 0.98 and 0.97 for O1, O2, and O3. These results confirm the high performance of seedOA to measure the odour concentrations at the WWTP.

Validation of OEC measurements by multisensor array system

Fig. 4 shows the OEC calculation for the last samples taken in June. In detail, the comparison between the odour concentrations measured at different striping time by dynamic olfactometry analyses versus the odour concentration predicted by seedOA applying the PLS models were shown. The results show that there is a good fit between the predicted and measured values.

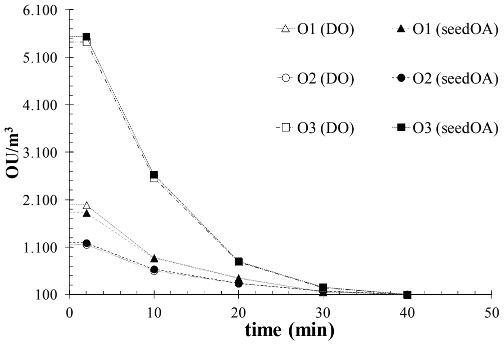

Fig. 4. Comparison of predicted and measured odor concentrations during the OEC stripping test.

Table 2 shows the OEC values calculated using the odour concentration measured by both dynamic olfactometry (DO) and seedOA.

The results suggest that the new method can be considered highly reliable since there is almost no difference in terms of OEC values (i.e. < 5%) between the responses of the two presented tools.

Table 2. Comparison between OEC measured by dynamic olfactometry and predicted by multisensor array system (seedOA).

Investigated treatment units	**Sample**		
	DO	**seedOA**	**spread**
	OEC (OU/m$^3_{liquid}$)		(%)
O1	7.008	6.764	3,6
O2	4.588	4.823	4,9
O3	19.311	19.804	2,5

Concluding remarks

The comparison of OEC values measured by dynamic olfactometry and predicted by multisensor array system (seedOA) have shown a minimum margin of difference, ever lower than 5%.

The use of multisensor array system in the determination of OEC reduces drastically the costs and the time of analyses, making real and sustainable it use in the management of odour emission in wastewater treatment plants.

Further studies will improve the use of the seedOA for direct and continuous analysis on site making possible a constant monitoring of potential odour emissions.

Keywords: dynamic olfactometry, e.noses, multisensor array system, odour emission capacity (OEC), wastewater.

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AN EXPLORATION OF DATA DRIVEN MODELS FOR ODOR ASSESSMENT

Extended abstract

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Background

Odor perception, occurring in correspondence of single inspiration acts, is characterized by a time scale in the order of 12 seconds (Schauberger et al., 2012). Ideally, modeling odor concentration should then be made on a comparable time frame. The concentration of odor-carrying compounds may change significantly over such a short period, often exhibiting intermittency (Hildeman and Wilson, 1999) and other complex features (Nicell, 2009).

Conventional dispersion models and the meteorological data feeding them are not typically able to resolve so a short range, their long term (most often hourly) averaging actually filtering most interesting variation out (Nicell, 2009; Scauberger et al., 2012). To circumvent this problem various strategies have been developed, as for example using probabilistic models allowing estimation of concentration distribution instead of just hourly means (e.g. SciPuff, online at http://www.sage-mgt.net/services/modeling-and-simulation/scipuff-dispersion-model, and coupled particles models), or adopting an estimate of maximum concentration from its hourly value using peak-to-mean ratio (Nicell, 2009; Schauberger et al., 2012).

In this work an alternative model, developed by the authors, has been explored. It is based on a modified version of Lagrangian particle models in which frequently updated measured statistics replace estimates based on similarity theory. Further work is in progress and will be addressed in a more extensive paper, currently under preparation. In conventional Lagrangian particle models like Flexpart (Stohl et al., 2005) wind statistics are modeled by particular solutions of Langevin-type equations, usually derived under the assumption of a time scale significantly longer than typical Lagrangian decorrelation time (e.g. hourly). These solutions, characterized by quite a simple analytical form, are well suited to estimating hourly concentration, but tend to not provide detailed information about instantaneous concentrations.

Therefore a need exists of a different approach to modeling, in which short time frame is explicitly considered. In this exploration, a particle model has been used in which Langevin-type equation has been replaced with empirical multivariate distributions obtained from high-frequency 3D wind measurements by a three-axial ultrasonic anemometer. This approach, suitable for efficient implementation, has the potential of real-time operation on small-scale, easy to deploy computing devices. The new class of models built this way has been provisionally named of data-driven models. The specific data-driven model used in our exploration is named NanoPart.

Methods

The general Langevin equation for transport and diffusion is (Eq 1):

$$dv_{ti} = a_i\left(x, v_i, t\right) \cdot dt + b_{ij}\left(x, v_i, t\right) \cdot dW_j \qquad (1)$$

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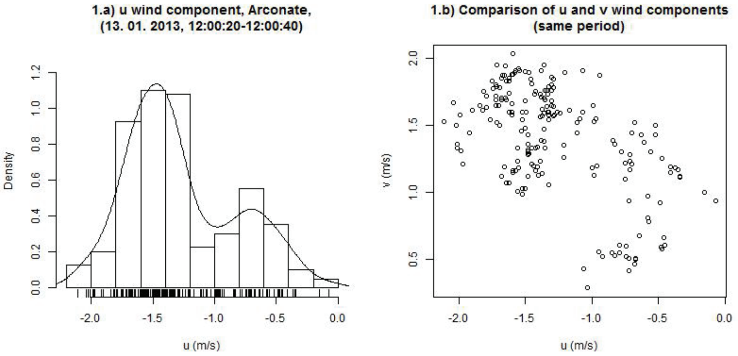
where: $\mathbf{x}, \mathbf{v}_i$ are the position and velocity, respectively, and $dW_j, j = 1,2,3$ are the components of a Wiener process with zero mean and unit standard deviation.

Eq.1, of generic type, is not directly suitable for use in particle dispersion models, and is used as a basis to derive application-specific analytical forms. For example, in FLEXPART eq.1 is simplified to a set of three independent equations for du, dv, dw. The equation for vertical wind component is (Eq. 2):

$$\mathrm{dw} = -\mathrm{w}\frac{\mathrm{dt}}{\tau_{\mathrm{L_w}}}\frac{\partial\sigma_{\mathrm{w}}^2}{\partial \mathrm{z}}\mathrm{dt} + \frac{\sigma_{\mathrm{w}}^2}{\rho}\frac{\partial\rho}{\partial \mathrm{z}}\mathrm{dt} + \left(\frac{2}{\tau_{\mathrm{L_w}}}\right)^{1/2}\sigma_{\mathrm{w}}\mathrm{dW} \tag{2}$$

where: dW is a Wiener process of mean 0, τ_{L_w} is the Lagrangian decorrelation time along *z* axis, ρ is air density, σ_w the standard deviation of vertical wind component. Eq. 2 represents a special case of Eq. 1, in which all the involved quantities can be directly measured or estimated through similarity theory. This allows using (Eq. 2) (and similar relations for horizontal components) as a device for generating random wind values whose values can then be imparted to pollutant "particles", simulating transport and turbulent diffusion.

Equations like (Eq. 2), derived under the assumption $dt >> \tau_{L_w}$, imply that probability distribution is normal for all wind components, and wind components are pair-wise uncorrelated. These two statements are approximations to reality, valid if a scale much longer than Lagrangian decorrelation time is used. If $dt \le \tau_{L_w}$, then neither normality nor lack of correlation hold, an example on real data is given in Fig. 1.a and 1.b.


1.a) u wind component, Arconate, (13. 01. 2013, 12:00:20-12:00:40)

1.b) Comparison of u and v wind components (same period)

Fig. 1. Example of wind non-normality and correlation in short-term (20s) time frame

In data-driven models Eq1 is replaced by (eq. 3)

$$\mathrm{x_p}(\mathrm{t} + \mathrm{dt}) = \mathrm{x_p}(\mathrm{t}) + \mathrm{V}(\mathrm{t}) \cdot \mathrm{dt} \tag{3}$$

where: $\mathbf{x}_p(t)$ represents particle position at time *t*, and $\mathbf{V}(t)$ is a random variable whose statistical distribution (of unspecified analytical form) coincides with the multivariate distribution of wind components as determined by experimental measurements. To apply Eq. (3) in a data-driven model, random values should be generated from the instantaneous distribution of wind components, $F(\mathbf{v},t)$. As this distribution is not constricted to a specific analytical form, its estimation $\hat{F}(\mathbf{v},t)$ is made from the set of wind data sampled from $t - \Delta t$ to t (Eq.4),

$$S_{\Delta t}(t) = \{\mathbf{v}_k | t - \Delta t \le t_0 + k \cdot \delta t \le t\} \tag{4}$$

where: Δt is a user-selected time sequence duration (typically in the order of τ_{L_w}), δt is the anemometer's sampling rate, and t_0 a reference time.

In principle the estimate may be computed in different ways. For example, the joint frequency distribution could be approximated using a continuous function (like for example a "gamma estimate" or a combination of B-splines), and random values $\hat{\mathbf{v}}_j$ extracted from it by means of one of the many existing algorithms. In this work, an *implicit* method is preferred, in which random values $\hat{\mathbf{v}}_j$ are obtained by sampling with repetition from the measurements data belonging to $S_{\Delta t}(t)$. If the number of elementary wind data in $S_{\Delta t}(t)$, $N = \left\lfloor \frac{\Delta t}{\delta t} \right\rfloor$, and the number of random values are sufficiently large so that the joint frequency function of the values approximates the original wind distribution, at a fraction of the computational cost. The ability to reproduce the short time-scale distribution of wind, including its non-normality and correlation structure, without heavy assumptions permits data-driven models to address situations like odor assessment, accidental toxic releases, defense and civil protection.

In analogy to conventional particle models, in data-driven models the wind values $\hat{\mathbf{v}}_j$ are fed into (Eq. 3) and use relation (Eq. 5) to update particle positions:

$$\mathbf{x}_j^{i+1} = \mathbf{x}_j^i + \hat{\mathbf{v}}_j \cdot \tau \tag{5}$$

where index j spans the set of particles existing at time $t_i = t_0 + (i-1)\cdot\tau$, and τ is particle release time. If τ is small enough, many concentration "snapshots" can be computed on each hour, in number sufficient to compute both mean and standard deviation, and potentially to determine point-wise non-parametric estimates of concentration distribution.

Finite particle life time is modeled through the combination of a maximum particle time span T and an exponential decay function $M(a) = M_0 \exp(-\beta a)$, being a the particle age, and different values of β coefficient account for different chemical species. The final model output is a sequence of ground concentration fields. These may be estimated in two ways, selected by the user. The first method counts the N_p particles contained in a box with basis centered at a receptor $\mathbf{x}$ and with edges of length Δx, Δy and Δz. Concentration is expressed as (Eq. 6):

$$C(\mathbf{x}) = \frac{1}{\Delta x \Delta y \Delta z} \sum_{k=1}^{N_p} M_k(a_k). \tag{6}$$

where: $M_k(a_k)$ represents the mass of k-th particle, and the sum is restricted to particles belonging to the box. In the second method each particle is represented as a Gaussian distribution

$$\mathrm{C_p(x)} = \frac{\mathrm{M_k(a_k)}}{\sqrt{(2\pi)^3}\,\sigma_x\sigma_y\sigma_z} \exp\left\{-\left[\frac{(x_p - x)^2}{2\sigma_x^2} + \frac{(y_p - y)^2}{2\sigma_y^2} + \frac{(z_p - z)^2 + (z_p + z)^2}{2\sigma_z^2}\right]\right\} \tag{7}$$

where: $\mathbf{x}_p$ represents the particle position, and $\sigma_x^2, \sigma_y^2, \sigma_z^2$ are estimated from measured wind component standard deviations and Lagrangian decorrelation times. Final concentration at a point is then estimated as

$$C(\mathbf{x}) = \sum_p C_p(\mathbf{x}). \tag{8}$$

where: the sum extends to the whole particle set.

Results and discussion

Fig. 2 shows the distribution of particles obtained from running the NanoPart model on a test case characterized by wind meandering. The particle survival time has been fixed to 7200s, with 10 particles emitted every second from the only point source placed at origin with a zero initial speed and at ambient temperature, so that buoyancy can be excluded; Δt was assumed to be 20s, and ultrasonic anemometer data rate set to 10Hz.

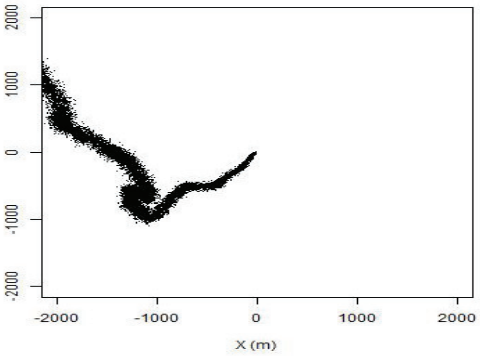


Fig. 2. Example of NanoPart particle distribution, at instant 03:31:45 from simulation start

Respect to the cloud of points typically visible using conventional particle models, Fig. 2 shows a defined plume advecting and widening due to turbulence, with meandering effects clearly visible. Other advantages of data-driven models include extreme simplicity (the Fortran 2003 code used to generate the data presented in Fig. 2 is 609 lines long, comments and spaces included), computational efficiency (especially if implicit estimation of wind joint frequency function is used), and possibility of real-time implementation.

Concluding remarks

For a Fig. 2 like to be meaningful, wind measurements in $S_{\Delta t}(t)$ must contain detailed information about turbulent fluctuations. This virtually rules out mechanical anemometers, whose inertial low-pass filtering and vulnerability to wind calms cut essential information away. Ultrasonic anemometers or other fast and accurate advanced sensors have then to be used to feed data-driven models. As the vertical wind must be considered, too, three-dimensional instruments are needed.

In addition to the need of advanced anemometers, data-driven models have shown some points susceptible of possible improvement. Among them are worth mentioning the modeling of wind distribution change with position, and the possibility of an optimal selection of Δt.

Next planned developments include validation campaigns made using non-reactive tracers, mean and standard deviation comparison with prediction of existing probabilistic dispersion models, and the realization of an integrated data acquisition and real time modeling for field use.

Keywords: dispersion models, odor assessment, pollutant instantaneous concentrations, ultrasonic anemometer

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A NOVEL APPROACH FOR ODOUR REGULATION BASED ON "BUFFER ZONE" CRITERION

Extended abstract

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Background

Odours produced by anthropic sources represent a complex issue to face because they directly affects both the environmental and human quality. In fact, the proximity of industrial plants and farms, very often source of bad odours, to residential zones, really limits the acceptability of such activities and leads to citizen's complaints (Nicell, 2009). Furthermore, odours strongly affect people's daily life and health, as, although they do not represent a risk for human health, smells could cause both physiological symptoms (respiratory problems, nausea, headache) and psychological stress (Schiffman, 1998).

Odour emission monitoring and its regulation are characterized by a great complexity due principally to the strict association of odour pollution to human perception. For this reason, odour emission control can not be rigorously equalled to air quality monitoring and different legislative approaches have been applied for preserving air quality from industrial odour emissions.

Objectives

The aim of this work is to provide a description of a novel approach for the regulation, developed in Puglia Region, located in the South of Italy. The main purpose is to present the innovative aspect of this regulation, based on a "buffer zone" criterion, compared to the most widely applied at international level.

Outline of the work

This work is divided in two main parts:

- The first part discusses the state of the art of the legislative approaches used in international regulation and in national one. This part provides the necessary background for understanding the complexity in regulating of odour emissions from industrial plants and for underlining the lack of a unique approach for this matter.
- The second part is dedicated to the development of the innovative methodology, applied in a region of the South of Italy, Puglia region. It describes the principal features of the regulation, providing examples of applications.

Methods

The odour emission regulation generally considers two main aspects:

- emissions, expressed as the odour concentration released by a particular source. In this case, two approaches have been adopted by the legislations of the different countries, establishing precise limits for the whole odour mixture and/or for single chemical compounds. In the first case, the odour concentration is expressed in odour units

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(ou/m^3) and detected through dynamic olfactometry (CEN, 2003). In the second one, only the concentrations of specific compounds are set, expressed in typical mass/volume units. Such odour limits are related with compounds that have a typical odorous impact (e.g., ammonia, hydrogen sulphide, methyl mercaptans) (Nicell, 2009). Because of the wide range of odour industrial processes and sources (punctual or active/passive areal sources), the prescriptive limits for the odour mixtures usually refer to specific sources (above all punctual or active areal sources) and to precise plants (above all composting plants). For instance, in Austria and in the Netherlands, there are guidelines fixing limits to the emissions from livestock productions (Schauberger et al., 1997; VROM, 2006); in France, limits to the odour emissions from composting plants have been recently fixed by the Arrêté 22/04/2008 (JORF, 2008). In other cases, guidelines are horizontal, i.e. they apply to all the activities that may potentially represent a cause of odour nuisance. Examples there are given by the guidelines in Germany (GIRL, 2008) or in the UK (UK-Environmental-Agency, 2002).

- odour impact criteria, defined as odour concentration limits considered acceptable for avoiding odour annoyance at receptors. They are typically expressed in terms of a concentration (i.e., in ou/m^3) considering an averaging time and a frequency of exposure (e.g., 98th percentile of hourly average concentrations in one year). This aspect is generally attained by means of decision making support tools and, in particular, of dispersion models that estimate the downwind concentration according to emission rates, meteorological parameters, that affect the transport and the diffusion of the pollutants, and topography of the site. More in detail, the guidelines of the UK, Netherlands and France provide to simulate the odour concentration on the territory by dispersion modelling, and give limits expressed in terms of 98th percentile, on an yearly basis, of the peak odour concentration values.

In the last years, the trend in legislative approaches is to avoid to fix limits at emission sources and to consider acceptability criteria at receptors (immissions). This last aspect is more complicated to realize, compared with the emissions control, for which reproducible measurement techniques exist. This requires the definition of the simulation procedures, which allow to estimate ground concentration levels (e.g., dispersion model, quality of input data) based on the measured emission data, in a detailed manner, in order to produce reliable and reproducible results.

In Italy there is no national legislation disciplining odour emissions. This lack has led some Italian regions to adopt regulatory measures and guidelines, specifically for odours, useful to support their control activities. The first odour emission limits were fixed by the Region of Lombardia and applied to composting plants ("Guidance for the construction and operation of compost-producing plants" (D.G.R.n.7/12764, 2003)). This limit provided a maximum odour concentration at the outlet of treatment systems at 300 ou$_E$/m^3, as measured by dynamic olfactometry. Later, other Italian regions like Sicilia (Sicilia-Ordinanza-Commissariale, 2002), Abruzzo (D.G.R.n.400, 2004) prepared similar directives with the same emission limits for composting plants. This approach showed some drawbacks in its application; the most important being that the prescribed limit was applied not only to treatment systems in composting plants, but indiscriminately to any other industrial plant and source. For this reason, Regione Lombardia (D.G.R.n.IX/3018, 2012) has recently published a legislative act, fixing no more emission limits but evaluating the odour impact at receptors through the use of dispersion models. Emilia Romagna Region (D.G.Rn.1495, 2011) has recently published a regulatory act setting a limit for digester plants producing biogas equal to 400 ou$_E$/m^3 and 5 mg/m^3 for ammonia.

In Puglia Region, a specific regional law was adopted for the point emissions of olive residues treatment plants (L.R.7/99, 1999). In this case, two different emission limits are fixed (in parts per million) distinguishing the substances according to their odour thresholds. This approach is hardly applicable because of the lack of unambiguous values of odour thresholds reported in literature for several substances. So, consistent with the actual trend in regulation, an innovative methodological approach for an odour guideline has been developed in this region with the purpose of defining acceptability and monitoring criteria for odour emissions. The present methodology suggests a coupling between a predictive approach, based on dispersion models, and a systematic approach to carry out the monitoring and the control through reliable methodologies.

Results and discussion

The focus of the proposal consists in the implementation of two approaches for the authorization of odour emissions (Brattoli et al., 2011):

- assessment of acceptability criteria using predictive methods. Similarly to international approach, it employs the use of mathematical models to predict the downwind odour concentrations at receptors on the basis of odour emission rates, topography and meteorological data referred to a selected period of time. Such models aim to determine whether the estimated emissions at sensitive receptors are in compliance with ambient air quality criteria, considered acceptable for the exposure of the population. These criteria can be defined on the basis of several parameters, such as: presence of sensitive receptors; distance between the plant and sensitive receptors; land use (residential, commercial, agricultural, industrial); existing or new plants; distribution of concentration values expressed as percentiles; averaged time considered for simulations.
- the buffer zone approach. The buffer zone identifies an area around the plant boundaries, outside of which a prescriptive limit, expressed in odour units and detectable through dynamic olfactometry, must never be exceeded. The buffer zone can have a more or less regular shape, individuated according to the predominant wind directions,

the presence of receptors and the geographic location. The buffer zone extension can be defined using dispersion models based on the meteorological scenarios that have determined the worst odour dispersion conditions in a defined period of time. These scenarios have to be described so that a possible exceeding, determined by a meteorological situation worse than those previously considered, could be permitted. If the prescriptive limit is fulfilled inside the plant boundaries, the buffer zone overlaps with the plant perimeter.

For better understanding the meaning of the buffer zone criterion, Fig. 1 and Fig. 2 explain how the buffer zone is defined according to the worst scenarios. For example, if the prescriptive limit, called Z, is equal to 50 ou/m^3, the buffer zone might comprehend the area where 50 ou/m^3 are overcome in the worst meteorological conditions. In Fig. 1 (case 1) the buffer zone is outside the plant perimeter, while in Fig. 2 (case 2) overlaps with it. In this last case, the Z value must be applied and verified at the plant perimeter.

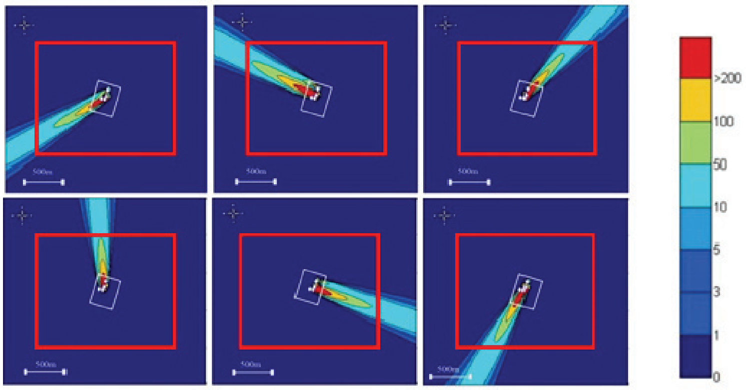

Fig. 1. Maps illustrating the individuation of the buffer zone considering the worst odour dispersion conditions for a landfill (case 1). The white rectangle delimits the plant perimeter while the red one individuates the buffer zone perimeter; the white points are the odour sources. In all maps, the buffer zone is defined on the bases of the isoline of 50 ou/m^3.

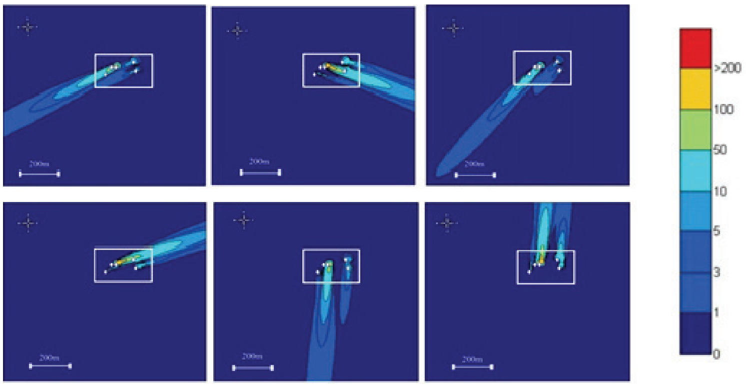

Fig. 2. Maps illustrating the individuation of the buffer zone considering the worst odour dispersion conditions for a landfill (case 2). The white rectangle delimits the plant perimeter; the white points are the odour sources. In all maps, since the isoline of 50 ou/m^3 falls within the plant perimeter, the buffer zone overlaps with the plant boundaries.

The definition of a buffer zone is a valid approach particularly for landfills that present areal emissions, usually located in ground-line; in fact, in this type of emissions the odour concentration decreases moving away from the sources. For this purpose, a monitoring plan should be proposed and verified. A greater extension for the buffer zone means more strict prescription for the plant in order to control its productive process; in fact the implementation of continuous monitoring systems can be planned in relation to the extension of the buffer zone and the presence of receptors inside, or near it. According to the different conditions, these systems can be located at the receptors and/or at the boundaries of the buffer zone and of the plant. It could be considered as adequate continuous monitoring systems, instruments that provide signals that have to be correlated with dynamic olfactometry data for the specific plant (e.g. electronic noses, sensors, conventional analyzers, sulfur compound analyzer).

In particularly complex cases, such as co-presence of other significant odour sources, this evaluation could be executed through chemical characterization of ambient air samples.

Concluding remarks

In this paper, a focus on the main legislative approaches for odour emission control is presented. In particular, it describes a methodological approach developed in an Italian region, in which the guideline integrates a predictive approach based on dispersion models and a systematic approach to carry out the monitoring and the

control. The novelty of the proposal is represented by the introduction of a buffer zone, that is a “respect area”, individuated by means of dispersion models, in which prescriptive limits have to be fulfilled and verified by standard measurement methodologies. In addition, the odour guideline endorses to perform a process control for particularly impactful plants, realized through continuous monitoring systems.

Keywords: buffer zone, dispersion models, dynamic olfactometry, odour regulation, process control.

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ODOUR IMPACT ASSESSMENT IN THE INDUSTRIAL AREA OF NARNI

Extended abstract

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Background

Most of biogas is produced during anaerobic digestion of organic matter (e.g., manure, vegetable wastes, municipal solid In the last 30 years odours have become a serious environmental concern, and odour nuisance problems are particularly worrying when more industrial activities exist near residential areas (Nicell, 2009). Odour nuisance problems are particularly worrying when more industrial activities exist near residential areas. One example of this situation is represented by the town of Narni (ca. 20'000 inhabitants), located in the Region of Umbria, in central Italy. Narni is a medieval town rising on a hill, at the foot of which there is a huge industrial area, which can be divided into two distinct industrial poles: one located in Narni Scalo, and the other one between Nera Montoro and San Liberato, both poles including several plants characterized by different activities and productions (Fig. 1).

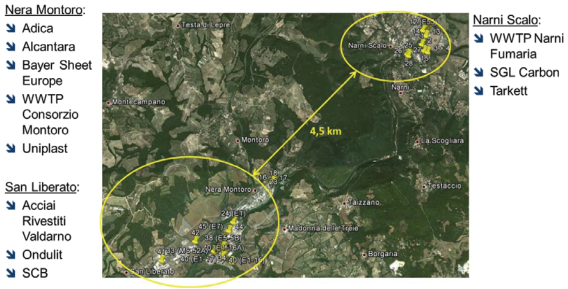

Fig. 1. Localization of the industrial poles and the considered odour sources

In order to evaluate the entity of the problem and to investigate its origins, an odour impact study was conducted, meaning the identification of the principal odour sources of the three industrial poles of the city, the quantification of emissions by specific techniques for odour sampling and measurement (dynamic olfactometry) and the simulation of the dispersion of odour emissions on the territory by application of a suitable mathematical model.

Methods

The first important step for odour impact evaluation is the identification of the major odour sources to be monitored, which was achieved with an accurate survey of the industrial poles under study. 35 emission sources distributed over 11 plants (8 in the industrial pole of Nera Montoro/San Liberato and 3 in that one of Narni Scalo) were identified. These include point sources, i.e. conveyed emissions, e.g. through a stack, as well as area sources, i.e. liquid or solid surfaces without an outward flow. The source typology must be taken into account in order to adopt specific sampling strategies and consequently to evaluate emissions correctly (Capelli et al., 2013). In the case of point sources, sampling involves the withdrawal of a fraction of the conveyed air flow In the case of passive area sources (e.g., wastewater treatment tanks), sampling is performed using so called "hood" methods, whereby a hood is positioned over the emitting surface and a neutral air stream is introduced at known airflow rate into the hood, thus

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simulating the wind action on the liquid or solid surface to be monitored. In this specific case, sampling on passive area sources was conducted using a neutral air stream from a synthetic air bottle, resulting in an air velocity inside the central body of the hood of 0.035 m s^{-1} (Capelli et al., 2009).

Odour samples were collected on all the identified potential odour sources. The sampling operations were performed on Monday, 16th July 2012 and Tuesday, 17th July 2012. The samples were then analysed by dynamic olfactometry for the determination of the odour concentration within the time interval of 30 hours allowed by the European Standard EN 13725:2003. Dynamic olfactometry is a sensorial technique, i.e. a technique that uses the human nose as a sensor, which is most commonly used for odour measurement. Dynamic olfactometry allows the determination of the odour concentration (c_{od}) of an odorous air sample, which is expressed in European odour units per cubic metre (ou_E m^{-3}), and represents the number of dilutions with neutral air needed to bring the sample to its odour detection threshold concentration (CEN, 2003). The analysis is carried out by presenting the sample to a selected panel at increasing concentrations by means of a particular dilution device called olfactometer, until the panel members start perceiving an odour that is identified to be different from the neutral reference air. The cod is then calculated as the geometric mean of the odour threshold values of each panellist.

An olfactometer model TO8 produced by ECOMA GmbH, based on the “yes/no” method, was used as a dilution device. This instrument with aluminium casing has 4 panellist places in separate open boxes. Each box is equipped with a sniffing port in stainless steel and glass, and a push-button for “yes” (odour threshold). The measuring range of the TO8 olfactometer starts from a maximum dilution ratio of 1:65536, with a dilution step factor 2. All the measurements were conducted within 30 h after sampling, relying on a panel composed of 4 panellists. The panellists were selected based on their individual threshold towards a reference gas (n-butanol in nitrogen) and on the standard deviation of their responses, in conformity with the requirements of the European Standard for dynamic olfactometry (CEN, 2003). In general, in order to characterize an odour emission, it is necessary to determine the so called “Odour Emission Rate” (OER) associated with each odour source, which is measured in ou_E s^{-1}. In the case of point sources, the OER can be calculated simply by multiplying the odour concentration value (in ou_E m^{-3}) by the air flow (in m^3 s^{-1}), normalized at 20°C, which is the reference temperature according to the EN 13725:2003. The evaluation of the OER relevant to area sources, e.g. wastewater treatment tanks, requires the calculation of the Specific Odour Emission Rate (SOER), which is expressed in ou_E s^{-1} m^{-2}. The SOER is calculated as the product of the odour concentration (ou_E m^{-3}) and the flow rate of the neutral air introduced into the sampling hood (m^3 s^{-1}), divided by the base area of the hood (m^2). The OER is finally obtained as the product of the SOER value and the emitting surface of the considered source (m^2) (Capelli et al., 2013). Based on its definition, the OER of an area source is a function of the air velocity, i.e. the wind speed, on the emitting surface. Once the OER relevant to the sampling conditions (i.e. air velocity) is evaluated (OER_1, v_1), the OER for any other air velocity (OER_2, v_2) can be calculated using Eq. (1) (Capelli et al., 2009):

$$OER_{v2} = OER_{v1}\left(v_2/v_1\right)^{0.5} \tag{1}$$

The OER values are used as input data for the dispersion model, together with other information regarding the emission sources, such as geographical coordinates, height, geometry and operating times. The model used is the CALPUFF model, a non-stationary puff atmospheric dispersion model, which is proved to be effective for the simulation of the dispersion of odours (Sironi et al., 2010). Given the distance, and the different geographical and terrain characteristics of the two studied poles (i.e., Narni Scalo and Nera Montoro/ San Liberato), for the purpose of odour emission dispersion, the two poles must be considered separately, thus applying two distinct models, each using suitable input data. Besides emission data, the model also needs other input data: orographical and meteorological data.

As far as orography is concerned, the dimensions of both receptor grids on the simulation domain are 4000 m x 4000 m, with a receptor point every 100 m. The dimensions of the simulation domains were chosen in order to include the whole industrial of Narni Scalo in one case, and the industrial areas of Nera Montoro and San Liberato in the other case. All orographical data were extrapolated from Google Earth. The meteorological data used for the simulation are the data registered over a complete year (from the 1st September 2011 to the 31st August 2012) from two different meteorological stations: one located at 42°33’56’’ North and 12°38’50’’ East (Narni Scalo) and the other one at 42°28'52" North and 12°27'52" East (Nera Montoro/ San Liberato). By means of a specific pre-processor, the micrometeorological variables such as the surface heat flux, the friction velocity, the Monin-Obukhov length, the convective velocity scale and the mixing height were calculated. The emission data for the simulation are based on the results of the olfactometric analyses. As already mentioned, in order to characterize an odour source, the OER, expressed in ou_E s^{-1}, must be evaluated. It is worth to highlight that, as the OER from area sources is a function of the wind speed over the emitting surface, the OERs relevant to area sources are calculated for each hour of the simulation domain based on the current wind speed, according to Eq. (1).

As output, the model calculates the hourly mean odour concentration for each receptor of the simulation grid and for each hour of the simulation period. The peak odour concentration can be obtained by multiplying the hourly mean odour concentration by a coefficient called peak-to-mean ratio. The peak-to-mean ratio could theoretically be evaluated as a function of wind velocity, stability and distance from the source (Shauberger and Piringer, 2012). In this case, the peak-to-mean ratio was set equal to 2.3, according to the indications of the regional guideline about the characterization and authorization of gaseous emissions from odour emitting activities, which has recently (2012) been issued in the Region of Lombardia, and is already used as a reference all over Italy (DGR 15 February 2012 – n. IX/3018). Also the choice of how to represent the modelling results should be based on current regulations about odour impact evaluation. According to the above mentioned regional guideline, which suggests the 98th percentile methodology for odour impact evaluation, the 98th percentiles were extracted from the matrix of the ground peak odour concentration values. The results of the odour dispersion simulation are therefore represented in maps reporting the isopleths relevant to the 98th percentile of the hourly peak concentrations.

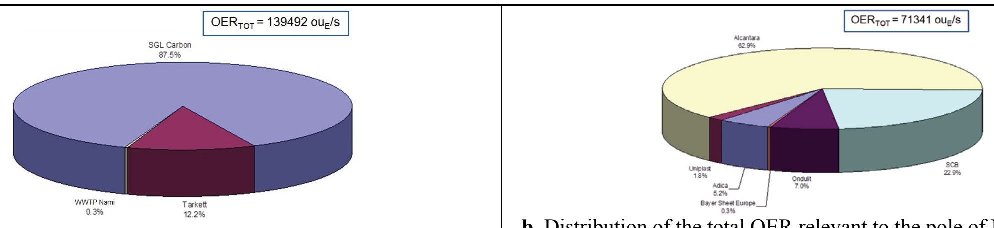
Results and discussion

The measured odour concentrations and the OER values for each source, expressed in ou_E m^{-3} and in ou_E s^{-1}, respectively, are reported in Table 1, together with a short description of the activity of the plant where the samples were collected. It is important to highlight that, as far as area sources are concerned, Table 1 reports the OER values referred to the sampling conditions, which correspond to an air velocity of 0.035 m s^{-1}, whereas for the dispersion modelling the OERs were calculated for each hour of the simulation domain based on the current wind speed.

Table 1. Odour concentrations and OER values relevant to the considered odour sources

Industrial area	*No.*	*Plant*	*Plant activity*	*Sample name*	*Type*	*c_{od} (ou_E/m^3)*	*OER (ou_E/s)*
Narni Scalo	2	SGL Carbon	Production of graphite electrodes	E202	PS	**810**	**1439**
	3-4	SGL Carbon		E25	PS	**885**	**120586**
	5	Tarkett	Linoleum production	E38	PS	**580**	**3583**
	6	Tarkett		E60	PS	**810**	**2167**
	7	Tarkett		E8	PS	**970**	**4285**
	8	Tarkett		E52	PS	**860**	**2089**
	9	Tarkett		E41	PS	**910**	**758**
	25	WWTP Narni Funaria	Wastewater treatment	Sludge storage	AS	**410**	**32**
	26	WWTP Narni Funaria		Biological oxidation	AS	**140**	**57**
	27	WWTP Narni Funaria		Sludge aerobic stabilization	AS	**150**	**132**
	28	WWTP Narni Funaria		Wastewater arrival	AS	**720**	**140**
Nera Montoro, San Liberato	17	Adica	Production of fertilizers and plant protection products	E 28	PS	**720**	**1600**
	20	Adica		E 30	PS	**770**	**1143**
	24	Uniplast	Production of plastic packing	E1	PS	**180**	**633**
	24	Uniplast		E2	PS	**180**	**636**
	29	Alcantara	Textile production (Alcantara®)	Sludge storage	AS	**19000**	**1583**
	30	Alcantara		S40-41-42	AS	**25000**	**26389**
	31	Alcantara		Sedimentation (MS50-41)	AS	**6500**	**6640**
	32	Alcantara		Biological treatment (S50)	AS	**290**	**434**
	33	Alcantara		MS52a	AS	**25000**	**7778**
	36	Alcantara		E4-15	PS	**170**	**950**
	40	Alcantara		E1-16a	PS	**200**	**552**
	41	SCB	Asphalt production	E3	PS	**44000**	**391856**

The overall odour emissions released into the atmosphere from each industrial pole (OER_{TOT}) was calculated as the sum of the OER values of all the odour sources being considered for each pole. The total OER relevant to the industrial poles of Narni Scalo and Nera Montoro/ San Liberato were estimated to be about 140,000 ou_E s^{-1} and 71,000 ou_E s^{-1}, respectively. The pie charts in **Error! Reference source not found.**a and Fig. 2b show the relative contribution of each plant to the total OER of the industrial pole.



a. Distribution of the total OER relevant to the pole of Narni Scalo among the considered odour sources

b. Distribution of the total OER relevant to the pole of Nera Montoro/ San Liberato among the considered odour sources

Fig. 2. Distribution of the total relevant OER among the considered odour sources

As far as the industrial pole of Narni Scalo is concerned, the plant that mostly contributes to the overall odour emissions is SGL Carbon, which produces graphite electrodes for steel plants, and accounts for 87.5% of the pole OER. This high OER is not due to the odour concentration of the effluents, but to the enormous flow rate of its main emission (stack named "E25"), which exceeds 450,000 m^3 h^{-1}. In the industrial pole of Nera Montoro/ San Liberato the plant that mostly contributes to the total OER is Alcantara (62.9%), followed by SCB (22.9%). It is important to highlight that this comparison is made considering just the odour concentrations and corresponding OER values measured at each source, without accounting for their effective functioning times. This consideration is particularly important in the case of SCB, which is a plant for the production of asphalt, which works discontinuously, for about 1 h a day. Of course, this has to be considered when simulating odour emission dispersion over a complete year. The results of the simulation of the odour emission dispersion relevant to the industrial poles of Narni Scalo and Nera

Montoro/ San Liberato are illustrated in Fig. 3. The maps report the isopleths of the 98th percentile, on an yearly basis, of the peak odour concentration values relevant to the three studied industrial poles, respectively, in a scale from 1 ou_E m^{-3} to 10 ou_E m^{-3}. The numbered bar in the upper part of the Fig.s indicates the odour concentration value in ambient air, in ou_E m^{-3}, which is constant on each isopleth. According to the definition of 98th percentile, these odour concentration values represent the odour concentration that is exceeded for 2% of the hours in a year.

Fig. 3. Map of the 98th percentile of the peak odour concentration values relevant to the emissions from the industrial pole of Narni Scalo (left) and the one of Nera Montoro/ San Liberato (right), in a scale from 1 ou_E m^{-3} to 10 ou_E m^{-3}

It is possible to observe that the odour impact relevant to the studied industrial pole is not negligible, especially in the case of the industrial pole of Nera Montoro/ San Liberato. In Narni Scalo, the major responsibles for the odour impact turned out to be Tarkett, i.e. the plant for the production of Linoleum, and the wastewater treatment plant. In Nera Montoro/ San Liberato, the major cause of odour impacts on the territory is represented by Alcantara, especially as far as its wastewater treatment tanks are considered. Also SCB turned out to have a not negligible impact, even though it is limited in time, given its low functioning frequency.

Despite the fact that, based on the olfactometric measurements results, the OER relevant to the industrial pole of Narni Scalo turned out to be twice the OER relevant to the industrial pole of Nera Montoro/ San Liberato (140,000 ou_E s^{-1} vs. 71,000 ou_E s^{-1}), the odour impact simulated by the model shows an opposite behaviour, i.e. the odour impact relevant to the industrial pole of Nera Montoro/ San Liberato is significantly higher than the one relevant to the industrial pole of Narni Scalo. The odour sources of the industrial pole of Narni Scalo, and especially those of SGL Carbon, having the highest OER, are the main point sources (high stacks). The main emission of SGL Carbon, which alone has an OER of over 120,000 ou_E s^{-1} is 130 m high, having an excellent dispersion capability, resulting in a negligible impact on the territory. On the contrary, the plant Alcantara located in the industrial pole of Nera Montoro/ San Liberato is characterized by the presence of odour sources with a poorer dispersion capacity, such as lower stacks (less than 20 m high). The modelled OERs are in general much higher than the OERs reported in Table 1, which are referred to the sampling conditions, i.e. to an air velocity of 0.035 m s^{-1}.

Concluding remarks

The combination of olfactometric analyses and dispersion modelling allowed the evaluation of citizens' exposure to industrial odours, resulting in both the quantification of emissions and the assessment of their impact on the territory. The overall odour emission rate (OER) relevant to the industrial pole of Narni Scalo was estimated to be equal to ca. 140000 ou_E s^{-1}, of which 87.5% deriving from a plant for the production of graphite electrodes for steel plants; whereas those relevant to the industrial pole Nera Montoro/ San Liberato was estimated to be equal to ca. 70000 ou_E s^{-1}, of which 63% deriving from a textile industry.

The simulation of the emission dispersion shows that the odour impact relevant to the industrial pole Nera Montoro/ San Liberato, despite its lower overall OER, is quite higher than the odour impact of the industrial pole of Narni Scalo. This difference is due to the different characteristics of the odour sources considered: the industrial pole of Narni Scalo is characterized mostly by the presence of point sources and high stacks, which provide a good dispersion of emissions. On the contrary, the higher odour impact relevant to the industrial pole Nera Montoro/ San Liberato may be attributed to the presence of several area sources at ground level, especially as far as the wastewater treatment plant of the textile industry is concerned, which are proven to have a very low dispersion capability.

Keywords: CALPUFF, dynamic olfactometry, odour concentration, odour dispersion modelling, odour emission rate

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ELECTRONIC NOSE FOR THE CONTINUOUS MEASUREMENT OF ODOUR CONCENTRATION AT EMISSIONS: INSTRUMENT DEVELOPMENT, TRAINING AND APPLICATION

Extended abstract

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Background

The presence of odour in ambient air is nowadays recognized as an environmental stressor that negatively affects the quality of life (Blanes-Vidal et al., 2012). In order to evaluate odour exposure at receptors, several methods can be applied. Different regulations provide to use dispersion modelling to simulate how odour disperses into the atmosphere, and consequently to calculate hourly ground odour concentration values in the simulation space-time domain (Cusano et al., 2010). Given that a detailed characterization of emissions over time would require frequently repeated olfactometric tests, thus resulting in a very expensive (in terms of money and time) approach, emission data employed as model inputs are usually represented by averaged odour emission rate values. This approach may provide a good description of the average odour impact, but doesn't take account of fluctuations that are typical of some emission typologies (Isaac-Ho Tin Noe et al., 2010). This study discusses the possibility of installing an electronic nose directly at an emission, in order to measure odour concentration continuously and therefore to obtain data that could be possibly used as real-time inputs for dispersion models as well as hourly data to use instead of averaged values. Such an application requires the development of a specific instrument, as well as a specific training. An EOS 507 electronic nose, developed in collaboration with Sacmi s.c. and Progress S.r.l., was used to evaluate the possibility to monitor the odour concentration at the emission of a plant for hospital waste treatment.

Laboratory tests were conducted to evaluate the electronic nose capability of quantifying odour concentration: samples containing pure compounds and mixtures were tested at different concentrations, as well as real samples collected directly from the odour source.

Methods

1. The EOS 507 electronic nose

The electronic nose used for this work is an EOS 507 (Dentoni et al., 2012).

The instrument has two inlets for air: one of them is connected with the system for the neutral air realization; the other one is connected with an electronic valve that regulates the sample flow that is sent to the sensor chamber, which contains 6 MOS sensors.

Moreover, the electronic nose is equipped with a temperature and humidity sensor. For the regulation of the sample humidity, the electronic nose regulates neutral air humidity to a certain value RH_{wk} that the software calculates from the external humidity value (RH_{ext}).

With the EOS 507, only one feature is calculated from the response of each sensor, defined as E.U. (EOS Unit). All measures are normalized using an internal standard consisting of n-butanol at a known and constant concentration and, as a consequence of this normalization, sensors responses in terms of E.U. should increase linearly with the concentration of the analyzed sample. The classification and quantification algorithm is a modified KNN-algorithm.

The electronic nose is trained with samples collected on the source to be monitored, diluted as to obtain samples at different concentrations. For sample recognition, the system compares the distance, in the 6-dimensional response space (6 sensors giving each 1 E.U. value), of the point relevant to the unknown measure to be classified and the broken lines between two neighbouring points belonging to the same olfactory class. The unknown measure is then classified as belonging to the olfactory class for which the minimum distance is measured. The odour concentration of the analysed sample is then calculated based on the odour concentrations of the points at the extremities of the segment, by evaluating the relative distance between the two points at known concentration and the position of the projection of the point representing the unknown measure.

2. Considered emission

The emission considered in this study is a chimney of a hospital waste treatment plant. More in detail, the chimney emits the air sucked from the grinder where the medical waste is first treated, as well as all the vents coming from the sterilization process. The plant operates with cycles and each cycle can be considered as composed by different phases. After collection, the medical waste is grinded and sent to a batch sterilizer. When the waste loading in the sterilizer is completed, the air inside the sterilizer is sucked by means of a pump and emitted through the chimney. After that, the sterilization process starts with the injection of steam. After 15-20 minutes, the sterilizer is vented, and this vent is emitted through the chimney, as well. The emission from the chimney is therefore variable. Based on the above described process, three different emissions typologies can identified: the air sucked from the grinder, the vent of the air sucked from the sterilization system before the steam injection and the vent after the sterilization process. Gaseous samples were collected at the emission during these three different phases, and then tested by dynamic olfactometry in order to evaluate their odour concentration. Moreover, chemical analyses were carried out in order to determine the chemical composition of the emission.

3. Tests with pure compounds

Pure compounds to be used for laboratory tests were chosen among compounds detected in the emission. More in detail, starting from chemical analysis results, and considering the odour threshold of each compound, the theoretical odour concentration related to each single compound in the emission was estimated. Laboratory tests were conducted using those chemical compounds having the major theoretical odour concentration in the emission: ethanol and ammonia.

Gaseous samples of each pure compound were analyzed with the electronic nose at different concentrations in order to train the electronic nose to estimate odour concentration. After the training phase, gaseous samples were analysed with the EOS 507, which estimated their odour concentration. Tests were performed using gaseous samples containing ammonia and ethanol separately, as well as mixtures of the two compounds. The odour concentration of analysed samples was in the range between 20 and 500 ou_E m^{-3}.

4.Tests with real samples

Different samples were collected at the emission during the 3 different phases of the process. All samples were analysed by dynamic olfactometry to determine their odour concentration. The electronic nose was trained with all real samples at different odour concentrations, between 10 and 100% of the measured odour concentration. The capability of the electronic nose to estimate the odour concentration of real samples was tested. For this purpose, different samples having different odour concentrations were obtained from collected real samples. Those samples were then analysed with EOS 507 and the estimated odour concentration registered. During the quantification process different training datasets were taken into account. First, for each odour typology, only the relevant training dataset was considered; second, a training dataset comprising all measures performed with the different odour typologies was created and used for odour quantification. The estimated and real odour concentrations were compared, to evaluate the performances of the instrument.

Results and discussion

1. Tests with pure compounds – results

Electronic nose responses to different odour concentrations of the different considered pure compounds were evaluated in order to verify the linearity between electronic nose responses (E.U.) and odour concentration. As an example, the electronic nose responses to different odour concentrations of a gaseous sample containing ethanol are reported in

Fig. **1**.

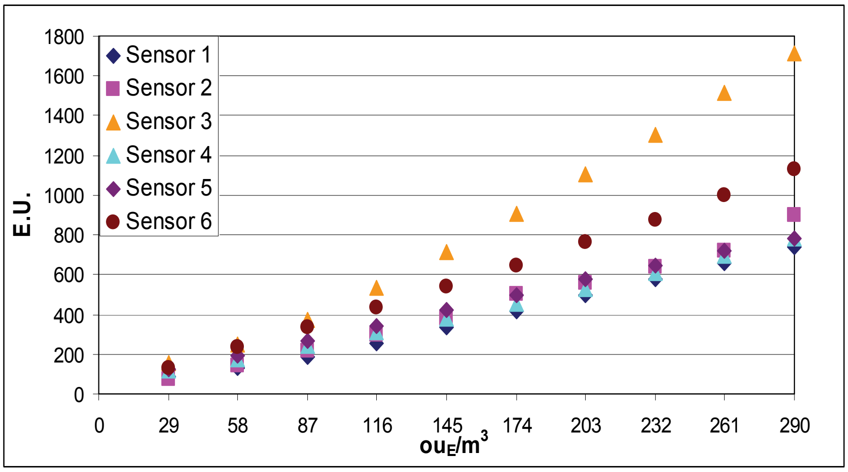


Fig. 1. E.U. registered for different odour concentrations of the ethanol sample

Some of the results of the odour concentration estimation performed by the electronic nose using the pure compounds are reported in Table 1.

In the table, the real and the estimated odour concentrations are listed; the error (per cent) of the concentration estimation is reported, as well.

Table 1. Real and estimated odour concentrations relevant to the tests with pure compounds

Tested Compound	***Real concentration [ou$_E$ m^{-3}]***	***Estimated concentration [ou$_E$ m^{-3}]***	***Error [%]***
Ethanol	145	150	3
Ethanol	145	149	3
Ethanol	290	255	12
Ethanol	290	255	12
Ethanol	290	283	2
Ethanol	290	275	5
Ethanol	580	593	2
Ammonia	82	99	21
Ammonia	164	141	14
Ammonia	246	208	15
Ammonia	328	301	8
Ammonia	411	417	1
Ammonia + Ethanol	62	70	13
Ammonia + Ethanol	125	118	6
Ammonia + Ethanol	187	194	4
Ammonia + Ethanol	249	260	4
Ammonia + Ethanol	312	306	2
Ammonia + Ethanol	124	120	3
Ammonia + Ethanol	187	193	3
Ammonia + Ethanol	312	314	1

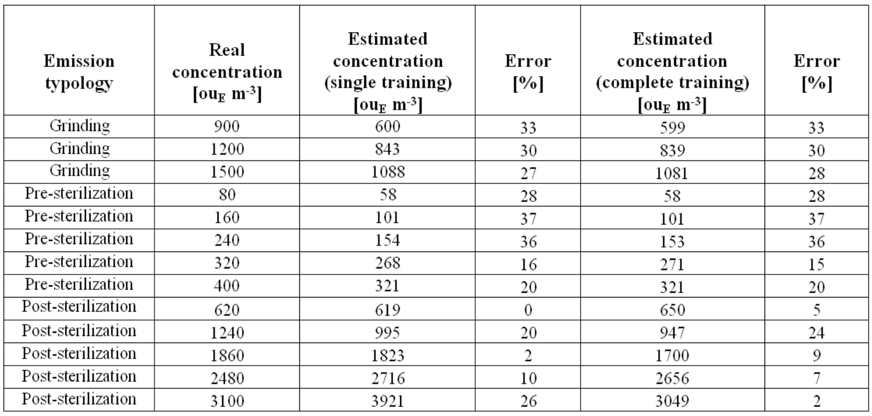
Odour concentrations estimated by the electronic nose are comparable with the real concentration evaluated by means of dynamic olfactometry, or obtained by diluting gaseous samples having a known odour concentration. The per cent error is comprised between 1 and 20 %, and the error decreases when the odour concentration increases.

2. Tests with real samples – results

Fig. 2 reports the results obtained with the real samples. More in detail, the real odour concentration, the odour concentration estimated using only the training data set of the same emission phase (single training dataset) and the odour concentration estimated using the complete training dataset are reported.

The electronic nose is able to estimate the odour concentration of real samples with an error between 2 and 37%. The quantification system guarantees the same performances both using the single training and the complete training. In general, it can be observed that the odour concentrations estimated by the electronic nose are almost always lower than the odour concentration measured by dynamic olfactometry.

This may be due to the losses through the sampling bags that may occur during the time interval between the two analyses (Hansen et al., 2011).



Emission typology	Real concentration [ou$_E$ m^{-3}]	Estimated concentration (single training) [ou$_E$ m^{-3}]	Error [%]	Estimated concentration (complete training) [ou$_E$ m^{-3}]	Error [%]
Grinding	900	600	33	599	33
Grinding	1200	843	30	839	30
Grinding	1500	1088	27	1081	28
Pre-sterilization	80	58	28	58	28
Pre-sterilization	160	101	37	101	37
Pre-sterilization	240	154	36	153	36
Pre-sterilization	320	268	16	271	15
Pre-sterilization	400	321	20	321	20
Post-sterilization	620	619	0	650	5
Post-sterilization	1240	995	20	947	24
Post-sterilization	1860	1823	2	1700	9
Post-sterilization	2480	2716	10	2656	7
Post-sterilization	3100	3921	26	3049	2

Fig. 2. Real and estimated odour concentrations relevant to the tests with real samples

Concluding remarks

Laboratory tests show that the EOS 507 is able to quantify the odour concentration of samples of pure compounds and of real samples.

The error obtained with pure compounds is comprised between 1 and 20%. The capability of the system to estimate the odour concentration turned out not to be influenced by the use of mixtures of different pure compounds in air instead of gaseous samples of pure compounds in air.

Tests performed with real samples demonstrate that the system is capable to estimate the odour concentration with the same accuracy using only a training dataset obtained with samples belonging to the same olfactory class as the sample to be quantified, as well as using a "complete" dataset, which contains data relevant to different olfactory classes. This of course is important information, meaning that the use of one single "complete" dataset will be sufficient in order to quantify the odour concentration of the monitored emission during all the phases within a satisfying level. The error relevant to the odour concentration estimation of real samples is comprised between 2 and 37%.

Laboratory tests proved the electronic nose EOS 507 to be able to quantify odour concentration with a error below 40%. Future studies will be carried out in order to verify the electronic nose performances directly in the field. Moreover, the instrument will be tested with different samples, collected on other odour sources, in order to evaluate its performances with different emissions.

Keywords: electronic nose, MOS sensors, odour emission, odour monitoring

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ODOUR IMPACT ASSESSMENT IN THE FIELD: THE PLUME METHOD

Extended abstract

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Background

Odours coming from human activities may cause adverse effects on citizens (Sucker et al., 2009), and therefore have recently become a growing social problem in industrialized countries (Ranzato et al., 2012). For this reason, odours are nowadays subject to control and regulation in many countries (Nicell, 2009). The need to regulate odour impacts entails the need of specific methods for odour of odour on citizens.

Different approaches can be used in order to evaluate measurement. Dynamic olfactometry (CEN, 2003) is now a widespread and common technique for the quantification of odour emissions. However, besides source characterization, it is important to evaluate the effective impact the odour impact on receptors, and therefore to regulate it. The two common approaches used are dispersion modelling and field inspection (Ranzato et al., 2012; Dentoni et al., in press). Odour dispersion modelling is commonly applied to simulate how odour disperses into the atmosphere, and therefore to calculate ground odour concentration values in the simulation space-time domain (Capelli et al., 2011). This approach may be useful for the definition of specific odour regulation. The wide diffusion of this approach is probably due to the fact that odour dispersion model is relatively cheap and results are easily understandable. Another important approach for direct assessment of odour impact in the field involves field olfactometric surveys, conducted relying on a panel of trained human assessors (field inspection) (Nicolas et al., 2006). This way of assessing odours entails the advantage of allowing the determination of ambient air concentration close to the odour detection threshold. The growing importance of this odour impact assessment method is proved by the current draft of an European Standard (Guillot et al., 2012).

The new European standard includes two methods of field inspection: the grid method and plume method. The differences between these methods are shortly described as follows: the grid method is a long period (one year) statistical survey method to obtain a representative map of a recognizable odour exposure over a selected area; the plume method is a short period method to determine the extent of recognizable odour from a specific source (Dentoni et al., in press). Both methods (grid and plume) are based on odour detection and recognition by human panellists (Guillot et al., 2012).

The aim of this work is to describe the application of a modified, site-adapted, plume method field inspection in order to evaluate the odour impact by determining the absence or presence of odour downwind relative to the considered source (plume extent), for the case of two different industrial plants: a food industry sludge composting plant and a biomass anaerobic digestion plant, both located in Northern Italy. As already mentioned, the plume method described in the draft European Standard had to be adapted according to the specific area on which the plants are located, and this paper has the aim of using these two case studies to discuss the feasibility of applying field inspections as odour impact assessment methods.

Methods

The plume method is used to determine the extent of the area where the plume originating from a specific odour source or an odour emitting installation can be perceived and recognised, under specific meteorological

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conditions. The odour plume extent is described by points where a transition from absence to presence of the recognizable odour under investigation, occurs. Panel members are used to determine the presence or absence of the specific odour under study at different points downwind of a source under well-defined meteorological conditions. The meteorological conditions during the field observations are measured and recorded. Usually, the measurement is repeated to reduce uncertainty to an acceptable level. In this way variability due to random variations in meteorological conditions, panel member performance and odour emission is averaged out. There are two versions of observation methods for plume measurement in this standard (Fig. 2): •Stationary plume method •Dynamic plume method

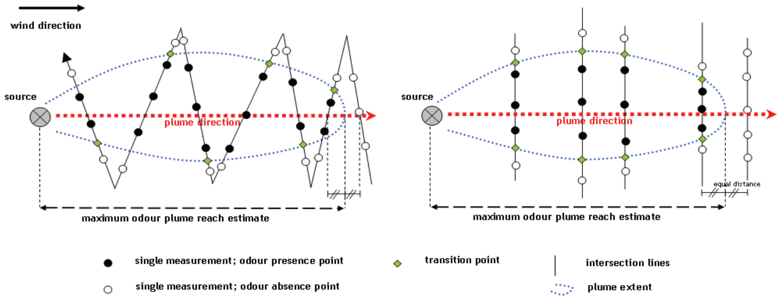

Fig. 1. Dynamic (left) and stationary (right) plume measurement

Using the stationary method, the panel members are located at specific intervals along intersection lines perpendicular to the plume direction. Each panel member determines the percentage odour time in the course of one single measurement. If the result of a single measurement reaches a percentage odour time <10%, the odour is considered as being absent; at higher values the odour is present. All observations at one intersection line are conducted simultaneously.. At least one intersection line has to be at sufficient distance to ensure that no recognizable odour is present at any measurement point to be able to determine the maximum odour plume reach.

Using the dynamic method, the panel members are traversing the plume, while conducting single measurements at frequent intervals. By successively entering and exiting the plume and in this way determining the transition between absence and presence of recognizable odour, the extent of the plume is defined. This approach helps to avoid adaptation. For both the stationary and the dynamic method the plume extent is defined by the transition points. A transition point is the point halfway between the last odour absence point and the first odour presence point for the odour type under study. In order to prevent possible adaptation effects causing incorrect observations, transition points are in the dynamic plume method only determined while entering the plume, and not while exiting.

1. Site description

The first site studied performs the composting of agro-alimentary sludge produced by a food industry for the production of cheese located in Northern Italy. The studied emission sources were the composting sludge heaps and the final product storage. The composting sludge heaps has an emitting surface of about 1600 m^2, whereas the final product storage surface is about 320 m^2. The second plant studied performs the anaerobic digestion of agricultural biomasses, and is located in Northern Italy, as well. The sources of odours of this plant are: the emissions from the biogas combustion, the shed for the biomass grinding and preparation, and the pond for the digestate storage, which, having a surface about 7100 m^2, represents the main source of odours.

2. Site-specific adaptation of the plume method

For this study it was decided to perform field inspections by applying the plume method with a dynamic approach. In both cases (plant 1 and plant 2) the dynamic plume measurement had to be adapted to the specific area where the plants are located. A preliminary study was performed in order to set up the plume measurement. This study involved the simulation of the odour dispersion at different times using the historical meteorological data relevant to the same month in which the field inspection should be run. This allowed planning the field inspection by evaluating the expected extension and direction of the odour plume in function of the time of the day. In addition, the area to be studied was mapped in a detailed way, in order to identify the paths around the source that could be used by the panellists for the field inspection. The field inspection planning also involved the training of the panel to recognize the characteristic odour of the considered source. For each measurement, 5 panellists divided in two groups were involved. More in detail, each group (A and B) was asked to go along the different paths identified during the preliminary study towards the odour emission source and to indicate the point at which they started to perceive the characteristic odour from the plant on each path. As soon as the panels perceived the odour, they had to stop in the position where they started perceiving the odour for 10 minutes, breathe normally, and fill in a specific form. After having indicated the time (hour and minute) at which they started perceiving the odour, every 10 seconds they have to fill in the grid indicating whether they continue to perceive the odour or not. Meanwhile, the group leader, by means of a GPS, registers the geographic coordinates of the point where the odour was first perceived.

Results and discussion

Plant 1 - The paths identified to be covered by the two groups of panellists (A and B) during the two field measurements are shown in Fig. 3. The results of the two field inspection campaigns (I and II) are shown on the left side of Fig. 3. More in detail, the maps reports, for both campaigns, and for each panel group (A and B, in different colours on the maps) the points on the different paths where the odour started to be perceived. In the right side of Fig. 4, there are shown the odour exposure simulated by running the odour dispersion model at the same time when the I and the II field inspection campaigns took place, i.e. with the meteorological conditions that were present at the time of the field measurement, in order to make it possible to compare the two assessment methods. In order to compare the dispersion modelling results with the outcomes of the field inspection, the lines connecting the points where the odour started to be perceived during the field measurements should be compared with the modelled iso-concentration lines. More in detail, the lines resulting from the field inspection should not be compared with the iso-concentration line of 1 ou_E m^{-3}, which corresponds by definition to the odour detection threshold concentration, but rather with the iso-concentration line corresponding to the odour recognition threshold concentration, which is assumed to be about 3 ou_E m^{-3}. Thus, the odour impact assessed with the two different approaches seems to be quite comparable. Nonetheless, a slight overestimation of the odour impact may result from dispersion modelling, due to the experimental evidences of overestimation of odour impacts obtained when Calpuff is applied to area sources. Moreover, based on the experience of our laboratory, in some cases, especially when dealing with odour emissions having an organic matrix located in an agricultural context, high odour concentrations are measured at the source, but odour becomes less perceivable when moving away from the source, probably because it tends to be confused with the background odour. In addition, the different shapes of the odour impacts may be due to an essential difference between the two compared approaches: while the odour dispersion modelling uses the hourly prevalent wind direction, the field measurements is affected by instantaneous wind direction changes.

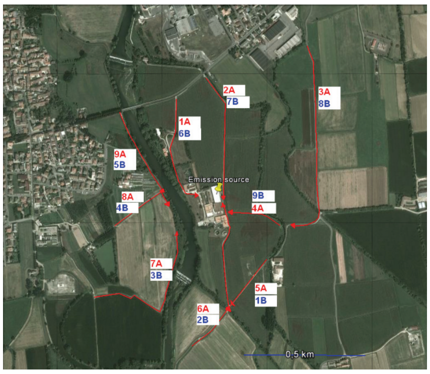

Fig. 2. Paths identified for field inspection

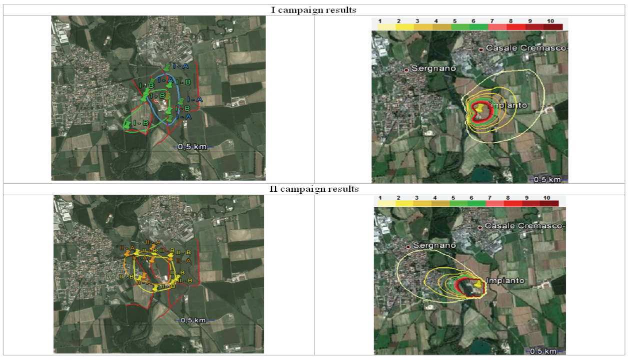

Fig. 3. Odour impact relevant to the I and II campaigns: assessed by field inspection (left) vs. simulated by odour dispersion modelling (right)

Plant 2

The paths identified to be covered by the two groups of panellists (A and B) during the field measurements are shown in Fig. 4. The results of the field inspection are shown in Fig. 5 (a).

Fig. 4. Paths identified for field inspection

The different lines (red and green) represent the results of the field inspection divided in two different time ranges: 16-17 (red line) and 17-18.30 (green line). Fig. 5b, 5c, 5d show the odour impact simulated by running the odour dispersion model at the same time when the field inspection campaigns took place, i.e., with the meteorological conditions that were present at the time of the field measurement, considering three different time ranges, i.e. 16-17 (b), 17-18 (c), and 18-19 (d). Comparing the plume obtained with field inspection with those obtained by dispersion modelling (comparison with iso-concentration line corresponding to an odour concentration of 3 ou_E m^{-3}), a slight overestimation of the odour impact assessed by dispersion modelling is observed: the odour impact evaluated by field inspection is about 1/3 in comparison with the results obtained by dispersion modelling, in term of maximum distance of odour perception/recognition.

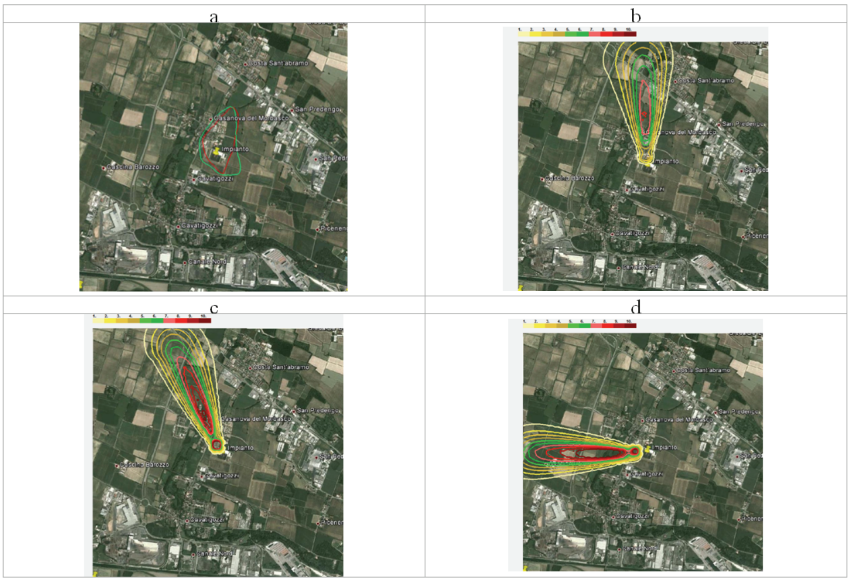

Fig. 5. Odour impact assessed by field inspection (a) vs. simulated by odour dispersion modelling considering different time ranges: 16-17 h (b), 17-18 h (c), 18-19 h (d)

Concluding remarks

The main purpose of this work was to describe the application of a modified, site-adapted, plume method field inspection in order to evaluate the odour impact by determining the absence or presence of odour downwind relative to the considered source (plume extent), for the case of two different industrial plants: a food industry sludge composting plant and a biomass anaerobic digestion plant, both located in Northern Italy. In both cases, the odour impacts resulting from the application of the field inspection turned out to be quite comparable with those obtained by simulating the dispersion of emissions by means of a suitable dispersion model (CALPUFF), thus indicating that both approaches may be effective and complementary for odour impact assessment purposes. More in detail, the dispersion modelling shows a slight overestimation of the odour impact. From the experience of our laboratory, this result could be explained by the fact that in some cases, especially when dealing with odour emissions having an organic matrix located in an agricultural context, high odour concentrations are measured at the source, but odour becomes less perceivable when moving away from the source, probably because it tends to be confused with the background odour. Further studies will be necessary in order to consolidate the experience with field inspections and to verify these preliminary results.

Keywords: dispersion modeling, field inspection, human panellists, olfactometry

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ODOUR EMISSIONS FROM INTENSIVE PIG FARMS

Extended abstract

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Background

Odour is a local problem but is an issue that is becoming increasingly important as the livestock industry expands and as ever increasing numbers of rural residential developments are built in traditional farming areas, bringing residential areas closer to livestock farms. The increase in number of farm neighbours is expected to lead to increased attention to odour as an environmental issue. Odour can be emitted by stationary sources, such as from storage, and can also be an important emission during farm activities, such as landspreading, depending on the spreading technique applied. Its impact increases with farm size. Dust emitted from farms contributes to odour transport. In areas with a high density of pig production, plumes from one farm can potentially transfer diseases to other farms (Valli et al., 2008).

Odour emissions can give rise to problems with neighbours. Emissions of odour are related to many different compounds, such as mercaptans, H_2S, skatole, thiocresol, thiophenol and ammonia, but although not all compounds that are involved have been identified yet (BREF, 2013).

Generally, housing systems vary mainly based on the proportions of fully – slatted, partly – slatted or solid (concrete) floors. Directive 2008/120/EC of 18 December 2008 lays down minimum standards for the protection of pigs and, among other things, imposes a maximum width of openings in concrete slatted floors according to the type of pigs (Council Directive, 2008). In addition, the ventilation of pig housing varies from manually controlled natural systems to fully automated fan – based systems. With dynamic systems, the distribution of air can be accurately adjusted by means of valves, positioning of the fans and diameter of the air inlets. Natural ventilation depends more on the natural fluctuations of the outside air temperature and on the wind. In the Northern of Italy, the pig houses are generally characterized of fully – slatted floors with natural ventilation. In this paper, we collected odour samples in more kinds of intensive pig farms, to understand which permit lower odour emissions, in relation with BAT.

We can use emission factors of different livestock farms in more than one situation. In first place they are used to valuate odour impact of farms in project for which it is not possible make measures. The odour impact calculated using a standardized procedure is used by the authorizer to determine the sustainability of the work. The emission factors are important not only before the construction but also when the farm is working: I mean in the monitoring plan. Sometimes the EIA monitoring plan is not developed with the proper attention, sometimes it is remanded to a later stage that is not well defined. This is true especially for those impacts with difficult evaluation. It is so that in monitoring plan we'll find all those impacts for which it was not possible to quantify the amount and therefore the monitoring plan will be a list of measures to assess those impacts that could not be estimated beforehand. The livestock farms could fall in this trap because of the absence of information about odour emissions or because we don't have a good database for emission factors

Use the monitoring plane to assess unknown impacts is a practice that should be avoided. Assess the unknown impacts would not be a cheap practice, in particular for odorous impacts for which the verification of the disorder is complex, costly and not free of uncertainties. Furthermore, actions to mitigate after construction of the livestock farm, are likely to be expensive because structural rather than management. For odour impact, in particular, the

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monitoring plan should be oriented to the verification of the emission factors rather than of entries, leaving the extent of these only as a last step of a procedure that involves, firstly, the verification of the expected emissions.

This procedure, which is currently a work in progress, was created by ARPA FVG for monitoring plans for farms which give rise odour impacts unsustainable. The basic idea is to proceed in stages aimed at identifying the sources of the odour impact and act with mitigation measures oriented and calibrated. The early stages of this procedure are of managerial type and provide for verification of the "factors" which are actually implemented (e.g. how much pigs.) If the odor remains we pass to the subsequent stages which provide for the control of the emission factors used for the preventive estimation. The control is performed by means of olfactomety measures directly in the company in order to identify any specificity or errors in the emission factor used by the literature. The transition to the next phase is in the case in which the mitigations implemented not solved the problems. Only the final phase includes measures of odour directly to the receptor. Therefore, the method is based on a solid assessment of the emission factors of the system to be used as a preventive measure and to be controlled afterwards. The test results can help to implement the emission factors database which should be built.

Objectives

The main objective of this work is to obtain odour emission factors for intensive pig farms and understand, with the application of dispersion models, which is the odour dispersion in the surroundings of a plant. The experimental data are collected in several intensive pig farms, with the method of dynamic olfactometry (CEN, 2003). Then we used a dispersion model, such as Calpuff, to evaluate odour dispersion in the surrounding of every intensive pig farms and compared our results with report of smell of resident people.

The main objective of this work is to obtain odour emission factors and understand which kind of facility and ventilation permit lower odour emission, in relation with BAT.

Outline of the work

This work is divided in three main parts:

- The first part covers samples collection at several intensive pig farms with dynamic olfactometry. Results are expressed in ou_E/m^3, in compliance with EN 13725.
- The second part covers validation of olfactometric results, with application of dispersion models. The results obtained are compared with report of smell of resident people.
- The third part reports results of animal house measurements. Results are expressed as odour emission referred per animal ($ou_E/s/ap$, as explained in BREF, 2013). Results obtained in our Laboratory are compared with standards, that are illustrated in BREF (2013).

Methods

This paper presents the results of the olfactometric analysis which are realized in several intensive pig farms. The results are elaborated to obtain emission factors which described the odour emission in function of the type of pig houses and ventilation. In general, European Standard EN 13725:2003 is the method used for monitoring of odour emissions.

The method is based on odour detection by trained human assessors by using a specific apparatus (olfactometer) of diluted gas samples at progressive degree of concentration, until the same threshold response is elicited as from the reference odour (n-butanol). The odour concentration is expressed in European odour units ou_E/m^3. In this case, we collected several odour samples with a vacuum sampler. In every type of intensive pig farms, measurements were made at the exhaust outlet of the air exchange fans or, if there was natural ventilation, at air outlets. The numbers are also used as input in dispersion models, such as Calpuff. CALPUFF is a puff Lagrangian dispersion model, in which the conservation equations of mass are written and solved by reference to emission releases called puff, which approximates the continuous emission. The equation for each puff is determined from the wind field. This wind field is calculated using a meteorological pre-processor (CALMET), which uses as input data, the data coming from the meteorological and mapping refer to the concerned site and for the simulation period. The output file of CALMET is processed by CALPUFF, together with the emissions data to get the desired concentration field. For the development and evaluation of results, the document of Regione Lombardia has been taken as reference (Regione Lombardia, 2012).

Results and discussion

This paper presents odour emission factors for intensive pig farms. The data were collected in several intensive pig farms. In the Northern of Italy, pig houses are generally characterized of fully – slatted floors with natural ventilation. We collected odour samples in intensive pig farms with:

- Fully – slatted floor (FSF) with deep pit: a deep pit lies under a fully – slatted floor with concrete slats. The slurry manure is removed at variables intervals, usually every fattening period, or even less frequently (BREF, 2013). In the case of forced ventilation, the air introduced removes gaseous components emitted by the stored slurry manure. Exhaust air is normally expelled through side wall vents.

- Fully – slatted floor with a vacuum system: on the bottom of the pit under a fully – slatted floor, outlets are placed that are connected to a discharge system moving the slurry to the external storage units (Fig. 1). Slurry is discharged by opening a valve in the main slurry pipe. A slight vacuum develops and allows for a through slurry removal, better than by gravity alone. A depth of slurry needs to be obtained before the system can operate properly to allow the vacuum to develop and empty more slurry (BREF, 2013).

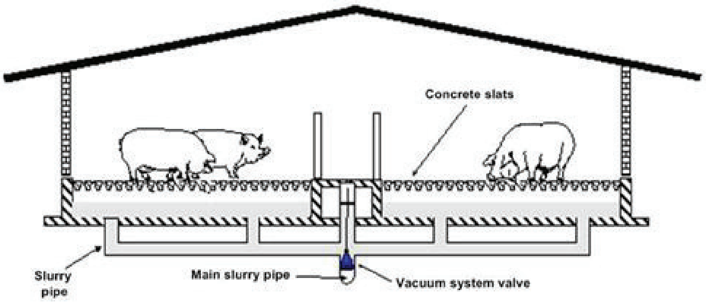

Fig. 1. Fully – slatted floor with vacuum system (BREF, 2013)

After the data collection, using dynamic olfactometry, we used the numbers as input in dispersion models. The mathematical modeling of emissions, based on assumptions made for the source, anemometry data, weather and terrain can evaluate the dispersion of odors. The dispersion models use complex algorithms to simulate the transport and kinetic pollutants in the lower atmosphere where the air is more affected by pollution. To achieve this, the models require input data divided into the following categories:

- meteorological data: wind (direction and intensity), temperature and humidity, atmospheric stability;
- mapping data: topography, cartography, land use;
- emission data: geometry and location of emission sources, type of polluting and mass flow.

The choice of model is often made based on the characteristics of the plant, defined as the set of elements that characterize a specific application. Based on the guidelines of the UNI 10796 (2000), a scene can be described based on five elements:

- spatial scale: computational domain for the dispersion. Can be distinguish between microscale applications (up to 1 km), local scale (up to 10-20 km), mesoscale (up to 100-200 km) and large-scale (up to 1000-2000 km);
- time index: short-term application (from minutes to days), medium term (from one hour to one week) long-term (seasonal and annual);
- geographical area: simple site (flat, uniform spatial features) or complex site (complex terrain, not constant spatial characteristics);
- types of sources: point, linear or aeral;
- simulated species: odour.

Fig.2 shows the odor dispersion model of the actual situation for a livestock facility with 1.100 fattening pigs, pointing out the values of 1.3 and 5 ou_E/m^3 reported by the Guideline of the Lombardy Region (Regione Lombardia, 2012).

The results of dispersion model are compared with reports of smell of the resident people. Results of the comparison between simulated and experimental data show that model is capable to predict satisfactory the odour dispersion on the surrounding of a plant. After that, we calculate odour emission factors. Results are expressed as odour emission referred per animal (ou_E/s/ap, as explained in BREF, 2013).

This paper presents the emission factor for intensive pig farms. We analyzed pig houses with fully – slatted floor. Our results differentiate the kind of ventilation used in the f intensive pig farms: the ventilation of pig housing vary from manually controlled natural systems to fully automated fan – based systems. With dynamic systems, the distribution of air can be accurately adjusted by means of valves, positioning of the fans and diameter of the air inlets. Natural ventilation depends more on the natural fluctuations of the outside air temperature and on the wind.

All the analyses referred to natural ventilation were conducted in the summer time. We compared results of our laboratory with values quoted in BREF, 2013. The data are similar and confirm that the measurements were conducted in a right way.

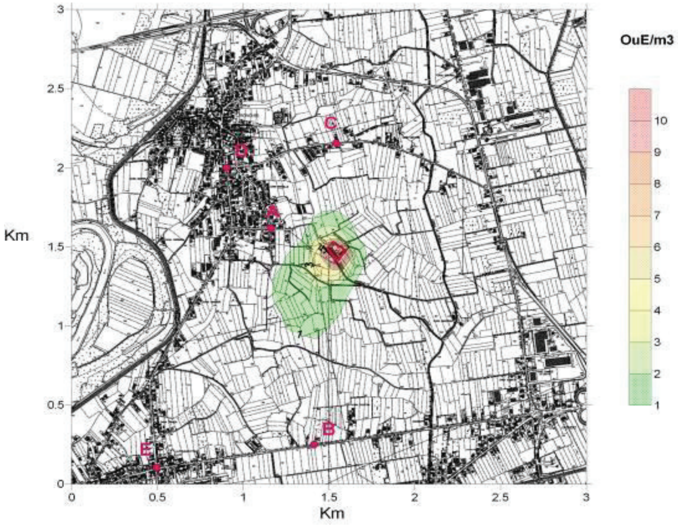

Fig. 2. Odour dispersion on the surrounding of a plant

Table 1. Odour emission factors for intensive pig farms.

Description	***Odour calculated by our Laboratory (ou_E/s/ap)***		***Odour (ou_E/s/ap) (BREF, 2013)***
	Forced ventilation	Natural ventilation	
Fully – slatted floor with deep pit – fattening pigs	5.8	10.6	6.5
Fully – slatted floor with vacuum system – Weaned piglets	1.4	5.8	3
Fully – slatted floor with vacuum system – fattening pigs	13.1	_	7
Fully – slatted floor with vacuum system – gestating sows (individual)	–	6.3	6

Concluding remarks

This paper presents the results of the olfactometric analysis which are realized in several intensive pig farms. The results are elaborated to obtain emission factors which described the odour emission in function of the type of pig houses and ventilation.

We compared results of our Laboratory with values that are quoted in BREF, 2013. The data are similar and we understand that, to minimize the diffusion of odour emissions from pig housing system, it is possible to select a suitable ventilation system, with low air velocity at the floor level.

Keywords: dispersion models, dynamic olfactometry, fattening pig houses, livestock facilities, odour emission

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MONITORING PLAN AND ODOUR CONTROL FOR IPPC PLANTS – CASE STUDY

Extended abstract

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Background

Industries subject to IPPC (Integrated Prevention and Pollution Control) have to present annually to the competent authorities the results of their monitoring and control plan. It contains technical and operational parts which describe the physical and chemical parameters to monitor, like also the odour. These requests of the competent authorities on the odour are affected by a gap in the present national legislation, so the companies risk to spend a lot of money and energy to answer them.

The European Standard EN 13725 (2003) and the Guide Line of Lombardia (2012) are adopted to cover this gap and followed for odour sampling and analysis. So it's edited an odour monitoring and control plan following these norms and according to the competent authorities and the plant manager.

This case study shows the olfactometric analysis, as the first step of IPPC odour Monitoring and Control Plan decided by LOD (Laboratory of Dynamic Olfactometry), ARPAV (Environmental Protection Agency of Veneto region) and a chemical plant, producing inorganic compounds, sited in Veneto.

Objectives

The main objective of this work is to answer to requests in IPPC of the chemical plant about the odour.

At section 7 "Monitoring and control plan" is written that the manager of the plant must present, until 24 months after the issue of IPPC, a plan for odour control, to estimate, control and analyze odour impact generated by the plant on the surrounding.

Outline of the work

This complete work is divided in subsequent steps:

- Inspection and identification of odour emission sources, basing on production cycle and raw materials used by the plant;
- Sampling of the emission sources identified, as described in European Standard EN 13725 (2003);
- Evaluation of the odour emission sources responsible of possible odour impact;
- Chemical analysis to identify the chemicals responsible of odour impact;
- Characterization of the odour emission parameters, comparing the odour threshold of the chemical with the concentration inspected (Odour protocol);

Evaluation of the odour impact in the territory nearby the plant, can be done using an odour dispersion model.

This model uses meteorological, orographic, and odour data as input data. So it's possible to understand how odour fall down at sensible receptors, previously identified in the territory.

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Methods

The sampling method for punctual sources is described in par. 7.2.2 “Sampling for delayed olfactometry” of European Standard EN 13725:2003: “the lung principle where the sample bag is placed in a rigid container, the air is removed from the container using a vacuum pump, the under pressure in the container causes the bag to fill with a volume of sample equal to that which has been removed from the container.”

To measure the odour concentration and flow rate from passive areal surfaces, like pools and muddles, it’s used the “wind tunnel” (Fig. 1). This system is composed by a “Zero grade air” cylinder, a flowmeter and the “wind tunnel”. The flow rate to input in the “wind tunnel” is controlled by the flowmeter. As described in the VDI 3880 Draft, (2011), “Olfactometry – Static sampling” the flow rate to the “wind tunnel” is regulated at 1.2 L/s. Then, the sampling is made by a vacuum pump, used to strip the air to analysis to the sample bag (Fig. 2).

Fig. 1. Wind tunnel

For the olfactometric analysis assessors are selected on their responses to a substance (n - butanol in nitrogen), to represent the “smell average" of population, as say par. 6.7.2 “Selection of assessors on individual variability and sensitivity” of European Standard EN 13725:2003: “in order to obtain a reliable sensor, composed of a number of panel members, assessors with specific qualities shall be selected from the general population to serve as panel members. In order to ensure repeatability of their result, their olfactory responses should be as constant as possible from day to day, and within a day. In order to ensure repeatability of the sensor, formed by a panel composed of individual panel members, their olfactory sensitivity shall be within a defined bandwidth, much narrower than the variability within the population. To achieve this aim assessors with a specific sensitivity to the reference odorant n-butanol are selected to be panel members. Then at least 10 individual threshold estimates for the reference gas shall be collected for selection purposes. The data for each assessor shall be collected in at least 3 sessions on separate days with a pause of at least one day between sessions.”

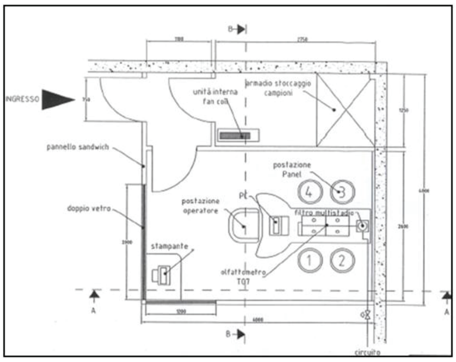

Fig.2. Olfactometric chamber

The principle of measurement is defined by European Standard EN 13725: “the odour concentration of a gaseous sample of odorants is determined by presenting a panel of selected and screened human subjects with that sample, varying the concentration by diluting with neutral gas, in order to determine the dilution factor at the 50% detection threshold (Z50). At that dilution factor the odour concentration is 1 ou_E/m^3 by definition. The odour concentration of the examined sample is than expressed as a multiple (equal to the dilution factor at Z50) of one European odor unit per cubic metre [ou_E/m^3] at standard conditions for olfactometry”.

Results and discussion

The OER (Odour Emission Rate) of the punctual odour emission sources are shown in Fig. 3.

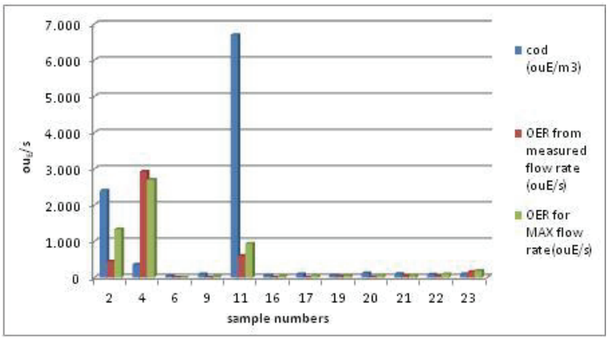

Fig.3. OER of the punctual odour emission sources of the plant

The OER for the punctual sources monitored was calculated, as expressed in (Eq.1):

$$OER = C_{od} x Q_{effl} \tag{1}$$

where: C_{od} is odour concentration measured (ou_E/m^3); Q_{effl} is flow rate (m^3/s).

Data shown in Fig. 3 lets to visualize the potential odour emissions of the plant. In fact, as written in Attached 1 – "Requirements of odour impact studies by dispersion simulation" of Guide Line of Lombardia - "General requirements concerning the characterization of gas emissions into the atmosphere by heavy odour impact plants - 2012": in the emission scenery to use in the simulation of the odour impact must be considered all the emission sources (piped, widespread and fugitive) with an odour emission rate greater than 500 ou_E/s, excepted the sources for which, whatever is the flow rate emitted, the odour concentration is lower than 80 ou_E/m^3."

Concerning the wastewater treatment plant, the principal odour emission (Table 1), comes from the sludge thickening pool, where the odour concentration measured is 1.600 ou_E/m^3. This value is in line with values reported in European Standard UNI EN 12255-9 (2002) "wastewater treatment plants, ventilation and odour control."

Table 1. SOER and OER for areal passive sources

Type of emission		*Flow rate pushed (l/h)*	*Emission surface (m^2)*	*c_{od} (ou_E/m^3)*	*SOER (ou_E/m^2s)*	*OER (ou_E/s)*
12	Sludge thickening pool	4.500	63	1.600	3,75	240
13	Homogenization pool	4.500	32,55	45	0,10	3

For these samples, the values of SOER (Specific Odour Emission Rate) and OER were calculated basing on the values of odour concentration and the flow rate pushed into the "wind tunnel"., as reported in Table 4. These calculations were done following par. 5.4.2 of Attached 2 – "Olfactometric Sampling" of Guide Line of Lombardia - "General requirements concerning the characterization of gas emissions into the atmosphere by heavy odour impact plants - 2012". In detail: "for the OER (Odour Emission Rate) evaluation, it's necessary to calculate another important parameter, the SOER (Specific Odour Emission Rate), expressed in odour units for surface unit and time ($ou_E/m^2/s$) (Eq. 2).

$$SOER = \frac{Q_{effl} x C_{od}}{A_{base}} \tag{2}$$

where: SOER is Specific Odour Emission Rate ($ou_E/m^2/s$); Q_{effl} is flow rate from the "wind tunnel" (m^3/s); c_{od} is odour concentration measured (ou_E/m^3); A_{base} is base surface of the "wind tunnel" (m^2).

At the end, to calculate the (OER) is to multiply the SOER for the emission surface, i.e. the total surface of the source considered (Eq.3).

$$OER = SOER \times A_{emiss} \tag{3}$$

where: *OER* is Odour Emission Rate (ou_E/s); *SOER* is Specific Odour Emission rate ($ou_E/m^2/s$); A_{emiss} is emission surface (m^2).

As reported in Attached 1 – "Requirements of odour impact studies by dispersion simulation" of Guide Line of Lombardia - "General requirements concerning the characterization of gas emissions into the atmosphere by heavy odour impact plants - 2012" there aren't significant emission sources because the OER for every emission monitored is lower than 500 ou_E/s.

Concluding remarks

As reported in Attached 1 – "Requirements of odour impact studies by dispersion simulation" of Guide Line of Lombardia - "General requirements concerning the characterization of gas emissions into the atmosphere by heavy odour impact plants - 2012" the significant emissions are:

- Stack 1 Scrubber for sulfur fuser;
- Stack 3 – sulfuric acid;
- Stack 11 - HCL tanker unloading.

The sample collected at the vent of the liquid sulfur tank has the highest value of odour concentration of all the emission sources, 11.000 ou_E/m^3. Even if this emission is discontinously it must be monitored for its high odour concentration.

Concerning the wastewater treatment plant, there are not emissions to simulate in an odour dispersion model. After this, the odour monitoring and control plan to show to the Competent Authorities, for IPPC; they can include a limited number of plant emission sources.

Table 2. Possible olfactometric samples

Stack	*Features*	*Sample number*
1	Scrubber for sulfur fuser	Sample 1 (IN) Sample 2 (OUT)
3	Sulfuric acid stack	Sample 3 (IN) Sample 4 (OUT)
11	HCL tanker unloading.	Sample 10 (IN) Sample 11 (OUT)
	Sulphuric acid tank vent	Sample 8
	Liquid sulfur tank vent	Sample 7
	Sludge thickening pool	Sample 12

Based on these evaluations, the remaining steps to make for IPPC odour Monitoring and Control Plan are:

- chemical analysis of the significant odour emission sources identified by the olfactometric sampling to identify the chemicals responsible of odour impact;
- characterization of the odour emission parameters, comparing the odour threshold of the chemical with the concentration inspected (Odour protocol). So another olfactometric analysis will be conducting during the chemical analysis at the significant odour emission sources to connect the chemicals concentration with the odour concentration.
- evaluation of the odour impact in the territory nearby the plant, using an odour dispersion model. The input odour data are the results of the olfactometric analysis done together the chemical one.

Keywords: emission, IPPC, odour, olfactometric analysis

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DISPERSION MODELING SUPPORTING URBAN PLANNING CASE STUDY: UDINE INDUSTRIAL ZONE (Z.I.U.)

Extended abstract

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Background

The "area industriale Udine-Sud (ZIU)" is the main industrial area of Udine, it is located in south-east of the city and extends in 5.190.000 sqm ha for the location of new initiatives (Productive and services and community facilities and public interest).

The ZIU area is managed by the Consortium for Industrial Development of Central Friuli, public economic Autority whose purpose is the promotion of the necessary conditions for the creation and development of productive activities in industry. The Consortium has also specific competencies in urban planning with the adoption of the urban "PTI" (Infraregional Territorial Plan).

Objectives

Within the redaction of the new urban plan of the industrial area, in force since August 6, 2013, whose most important change involved the expansion of the ZIU (+10% of the area), the Consortium made some studies to support this plan in particular preparing, together with LOD, the definition of criteria to be followed in the preliminary establishment of new industrial activities, in order to maintain the conditions for a good environmental quality according to the objectives of the regional plans and national regulations.

For this purpose it was first realized a census of all the authorized emissions present within the ZIU and subsequently modeled the dispersion in the atmosphere for certain pollutants.

The dispersion modeling results have been compared with the values of the ARPA control units (already placed on the territory) and have demonstrated a substantial correspondence with the previous data, validating the model simulation and the preliminary evaluations conducted.

This dispersion model will be also useful to make an air quality assessment for the introduction of the new plants by evaluating local pollution values at different specific sites.

Outline of the work

This work is divided in three main parts:

- The first part covers the census of all authorized emissions of the 116 companies inside the ZIU. This census verified that, on a total of 116 plants located in ZIU, 35 are equipped with an authorization for their emissions (about 30%). So we can say that 70% of the companies located in ZIU has no atmospheric emissions or, in any case, the emissions are not significant (according to Legislative Decree 152/2006 and subsequent amendments).

The emissions authorizations allowed to divide the companies, according to chemical compounds emitted:

  - NOx;
  - PM10;
  - Metals (Cd, Mn e Ni).

- The second part consists in the modeling of pollution dispersion and the correlated impact assessment.

- Finally, to confirm the validity of this study, we compared the results of the simulations with the values obtained from the ARPA stations located on the territory of ZIU.

Methods

The evaluation of odor dispersion and pollutants has been done using CALPUFF dispersion model, recommended by U.S. EPA for planning, monitoring and control of air quality. CALPUFF is particularly useful for the simulation of the dispersion of pollutants and odors on a local scale.

The dispersion models use complex algorithms to simulate the transport and kinetic pollutants in the lower atmosphere where the air is more affected by pollution. To achieve this, the models require input data divided into the following categories:

- meteorological data: wind (direction and intensity), temperature and humidity, atmospheric stability;
- mapping data: topography, cartography, land use;
- emission data: geometry and location of emission sources, type of polluting and mass flow.

CALPUFF is a puff Lagrangian dispersion model, in which the conservation equations of mass are written and solved by reference to emission releases called puff, which approximates the continuous emission. The equations for each puff are determined from the wind field. This wind field is calculated using a meteorological pre-processor (CALMET), which uses as input data, the data coming from the meteorological and mapping refer to the concerned site and for the simulation period. The output file of CALMET is processed by CALPUFF, together with the emissions data to get the desired concentration field.

For the selected area were acquired meteorological data taken on the ground level and data soundings (Scire et al., 2000a, b).

- Meteorological ground data were taken from Friuli Venezia Giulia OSMER center and refer to the meteorological station of Fagagna (Udine) located about 5 km far from the area site.
- Soundings data were taken from the meteorological station of Udine Campoformido (46 ° 02'N 13 ° 11'E) which is about 8 km far from the site.
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a. Preliminary analysis

The data analysis conducted in the first step has allowed us to acquire information about the expected behavior for pollution dispersion. As can be seen from the analysis of the wind rose shown in Figure 1, in 2007, there has been a strong head wind from the ENE and, secondly, from the NE directions; in other directions have recorded winds with frequencies below 10%. This result allows us to say that the disperse pollutants emitted by the plants located in ZIU will mainly spread in the SW direction.

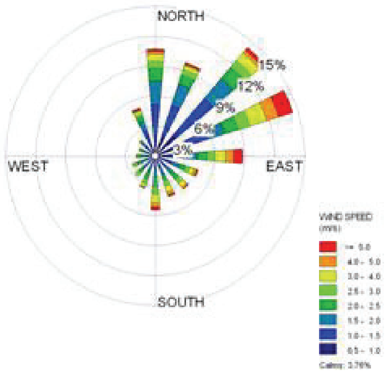

Fig. 1. Wind rose for the year 2007, referring to the meteorological station considered: the radial coordinate (length of the circular sector) is the frequency, the color of the wedge indicates the intensity of the wind.

b. Landuse and orographic data analysis

The dispersion model CALPUFF allows you to take into consideration the effects of orography characteristic of the territory. This kind of information was given through a matrix composed by array of elevation sand land uses data into the spatial domain. In this case study we decided to study the dispersion of pollutants on a local scale and work with a computing grid of 7 x 8 km and a grid spacing of 250 meters. The center of the grid was set in the South part of the ZIU Area. Within the computational grid were also identified particular receptors corresponding to specific houses or settlements located near the industrial area farm in which have been quantified pollutants and caused by the plants considered.

To confirm the validity of this study, we compared the results of the simulations with the values obtained from the ARPA stations located on the territory of ZIU (Friuli Innovazione – cfr. Point A,Via Casali Caiselli cfr. Point B and C, Via Manzoni, Via del Lavoro and Via delle Industrie cfr. point D).

c. Emission data

The pollution sources have been considered from the census of all authorized emissions of the 116 companies inside the ZIU (UNI 10796, 2000; UNI 10964, 2001):

- **Technical characteristics**: emission eight, length /frequency, velocity, temperature emisiilor and the flow rate of the effluent at the outlet.
- **Pollutants:**
    - **PM10:** companies have limits for PTS but not for the PM10. The emission value has been:
        - measured values +20% for the average working condition,
        - 80% of the emission limit when the measured values were not available.

      Dust emitted has all been considered as PM10.
    - **Metals:** companies have limits for Ni, Cd and Mn, the assessment of metal has been provided starting from the P10 values, based on studies conducted by ARPA in ZIU (since 2003). The correction values are shown in Table 1.

    - **Nitrogen Oxides (NOx):** The emission value has been:
        - measured values +20% for the average working condition,
        - 80% of the emission limit when the measured values were not available.
        - NOx has been considered like NO2; Nitrogen Dioxide has a much higher toxicity than the monoxide, it is very reactive and contributes for the formation of “photochemical smog”.

Table. 1. Correction values for PM10 and metals

PTS	PM_{10}	Ni	Cd	Mn
	PTS*0.87	PM10 * 0.0244	PM10 * 0.0012	PM10 * 0.16
ug/m^3	ug/m^3	ng/m^3	ng/m^3	ug/m^3

Results and discussion

The impact assessment on the domain has been referenced to D.Lgs. 155/2010 “Attuazione della direttiva 2008/50/CE relativa alla qualità dell’aria ambiente e per un’aria più pulita in Europa” which defines the reference limits not to be exceeded (different statistics as the annual average shown in Fig. 2).

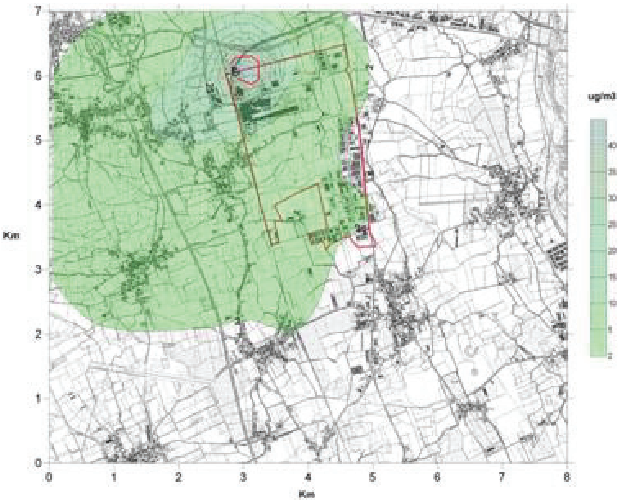

Fig. 2. Isoconcentration values referred to PM10 annual mean

In Table 2 there is the comparison between the model values calculated at the receptor and the previous models made by ARPA and CRMA at the same point.

Table 2. Comparison between model values at different points

	Simulation annual mean	***ARPA (2010) annual mean***	***ARPA (2011) annual mean***	***ARPA - CRMA***
Friuli Innovazione (A)	PM10: 0.3 NO_2: 3.6 Ni: 7.24 Cd: 0.33 Mg: 0.047	Ni: 3.0 Cd: 0.2 Mn: 0.01	-	PM10: 18.95 NO_2: 29.24
Casali Caiselli (B)	PM10: 0.6 NO_2: 3.2 Ni: 11.9 Cd:0.58 Mg: 0.077	PM10: - Ni: 4.3 Cd: 0.2 Mn: 0.05	Ni: 4.0 Cd: 0.2 Mn: 0.06	
Casali Caiselli (C)	PM10: 0.7 NO_2: 8.1 Ni: 16.3 Cd: 0.8 Mn: 0.1	-	-	
Rotonda Via del Lavoro e delle Industrie (D)	PM10: 0.4 NO_2: 2.4 Ni: 7.77 Cd: 0.4 Mn: 0.04	-	-	
Via Manzoni - Udine	-	PM10: 26 NO_2: - Ni: 4.0 Cd: 0.2 Mn: 0.02	PM10: 26 NO_2: - Ni: 4.4 Cd: 0.3 Mn: 0.02	

Concluding remarks

The modeling results are consistent with the pollution measurements data considered in the ZIU plan (already approved) and this attests to the correctness of the model and its input data.

The dispersion simulation implemented in the study, is also an important instrument for future evaluation of new production facilities in the industrial zone. It is possible to verify that emissions from future plants are compatible with the environmental and territorial quality objectives, by adopting an approach of "wide area", thus abandoning the concept of assessment “in local”. This can also be applied in case of significant emissions changes for existing plants (revamping, adjustments, upgrades).

According to this approach, it will be necessary to take into consideration all existing significant emissions in all surrounding areas, in order to obtain the future scenario of the whole area and assess their compatibility with the quality environmental objectives.

The modeling of the entire industrial area, if considered as a "dynamic system", can progressively provide useful data on the total amount of released emissions into the atmosphere and therefore make possible the emission management fixing limits in terms of mass flow (e.g. kg / year) instead of concentration.

The adoption of new regulatory measures can provide further useful information about the air quality compatibility compared to existing situation o and help the environmental Authority in the suitability assessment of a new plant in a specific geographical area.

Keywords: dispersion, model, urban, planning, pollution

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HEALTHY INDOOR ENVIRONMENTS: HOW TO ASSESS HEALTH PERFORMANCES OF CONSTRUCTION PROJECTS

Extended abstract

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Background

The indoor environments, designed as integrated systems of physical and anthropogenic factors, have a significant impact on the health of communities and are currently one of the major environmental risk factors for humans. The health risk due to a low indoor air quality was strongly acknowledged in the last century when numerous health and hygiene laws have been adopted in order to ensure a higher level of indoor safety and comfort.

In recent years, however, (in developed countries) there is a radical evolution of hygiene and well-being needs related to building systems in which individuals live and work, but at the same time laws and regulations have not been upgraded for meeting the emerging needs. The key factors that affect the state of health of individuals and, more generally, of a population are now numerous, interrelated and sometimes conflicting with each other. In the construction field, for example, the energy efficiency is considered a more and more important requirement for the sustainability, but it causes low permeability to air and reduced spontaneous flow of natural ventilation, thus increasing the concentrations of pollutants within the environment (Capolongo et al., 2001). The current welfare needs nowadays more than ever require architectural, technological and engineering solutions, with the aim of protecting the health and actively participating in prevention by parameters no longer associated with perceived well-being as temperature and humidity, lighting, sunshine, humidity control, water supply, waste removal and air quality.

However this awareness has not been received into regulations for addressing and controlling the design practice, that have not been updated mostly from the 70s and 80s, with the result that the references contained therein are not anymore comprehensive (Buffoli et al., 2007).

In recent years, the World Health Organization has focused its policies and directives towards strategies aimed at enhancing indoor and outdoor conditions that promote the well-being and protect health in its broader definition ("complete physical, mental and social health and not just the absence of disease"). It is therefore confirmed that health is the result of different socio-economic, cultural and environmental issues directly or indirectly related to the specific characteristics of the environments in which we live. The importance of considering all aspects that contribute to the indoor well-being as driving forces for the human health is also emphasized by the fact that, on average, everyone spend more than 90% of their time in confined environments (home, place work, meeting places, public transport).

According to this strong relationship between built environment and health every government should adopt more significant strategies for the achievement of well-being in this context. In Italy the local health authorities (ASL) are required to verify the compliance of construction projects with health and hygiene regulations. This assessment mainly consists in a mere verification accompanied by opinions often considered as subjective.

This context highlights the importance of defining an instrument in order to objectively evaluate the quality of indoor spaces in terms of health, comfort and prevention and to effectively address designers towards high performance buildings. This instrument called Multicriteria Evaluation Tool for Health (METH) was defined in a

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study carried out by the ABC Department (Politecnico di Milano) in collaboration with the ASL Milano, which currently uses it for the evaluation of all construction projects (new construction and rehabilitation) (Oppio, 2007a, b).

The tool evaluates the strategies adopted at the building scale with a special focus on the air indoor quality, while the health impacts at the urban scale have been considered in a specific complementary tool, always defined in synergy with the ASL Milano (Capolongo et al., 2011).

Objectives

Aim of this work is to define an assessment tool, effective and objective for the drafting of opinions regarding healthy housing projects in order to ensure a high level of indoor comfort. In Italy, in fact the local health authority (ASL) are required to verify the compliance of construction projects through health and hygiene, with the regulations and the drafting of subjective evaluations of the project. However, this assessment is often reduced to a mere verification of certain specific regulations recently updated (Building Regulations, Regulations Sanitation) no longer sufficient to ensure a high indoor comfort accompanied by opinions often too subjective.

In the instrument called Multicriteria Evaluation Tool for Health (METH), will also be included strategic directions to guide designers towards technologies and best solutions to wellness.

Through the use of METH, it is expected to improve the living conditions of indoor environments and design processes to trigger more virtuous and encourage a more conscious attitude towards issues of prevention and quality.

Outline of the work

The methodology followed for the definition of the assessment instrument was divided into three consequential phases.

The first phase required the comparative analysis of most frequently used assessment tools for environmental quality in Italy and abroad (Itaca, CasaClima, Ecolabel, LEED, BREEAM, HQE, SBTool, Nabers, CASBEE, Sustainable Building), in order to select widely shared parameters for assessing the quality of buildings, the indoor well-being and their effects on the individuals' health. Since there are not many tools focused solely on health, the research was addressed to the analysis of the buildings' environmental sustainability assessment systems. In order to better compare the criteria used by the evaluation systems investigated, it was therefore defined a matrix that highlights the importance attached to each parameter and the frequency with which the same parameters are considered within the different instruments. The matrix consists of 84 total parameters divided into 5 main thematic areas and it represents the outcome of the preliminary selection of the large amount of information collected.

This phase has played a fundamental role for the next stage of the process that consists in identifying the thematic areas and in the choice of the criteria for the evaluation of building systems (definitively 15 divided into 5 areas), that has been carried out with the technicians of the ASL.

Specifically, the instrument considers the current regulatory provisions as a minimum standard, assuming that if these were not satisfied the project under evaluation would not be considered entirely appropriate (Signorelli et al., 1999). However, according to a logic shared by the local health authority and aimed to increase the quality of design practice, the mere compliance with the above regulations has not be considered sufficient.

During this second phase, characterized by many focus groups designed to open a dialogue with the technicians of the ASL Milano, was also confirmed the need to differentiate the evaluation system according to the function and the typology of the building to be analyzed. The third phase of the research involved the testing and implementation of the Multicriteria Evaluation Tool for Health (METH). The test was conducted on a sample of 50 case studies located in the city of Milan, selected from an initial sample of 100 projects submitted to the mandatory hygiene opinion of ASL Milano. In order to get relevant feedback on the results obtained for all the different functions, the choice of the projects included in the sample was made with reference to the following building types: hospitals, nursing homes, schools and similar, housing, recreational activities and similar. According to the outcomes of the trial step, the instrument was then developed and improved in some of its critical features and has been developed a specific software. During the three stages of development of the METH has been given great importance to the experience of the technicians of the ASL by brainstorming and focus groups aimed to deeply discuss the emerging issues in the hygiene and health evaluation of plans and projects.

Methods

The METH is hierarchically divided into macro thematic areas, each of them is in turn divided into criteria. The thematic areas represent the main aspects of the construction project that may have direct and indirect impacts on health, while the criteria examine a more specific theme. The system developed and tested consists of 15 evaluation criteria grouped into five thematic areas according to the following scheme:

1.Indoor environmental quality - health (1. Thermohygrometric Comfort, 2. IAQ and ventilation, 3. Lighting natural/artificial and views, 4. Noise, 5. Ionizing and not ionizing radiation);

2.Outdoor quality (6. Parking, 7. Green areas, 8. Quality and efficiency of the open spaces);

3.Quality of the project (9. Functional mix, 10. Quality and efficiency, 11. Building and context);

4.Waste and Resources (12. Solid waste management 13. Liquid waste management-Waters 14. Building materials/finishings);

5.Quality of service (15. Building management).

For each criterion has been prepared an explanatory tab containing all the information necessary for evaluating the construction projects. These tabs also include a special section dedicated to the best practices in order to guide the designer. The explanatory tabs of each criterion are articulated in the following points: description of the criterion, health effects, goal, evaluation according to different functions, best practices, technical standard and regulations.

The definition of the performance judgment for each criterion has been carefully designed in order to minimize the subjectivity of the reviewer. Consequently, for each criterion has been specified three different qualitative performance judgment:

- a good judgment in the case of a significant improvement of hygiene performances compared to the standards established by the laws or regulations in force and to the common practice;
- a critical judgment in the case of a moderate improvement of hygiene performances compared with the standards established by the laws or regulations in force and to the common practice;
- poor judgment in the case of mere compliance with the minimum hygiene standard defined by the laws or regulations in force.

Each qualitative judgment has been linked to a quantitative score: 3 for good level, 1 for the critic and 0 for the poor. It is clear that the end of this kind of articulation of the judgment is to improve the current design practice beyond the legal requirements, assuming that if these are not fully satisfied the project would be not considered suitable. The judgments obtained at the level of the 15 criteria contribute to the definition of each macroarea's judgment (good, critical, insufficient) and to the final evaluation of the project analyzed (good, critical, insufficient). However, it is important to highlight that since the 15 criteria do not all have the same influence on the health status, they have been appropriately weighted. Specifically, to each criterion has been assigned a weight according to both health impact (low = 1, medium= 2; 3 = high) and to the number of components of the health status involved (physical well-being, social well-being, psychological well-being). The weight of each criterion, understood as its impact on the individual health, is given by the product of the scores thus obtained, subsequently normalized with respect to the sum of the weights.

The score of each area of evaluation is given by the weighted average of the scores obtained by each criterion, while the total score of the project is obtained from the weighted average of the each assessment area' score.

On the basis of the minimum and maximum scores 3 intervals of the rating scale, were identified which correspond to three different performance judgment: insufficient if the score is between 0 and 1; critical if it is between 1 and 2; good if it is between 2 and 3. In order to support the evaluation process and to facilitate the communication of the performance' level of the projects evaluated, an Excel software was developed (METH_vers01).

It is important to note that the proposed methodology to be used in its entirety by evaluating each criterion through the sub criteria and their judgment and not merely attributed to the reading of the final numerical data. Starting from the application of the METH on 50 case studies, it was noticed that in some sporadic situations specific criteria could not be considered. Thus was introduced the possibility of excluding the criteria to be not regarded as applicable. In the case of the absence of one or more criteria, the criteria's weights are automatically recalculated by the system.

The program also develops different graphs that can effectively communicate the outcome of the assessment, the strengths and the weaknesses of the projects evaluated: a radar diagram that shows the score obtained by each assessment area in the range between 0 and 3, a histogram showing the overall score, a histogram showing the distribution of scores for each area of assessment.The METH developed in collaboration with the ABC Department of the Politecnico di Milano and ASL Milano, has been tested on 50 projects related to buildings located in the city of Milan. The building projects on which it was decided to test the instrument were selected on a first sample of around 100 projects actually submitted to the ASL Milan for the mandatory hygiene opinion . The selection was based in order to include different building types, as hospitals, nursing homes and similar; schools (of different ages); homes, offices, buildings for the leisure and sports; retail. The application of the evaluation tool, carefully documented at every stage in order to have an adequate feedback, took about 6 months of work.

Each case study was analyzed by focusing on the description of the project, the location, the type of intervention (new construction, redevelopment total or partial), the qualitative judgment (15 criteria), the outcome of the analysis (matrix and graphics) and any comments found. The objectives of the trial were different: in the first place was important to verify the consistency of the assessments made by METH with the guiding principles of the experience. Consequently, for each case study carried out a comparison between the assessments made by METH and the hygiene opinion defined through the traditional assessment procedure ASL mostly based on to the subjectivity and the limited experience of technicians. Secondly, it was important to assess the applicability of the instrument, any critical and timing of use of the same.

Finally, the application of the tool has highlighted the current level of the quality and hygiene performances of construction projects. The evaluation tool it should also enhance the design healthier and more livable buildings beyond the mere compliance with the law, often outdated, contradictory or inadequate to ensure high level of indoor air quality.

Results and discussion

From the application of the evaluation tool to the case studies, it has emerged that in all cases the assessments made by instrument have touched all the major issues able to influence directly and indirectly on comfort. The strengths and weaknesses highlighted by the METH were greater, more complete and consistent than the traditional system linked to the experience and subjectivity of ASL assessors.

However, it was found that in some rare cases of projects evaluated (8%) certain criteria were not evaluable. For example the criterion parking or green space criterion in the case of a redevelopment of a surgical unit in a health facility: the endowment of green spaces and car parks in fact depends on the entire building project – all the hospital and not only the redevelopment the individual department-block. For this reason, in order to make the tool broadly applicable, it has been introduced the possibility to exclude from the assessment system (on the basis of a specific motivation) those criteria that “cannot be evaluated”. The application has also highlighted the need to request some technical integration to designers, as the sub-criteria are often not deeply explicated as it emerges from the technical reports traditionally delivered to the ASL. Specifically, the 28% of cases were judged as insufficient for the presence of sub-criteria that were not assessed due to the lack of documentation (90%) and for the presence of criteria not applicable (10%). Only for the 40% of the cases, the documentation has been considered sufficient and comprehensive for the evaluation of METH, an aspect that highlights the lack of attention to some specific issues. In the above mentioned cases, the instrument has detected simple, effective and rapidly implementable.

By comparing the assessments developed by different technicians on the same projects it has been possible to verify the objectivity of the instrument. Regarding the results of the application, the analysis has showed that among the cases analyzed, the 84% had achieved an overall low judgment, the 12% a critical one and only the 4% has pursued a good judgment. In particular, as regards these latter cases, it is possible to observe that has been paid a great attention to the following thematic areas: the indoor air quality, waste and resources and quality of service, while the most overlooked topics seem to be outdoor quality and quality of the project. Furthermore, by considering the prevalence of judgment “insufficient”, it must be highlighted that it does not mean that the project is not consistent to the regulations but simply that it was achieved the minimum standard neglecting the concept of quality and prevention. In this sense the use of METH should gradually address to design healthier buildings and more livable beyond the mere compliance with the regulations. The use of an Excel software could be considered as very effective as it allows to clearly focus on the strengths and weaknesses of the projects under evaluation, enhancing the introduction of appropriate corrective actions (short-term strategies) and addressing interventions towards the achievement of higher levels of sustainability (long-term strategies).

Concluding remarks

The need to promote health starting from the quality of the built environment, has led to the definition of a multi-criteria evaluation system with the aim of supporting the preparation of the hygiene opinions the ASL are called to draw about construction projects.

As for the efficiency, rapidity and clarity of sanitary assessments, testing of the tool gave a positive outcome and the implemented version of the METH is currently being used by the ASL Milano. For this reason, it is hoped that the METH will soon be also adopted by other Italian ASL calls to the evaluation of projects.

Keywords: assessment, comfort, health, hygiene, projects

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EVALUATION OF THE SOURCES OF ULTRAFINE PARTICLES IN RESIDENTIAL INDOOR

Extended abstract

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Background

While we often consider the effects of outdoor pollution on our health (Avino et al., 2011), we rarely think about how we are exposed to inside our home. In fact, even though there is a plethora of outdoor UFP sources, including vehicle emissions and outdoor air pollution, studies suggest that indoor sources are greater than outdoor sources for a typical non-smoking suburban consumer (Wallace and Ott, 2011). Nowadays, a person spends his time among his home, transportation and workplace leaving essentially in indoor environments. Basically, a person spends over 90% his time in indoor environments. In this case people are exposed to different gaseous and particle pollutants causing dangerous health effects. In this case, ultrafine particles are airborne particles that can cause personal discomfort and health reactions when inhaled by the occupants of a home. Fine particles show more immediate effects while ultrafine particle show more delayed effects on mortality (Air Quality Sciences, 2011).

During these last years, several studies have investigated the effects of particles in indoor environments, not only industrial as well as residential. In particular, a large number of sources are identified: among the most significant sources it should be considered tobacco smoke, cooking, fuel used for cooking and domestic heating (e.g., kerosene, wood). Other possible sources are anthropogenic, related to human activities in a house, including the resuspension of particulate matter from people and pets, activities such as dusting and vacuuming, the shower, the operation of humidifiers, electric motors.

Internal and external sources contribute and strongly influence the concentration and composition of the particles in the indoor environment. More information on the emission characteristics are usually available in the literature, such as the emission factors of the particle sources both in the ambient air and the indoor environment. However, the quantification of emissions from indoor sources is very important for the evaluation of human exposure to total particles.

Ultrafine particles (UFP) are defined as particles in the air that are less than 100 nanometers in size. Because of their small size, these particles can easily infiltrate the bloodstream and contribute to negative health effects or inhaled and travel deep into the human lung. It is important to study these particles, as people tend to spend most of their time indoors.

Airborne particles can be classified into three modes, according to their diameter and formation mechanisms, each of which may have very different sources and composition (Nazaroff, 2004; Manigrasso et al., 2012):

- ✓ nucleation mode. Measuring less than 100 nm, these are the UFP. They are formed by nucleation. These particles consist mainly of primary combustion products and reactions between gaseous compounds, and can grow in size either through condensation, when additional vapors condense on the particles, or through coagulation, when two or more particles combine to form larger particles.
- ✓ accumulation-mode. Particles receive this designation when they grow to a size of between 0.1 μm and 2.5 μm in diameter. They originate from primary emissions, chemical reactions, condensation, and coagulation.
- ✓ coarse-mode particles. These particles measure greater than 2.5 μm in diameter, and are most frequently generated by mechanical processes.

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In this paper we have focused our attention on the submicrometric fraction, in particular in the fraction 6-560 nm and we have investigated the particle concentration levels and the relative granulometric profiles during routinely operation occurring at home.

Objectives

Even if the information on this topic is relevant, the investigation of the release of UFPs from domestic activities is important for different reasons: (i) analyzing the impacts of UFPs on indoor air quality, (ii) assessing the personal exposure to ultrafine particles, and (iii) providing safe guidelines for activities in house. This article investigates the release and physical characteristics of particles during some popular operations occurring in a house. It should be noted that the focus of this study is on the particle numbers for determining the particle dynamic and behavior in relationship to selected sources and processes whereas chemical characterization or exposure quantification is out of the scope of this work.

Outline of the work

This work is would like to highlight preliminary information on the task related to the presence of submicron particle in indoor environments and how this pollutant can modify and influence the indoor air quality evaluation.

Factors governing indoor particle concentrations include direct emissions from indoor sources, ventilation supply and infiltration from outdoor air, deposition onto indoor surfaces, and removal from indoor air by ventilation and filtration. In some circumstances, transport and transformation processes within indoor environments may also influence particle concentrations (Nazaroff 2004). Our experiments were performed minimizing these occurrence.

Preliminarily, the effect of outdoor sources was investigated also considering our studies in this field; after the investigation was divided according the typical residential indoor lifestyles. Our concentration was focused in the predominant occurrences such as cooking (breakfast, lunch and dinner), cleaning and no (nighttime) operations. The measurements were performed in regards of the background measures performed at the beginning. These initial measures allowed to determine the steady-state of the area investigated and to correlate to them every determination carried out.

The final objective of this research will be the determination of the effects of each single source on the submicron particle concentration and the granulometric size profile as well (basically, a source apportionment of the different source affecting the residential indoor air quality).

Methods

Measurements were performed for studying submicrometric aerosol number-size distributions and their fast-evolution characteristics in different indoor house-environments where people doing different activities are usually exposed. The ultrafine measurement was conducted in a kitchen, living room and bedroom. During every measure the weather and the room condition was monitored for avoiding the influence of external parameters to the indoor air quality. The only anthropogenic sources were the domestic heating whereas the windows were opened after each measurement for 20-30 min allowing a rebalancing of the room atmosphere.

Aerosol number-size distributions were measured by means of a TSI Fast Mobility Particle Sizer (model 3091, FMPS, Shoreview, MN, USA) (Manigrasso and Avino, 2012; Manigrasso et al., 2013). The instrument counts and classifies particles, according to their electrical mobility, in 32 size channels, in the range from 5.6 to 560 nm, with 1 s time resolution. FMPS operates at a high flow rate (10 L min^{-1}) to minimize diffusion losses of UFPs. It operates at ambient pressure to prevent evaporation of volatile and semivolatile particles.

Results and discussion

First, we evaluated the contribution of the background of the investigated area before performing particle measurements in a house off home heating and cooking is not working. Fig. 1 shows profiles of submicron particles in the range 6-560 nm: it is interesting to note the presence of three mode, the first around 11 nm, the second (less pronounced) around 34 nm and the third around 70 nm.

In Table 1 the concentration of submicron particles in different intervals (total concentration, i.e., 6-560 nm; 6-16 nm; 16-560 nm) and for the situations studied, are reported. In the case of the background measurements, the total particles in the granulometric range of 6-560 nm are constant (coefficient of variation 7.2 %) with a high particle level (229,000±17,200 particle cm^{-3}). This high level is due mainly to the fraction 19-560 nm which represents about 87% of the total concentration while the fraction of particles 6-19 nm presents a much higher variability (coefficient of variation 25 %) due to itself nature (fraction with particles with a high capacity of aggregation and condensation). The ratio between the two fractions is approximately 7.

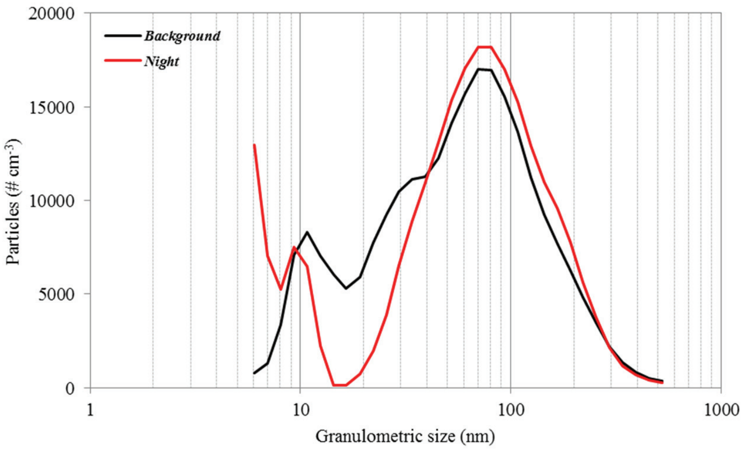

Fig. 1. Particle profile during background and nighttime measurements.

Table 1. Particle concentration during the different measurements performed (BG background; NT night time; BF breakfast; CL cleaning; LC lunch; DN dinner).

Particle	*BG*	*NT*	*BF*	*CL*	*LC*	*DN*
Total (6-560 nm) (# cm^{-3})	229+17	254+17	980+92	374+150	1273+694	196+14
Fraction 6-16 nm (# cm^{-3})	30+8	37+12	652+778	141+87	934+635	37+13
Fraction 16-560 nm (# cm^{-3})	199+13	216+9	328+174	233+69	338+110	159+7
Ratio 16-560 to Total (%)	86.8	85.3	33.5	62.2	26.6	81.1

The presence of these modes characterizes the measures in residential indoor without emission of anthropogenic and/or natural sources affecting the profiles. In fact, the background profile representation will be very similar to that obtained from measurements performed during nighttime, when, once again, there are no external interference or domestic heating or other heating sources in function. It can be noted two well-marked modes, at 9 nm and 70 nm, while it could be extrapolated a very intriguing mode with a maximum at a granulometric size below 6 nm (Fig. 1). The ratio between the two fractions decreases slightly (5.3) while the 16-560 nm fraction is still predominant (82 %).

The situation changes dramatically in the presence of sources and/or anthropogenic activities. Fig. 2 shows the profiles of submicron particles during the main activities characterizing a residential life, i.e., breakfast, cleaning, lunch and dinner. Each activity is accompanied by the use of the relative equipment (e.g., vacuum cleaners) or ignition stoves. In particular for the latter case the three main meals are separated because each of them is different in the load in terms of time and temperature that are reached.

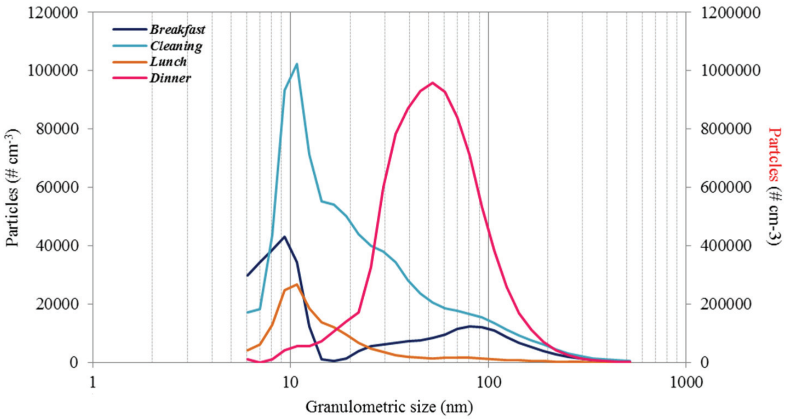

Fig. 2. Particle profile during breakfast, cleaning lunch and dinner measurements.

Particle levels are totally different from those determined during background and nighttime measurements (Table 1), but also the profiles are completely different, even between them (Fig. 2; please, note that the profile “dinner” is on the secondary y-scale).

The first three profiles (breakfast, cleaning, lunch time) are quite similar in terms of levels and trends even if during the cleaning procedure high concentration levels of particles between 10 and 30 nm are reached (ratio between the two fraction is 2 whereas total concentration particles are formed by 62 % of particles in the range 16-560 nm). Both the profiles are characterized to have a peak around 10 nm. This peak is totally absent in the profile "dinner" where the cooking is more strong as well as the cooking time is longer than the other two situation (breakfast and lunch time). This profile, almost Gaussian, is characterized by a single mode (around 50 nm) and very high levels of particles in the range 20-140 nm. Further, the ratio between the two fractions is around 20 and the main portion of the total concentration particles is due to the 16-560 nm fraction (average 82 % with maximum 95 % of the total during the maximum peak). In this case, the effect of the fuel used for cooking is relevant for the particle concentration levels.

Concluding remarks

The indoor air quality is an important task because it regards almost all the population. There are many factors affecting the air quality but the domestic heating, especially using gas (i.e., methane) as fuel, is one of the most important source of particle formation and aggregation. There are many factors that people cannot control, including the weather and traffic, but there are ways to reduce indoor air particles (for instance, keeping windows closed during heavy traffic time and using air conditioning, an alternative to opening a window). Finally, another important way to reduce exposure to particles is to avoid smoke and secondhand smoke (study in progress).

Keywords: domestic heating, FMPS, indoor, residential, ultrafine particle

Acknowledgements

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CAR COMMUTERS' PERSONAL EXPOSURE TO ULTRAFINE PARTICLES

Extended abstract

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Background

Ultrafine particles (UFPs, diameter < 100 nm) exposure has been associated to both short and long term health effects, however the specific or enhanced toxicity of UFPs with respect to other particle fractions has not been established yet. UFPs can be generated by indoor sources or can affect indoor environments due to infiltrations of particles outdoor generated. The main sources of UFPs are combustion related emissions, mainly, in urban settings, those from vehicles. People spent a minority, largely variable, though significant part of their time inside passenger cars. Recent studies (carried out in the US, Australia, central and north Europe) show that in-car exposure could significantly contribute to total integrated exposure estimates (Knibbs et al., 2011). In-car exposure studies in the Mediterranean basin area are scarce (e.g. Tartakovsky et al., 2013). To date, only one study assessing inside cars exposure within an Italian large urban settings is available (Cattaneo et al., 2009).

Rome, the Italian largest and most populated municipality with 2,724,347 residents in 1,285.3 km^2, is characterised by alternate zones of very high urbanisation and population density and zones where urbanization is lower or absent.

The main sources of particles originate from road traffic combustion. Traffic flow is rather high during work days with two rush hours (morning and late afternoon). Traffic flow easily exceed 20,000 vehicles per day in the main streets. Since 2001 particles number concentration (PNC), the parameter most used to estimate UFPs exposure, has been continuously measured in Rome, starting from the framework of the HEAPPS study (Aalto et al., 2005). A previous study shows a statistically significant decreasing trend for primary gaseous pollutants and PNC measured in Rome, mainly due to the progressive shifts towards vehicles meeting the most stringent European emissions standard, which was enhanced by national and local measures (Cattani et al., 2010).

To overcome some limitations of long term UFPs exposure studies, based on one or few outdoor measuring sites, data on indoor exposure to UFPs as well as their outdoor spatial variability, still lacking in Italy, are needed. Within the framework of the ongoing VIIAS project, aimed to assess the air pollution impact on health, this pilot study aims to assess for the first time in Rome, real-world UFPs personal exposure during systematic travel home to work of mid aged, roman office building employees as well as to estimate the contribution of in car exposure to the total integrated exposure.

Methods

To measure PNC four hand-held, real time condensation particle counters (CPC) were used (model 3007, TSI, MN, USA; minimum detectable particles size 10 nm). Measurements time resolution was 1s.

Two routes were selected for this study, with different origin and same destination. The first (R1) was 12,6 km long, from the city centre to the city south, through an high traffic urban street (three carriageway). The second (R2), 21,3 km long, has origin in the suburban periphery and gets the same destination throughout the Great Ring Junction (GRA), a dual-carriageway, three-lane, toll-free highway. Two vehicle ventilation modes were studied:

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- air conditioning (AC) and ventilation fan switched off and driver's window partially opened (WIN MODE);
- AC switched on, windows closed and cabin air internal recirculation switched on (REC MODE).

All experiments were carried out during working days.

Aimed to compare the in-car PNC with other indoor environments, PNC measurements have been undertaken in 3 private homes and one office building (during typical 8 hours working days). The investigated microenvironments were the kitchen (during cooking and while eating breakfast or dinner), the living room and the bedroom (during night). Measurements have been carried out following one selected inhabitants daily activities as the in-car experiments.

All the people involved in this study were non smokers. Moreover measurements have been carried out in 31 outdoor sites, to estimate spatial variability of outdoor PNC. Each site measurement lasts one week. Each day, three sampling periods have been selected, lasting two hours each, to estimate a daily average.

All the data collected were used to build a reliable integrated UFPs total exposure estimate. Descriptive statistics have been calculated starting from 1min averages of the 1s riding data set. The statistical analysis of collected data was performed by means of the *R* software (*R* Development Core Team, 2011).

Results and discussion

28 runs were performed during late spring/summer 2013. Average time spent in car during R1 was 40 min (±8 min) while average R2 lasted 28 min (±7 min) excluding an exceptionally long trip due to high traffic (115 min). About half of the R2 time (13 min ± 6 min) was spent in the GRA highway. The average R1 speed was 18.9 km h^{-1}, while the average R2 speed was 45.6 km h^{-1}.

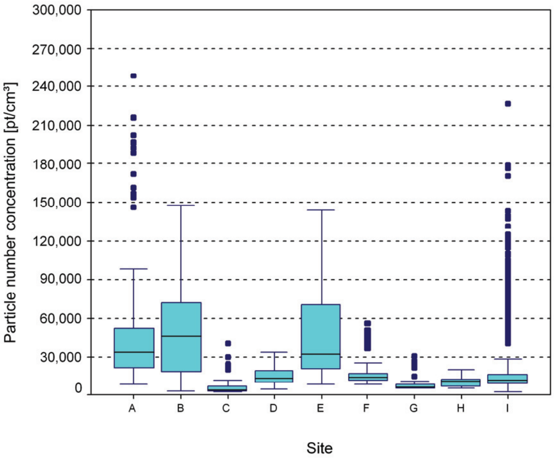


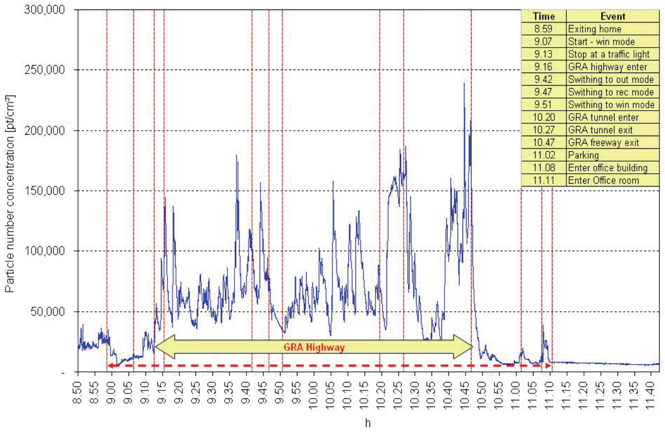
Fig. 1. Box plot of PNC (1 min averages) measured in several microenvironments: R1 WIN MODE (A); R2 WIN MODE (B); R1 AC MODE (C); R2 AC MODE (D); kitchen during cooking (E); living room (F); bedroom, night (G); office building (H); outdoor all measurements in 31 sites (I).

The PNC highest median was found during R2 trip in WIN MODE (46,293 particles cm^{-3}); R1 trip PNC median in WIN MODE was 33,520 particles cm^{-3}. Both data sets showed remarkable variability. Interquantile range was respectively 52,727 particles cm^{-3} and 30,768 particles cm^{-3}. The differences found are likely due to differences in traffic parameters between different routes. The R1 trip is characterised by lower average speed due to a number of traffic lights during the route; some tract was also often very busy. About half (13 min) of the R2 average time is spent on the GRA freeway, characterised by higher speed allowable, no traffic light, higher traffic volume and different vehicles composition with higher heavy diesel traffic volume. PNC median calculated over the R2 GRA section ranging between 47,994 and 87,471 particles cm^{-3}, in the WIN MODE.

In vehicles PNC can be efficiently reduced using the AC with recirculation (see Fig 1, box plot C and D, REC MODE). Also variability was reduced; the differences between the two routes were still evident. Personal commuters habits play a major role determining in-car exposure; particularly using AC (with or without recirculation) or keeping the car windows open. The last option is often the primary choice during the warm season in Rome, lasting from April to October, due to prevailing warm temperature during the morning day. Extensive use of AC is limited to the warmer months (i.e. July and August). These conditions are very different from those typical in central-north Europe, where the main studies available have been carried out. Using AC with recirculation raises the issue of CO_2 accumulation inside the vehicle's cabin: previous findings show that in a 30 min trip CO_2 concentration can easily increase over 2,000 ppm (e.g. Tartakoswky et al., 2013).

Both indoor and outdoor PNC measured in several other microenvironments were found to be much lower than those found in car cabins. The only exception was PNC median measured indoor in the kitchen during cooking

(32,296 particles cm^{-3}). Note that the kitchen data set include time spent during cooking and time spent after cooking during eating and cleaning activity. We observe that the mean time needed to PNC fall down to background indoor concentrations was 30 min.



Time	Event
8.59	Exiting home
9.07	Start - win mode
9.13	Stop at a traffic light
9.16	GRA highway enter
9.42	Swithing to out mode
9.47	Swithing to rec mode
9.51	Swithing to win mode
10.20	GRA tunnel enter
10.27	GRA tunnel exit
10.47	GRA freeway exit
11.02	Parking
11.08	Enter office building
11.11	Enter Office room

Fig 2. Pattern of PNC during a traffic congestion event; R2 route

Fig. 2 illustrate the short term traffic pattern during a traffic congestion event (measurements time resolution 1s). The highest spikes have been observed when the car was driven behind a heavy duty vehicle or older diesel cars. In car PNC decreased rapidly after switching from WIN MODE to REC MODE. Crossing the tunnel at reduced speed allows the PNC to rise up to 150,000; PNC was higher then 100,000 particles cm^{-3} until the tunnel exit. Mean PNC within the GRA tract of the trip was about 8 times the contemporary mean outdoor background PNC. Traffic congestion events though if occurs in a minority of days during the year, are quit frequent particularly during morning and late afternoon rush hours.

To estimate personal exposure to UFP we used the available micro-environmental concentrations and the time spent in these microenvironments from literature time–microenvironment–activity patterns (see Table 1).

The estimate was related to mid aged (30 – 65 years old), office building employees, that travel systematically home-to-work by car within the Rome municipality borders. Average time spent daily driving in Rome was estimated 74 min; this Fig. accounts for about half of systematic home-to-work travels (ANCI 2009); median total time spent indoor at home for Italian people was estimated by Schweizer et al. as 13.1 hours per day (ranging between 8.1 h d^{-1} – 22.5 h d^{-1}) and time spent indoor at office as 7.50 h d^{-1} (0.3 h d^{-1} – 12.3 h d^{-1}), (Schweizer et al., 2007).

Table 1. Estimated relative contributions of each considered microenvironment to UFPs exposure based on R1 route experiments

Microenvironment	Median time spent (h d^{-1}; %)	Median PNC (particles cm^{-3})	PNC exposure (particles cm^{-3} h)	Relative contribution to total integrated exposure (%)
In-car WIN MODE	1.1 (4,6%)	33,520	36,872	12.4%
Outdoor	2.3 (9.6%)	11,876	27,315	9.2%
Home - bedroom	7.0 (29.2%)	6,602	46,214	15.5%
Home - kitchen	1.5 (6.3%)	32,296	48,444	16.3%
Home - living room	4.6 (19.2%)	14,039	64,579	21.7%
Office	7.5 (31.3%)	9,934	74,505	25.0%

In this scenario commuting by car relative contribution to total integrated exposure became as important as others microenvironments, where time spent was higher but average PNC was much lower (e.g. bedroom or office). The effective contribution was strictly dependent upon drivers' habits and routes followed during travel. The R2 routes determine an higher contribute to total exposure (16.3%). Using AC plus recirculation allows for strongly reduce the in-car contribution to total exposure (1.8% for R1 route, 5.4% for R2 route).

Concluding remarks

Our study suggests that commuting by car significantly contributes to UFPs total integrated exposure. Short term high PNC and large variability characterised the in car cabin pattern of exposure. Drivers habits like driving with open windows is a key factor on determining exposure levels; driving with AC and cabin air recirculation completely changes the exposure pattern. Meteorological factor is the driving force for the commuter's choice. To improve the estimate, data collection during both warm and cold season, and a large scale survey on commuters' habits are needed.

Keywords: indoor exposure, ultrafine particles, vehicle occupants exposure

Acknowledgements

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OUTDOOR/INDOOR PARTICLE INFILTRATION FACTOR IN RESIDENTIAL BUILDINGS AND ITS RELATION WITH URBAN AIR QUALITY

Extended abstract

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Background

The majority of the people in the world lives in urban areas. According to the United Nations Population database, earth's population became more urban than rural in 2007 (UN-ESA, 2012), while, considering exclusively the more developed countries, the urban/rural ratio was greater than 1 since the '50s. Nowadays (2010) the percentage of urban population in developed regions is 75% and it is estimated that this percentage will reach 86% by 2050. Living in urban areas generally means spend a large amount of time indoors (homes, working places, cars or public transport vehicles) but, as well known, the information on air pollution inside buildings is very poor as compared to ambient air quality data provided by monitoring networks. So, necessarily, most epidemiological studies estimate personal exposure on the basis of outdoor concentration levels instead of indoor, really breathed, pollutants

Objectives

Human exposure to atmospheric pollutants in indoor environments is regulated by external pollutant penetration efficiency, time variability in air exchange rate and by internal source emissions. In view of this, the main objective of this work was to define an efficient, and easily reproducible, approach to overtake the basic indoor/outdoor concentration ratio, to evaluate air pollution in residential buildings and to estimate the particle infiltration factor without the need of sampling other gaseous pollutants to distinguish between internal and external sources.

Outline of the work

In this study we tried to assess the relationship between indoor air pollution and outdoor air in the city of Rome using, as an indicator, the Particle Number Concentration (PNC) measured in naturally ventilated houses for a year, respecting usual lifestyle and personal behaviours of the inhabitants; a record of the most influential activities of residents (opening/closing time of windows, cooking, cleaning or ironing) was kept during the sampling time.

The sampling devices used during the campaign were two TSI P-Trak Ultrafine Particle Counter (indoor and outdoor sampling, co-located in residential buildings, measuring particles between 0.02 and 1 μm in particle diameter, D_p, with 1-minute resolution) and one TSI 3022A Condensation Particle Counter (outdoor sampling, located in the Italian National Health Institute, ISS, monitoring station, measuring particles between 0.01 and 3 μm in particle diameter with 1-minute resolution).

Because of the limited availability of sampling instruments, simultaneous indoor and outdoor PNC measurements were taken one home at a time for seven consecutive days, six hours per day, every month from the first of July 2010 to the end of June 2011 to represent the complete year including the four-season meteorological profile.

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The selected sampling sites were two residential homes in Rome (the first one in a semi-central quarter, the second one in the eastern suburban area of the city) both located at eighth and last floor of residential buildings, with natural ventilation and no smoker inhabitants.

A third particle counter, located in downtown Rome, at the Italian National Health Institute (ISS) air monitoring station, provided continuous PNC measurements and it was used as the reference site, while the concentration data of particulate matter and primary gaseous pollutants recorded by the monitoring network of Rome, consisting of 13 monitoring stations that measure the standard 2008/50/EC Directive parameters, were taken into account to evaluate the variation in urban air quality patterns during the sampling periods and their relation with internal air quality.

Methods

During the four-season indoor and outdoor particle number concentration monitoring we observed that indoor source events (i.e. cooking or cleaning) can cause indoor/outdoor ratios to exceed one, particularly for less ventilated periods (winter). So the indoor PNC time series, in the absence of internal sources, were reconstructed in this work to better estimate the home infiltration factor.

The general infiltration factor equation is (Hänninen et al., 2010):

$$\mathrm{F_{Inf}} = \frac{\mathrm{C_{pin}}}{\mathrm{C_{out}}} = \frac{\mathrm{P \cdot Aer}}{\mathrm{Aer + k}} \tag{1}$$

where: F_{Inf} is infiltration factor (pt/cc); C_{pin} is penetrated particle concentration (pt/cc); C_{out} is ambient particle concentration (pt/cc); P is penetration efficiency (dimensionless); Aer is air exchange rate (h^{-1}); k is deposition rate (h^{-1});

The variability in the particle infiltration between different days, in buildings and between buildings, is mainly caused by the air exchange rate (in buildings with natural ventilation, the air exchange rate depends on the temperature difference between the indoor and outdoor air, the wind pressure outside the building and whether the occupants keep windows open or closed). Furthermore penetration efficiency and deposition rate are influenced by the geometry of the homes and air intake ducts and leaks, other than by the specific properties of the sampled aerosol (Hänninen et al., 2010).

For our objective was convenient to start from the indoor particle concentration that can be described as follow (Hänninen et al., 2004):

$$\mathrm{C_{in}} = \frac{\mathrm{P \cdot Aer \cdot C_{out}}}{\mathrm{Aer + k}} + \frac{\mathrm{Q_{is}}}{\mathrm{(Aer + k)V}} = \mathrm{F_{Inf} C_{out} + C_{ig}} \tag{2}$$

where: C_{in} is indoor particle concentration (pt/cc); C_{ig} is indoors generated particle concentration (pt/cc); Q_{is} is emission due to indoor sources (pt/h); V is home volume (m^3).

Consequently the infiltration factor, F_{Inf} is expressed by (Hoek et al., 2008):

$$F_{Inf} = \frac{C_{in} - C_{ig}}{C_{out}} \tag{3}$$

Among these parameters, only the ambient particle concentration (C_{in}, C_{out}) were variables routinely measured, whereas the indoors generated particle concentrations, C_{ig}, had to be estimated following these steps (schematically represented in Fig. 1):

- observe daily time series of indoor and outdoor PNC, comparing concentration peaks with the record of internal influential activities;
- identify indoor concentration peaks, separating those clearly related to outdoor sources from peaks ascribable to recorded activities of the inhabitants;
- extrapolate the baseline of the peaks generated by indoor sources;
- indoor peaks present a dilution time longer that outdoors, caused by the air exchange rate and the geometry of the apartment, and their aspect is typically asymmetric and tailed; therefore it is frequently possible to observe concentration peaks caused by outdoor sources on the tail. In these cases the baseline of the peaks generated by outdoor sources on the peak tailing have to be extrapolated at the same time, this step is illustrated in Fig. 1A and 1B (zoom shot);
- subtract the areas subtended exclusively to the indoor generated peaks obtaining the particle number concentration time series in absence of indoor sources (see Fig. 1C);

- it is now possible calculate, together with the indoor/outdoor concentration ratio, the particle infiltration factor on the basis of measured indoor/outdoor PNC.

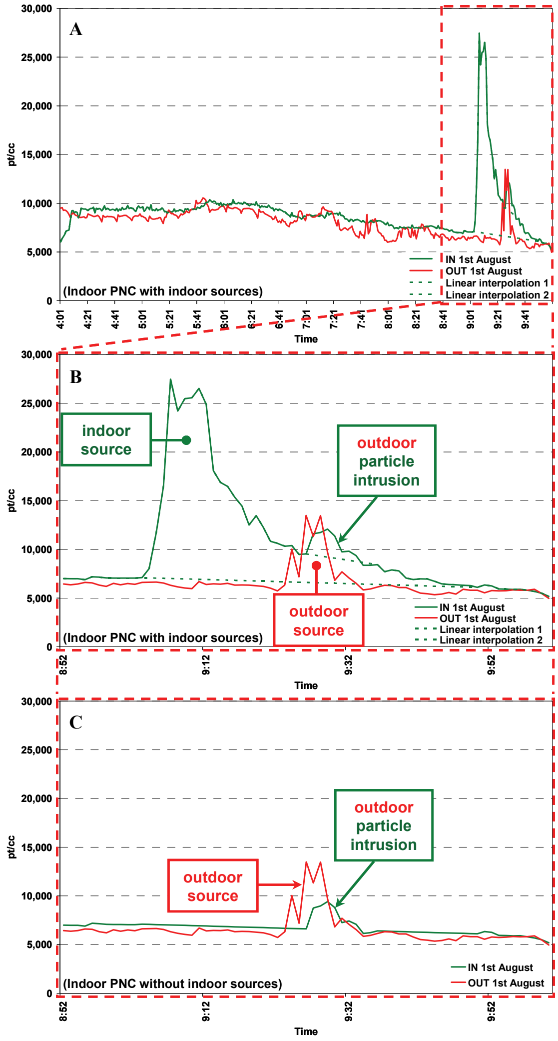

Fig. 1. Schematic representation of the method used for subtracting the internal sources (A: indoor, green, and outdoor, red, PNC profile in a summer day; B: magnified part of A with internal and external source related peaks; C: resultant profile after subtraction of internal sources)

Results and discussion

In this campaign we observed clearly different seasonal patterns in indoor and outdoor PNC; a good correlation between average indoor/outdoor daily values but huge differences in concentration profiles considering a shorter time scale between summer and winter (when the air exchange rate is slower because of different home dynamics; i.e. windows left open/closed).

It is remarkable that, during the whole year, a good correlation between PNC registered outdoors in the two sapling sites and the downtown reference site (distant respectively 3 km, ISS-H1, and 6 km, ISS-H2) was obtained (see. Fig. 2A); furthermore a good correlation between PNC registered indoor in the same sampling sites and the main primary gaseous pollutants measured in the urban network stations (see Fig. 2B) was registered.

Concerning the indoor/outdoor ratio compared to the particle infiltration factor, we applied the method for subtracting the internal sources discussed above to the entire sampling period, obtaining always an improvement in correlation between indoor and outdoor data (up to +0.42 at Home 1 during May 2011). The infiltration factor calculated on the basis of the reconstructed series showed an evident seasonal variation, with a minimum during the winter: $F_{inf} = 0.60$ at H1, $F_{inf} = 0.63$ at H2 (see Table 1) and an expected maximum during the summer (respectively $F_{inf} = 0.95$ and $F_{inf} = 0.99$). These differences were invisible considering the I/O ratio that presented, during several sampling weeks, a value greater than 1.

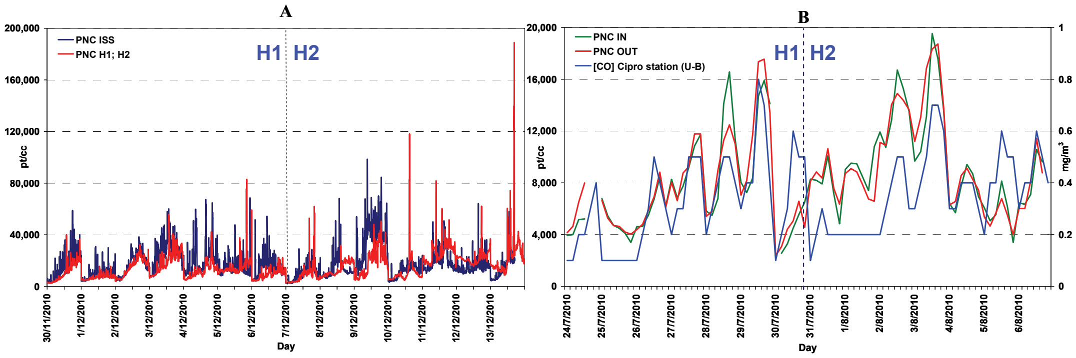

Fig. 2. A: time series of outdoor PNC measured in the two sapling sites (Home 1, Home 2) and in the ISS reference station; B: comparison between indoor/outdoor PNC and carbon monoxide concentration measured in a urban background station belonging to the air monitoring network of Rome

Table 1. Seasonal variation in infiltration factor measured in different homes

Indoor/Outdoor particle concentration ratio vs infiltration factor							
Home 1	I/O_{ratio}	F_{inf}	R^2_{Finf}	Home 2	I/O_{ratio}	F_{inf}	R^2_{Finf}
Summer	0.97	0.95	0.98	Summer	1.01	0.99	0.97
Autumn	0.99	0.84	0.56	Autumn	1.00	0.70	0.62
Winter	0.68	0.60	0.97	Winter	0.82	0.63	0.37
Spring	1.08	0.92	0.45	Spring	1.00	0.90	0.63
Year	0.97	0.85	0.72	Year	0.97	0.80	0.65

Concluding remarks

This paper presents an alternative approach for the determination of the infiltration of outdoor particles in the indoor residential environment based on particle concentration measures carried out with high-temporal resolution. This method allows quantifying the indoors generated particle concentration contributing to the sampled indoor particle concentration, so to better understand the real influence of urban pollution on indoor air quality.

Keywords: indoor air quality, indoor/outdoor particles, number concentration, urban pollution.

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LEATHER PRODUCTION: INDOOR INDICATORS FOR BATING PHASE IMPACT

Extended abstract

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Background

Traditional tanning process*es* for leather production have an important impact both on environmental and indoor conditions. The introduction in the 60s of rotating drums for tanning operations has permitted not only the perfect distribution of chemical agents and dyes the reduction of float volumes, but also a a significant reduction of indoor odour spread. This latter aspect can be further improved.

In the leather industry, the use of poultry dejections (PoDe) was historically abandoned on account of indoor odour impact as well. The use of technical products (TP) derived from PoDe as bating agents in the tanning industry to replace Standard Formulations (SF) was explored at the pilot scale in the LIFE project PODEBA (LIFE10 ENV/IT/365, Use of poultry dejection for the bating phase in the tanning cycle). Both TP and SF contain the proteolytic enzymes needed for de-limed pelt maceration, in order to obtain controlled weakening of the three-dimensional derma structure, through elastin and collagen breaking.

One of the main drawbacks of this kind of recycling is connected to foul smells that are typical of animal dejections but also of the tanning cycle. One of the project goals is to demonstrate how a poultry dejection treatment can reduce odorigen impact on the whole system, taking into account that standard conditions themselves are a source of foul smells (Dall'Ara et al., 2012).

Objectives

The goal of this paper is to present the strategy adopted to demonstrate PoDe deodorization after the treatment, and the evaluation of odor aspects connected with the use of this technical product in the bating phase compared with standard chemical formulations (SF).

Outline of the work

Because of difficulties in measuring indoor modifications or effects on the internal drum conditions (water, pelts and air during 0.5-1 hour rotation), the indoor impact of using TP during the bating phase was assessed by by experts of the tanning cycle (subjective perception), supported by objectively measuring the modification of standard odour conditions (obtained with SF).

The choice was to measure selected Sulphur compounds in TP and in the final bating floats, as incremental source of emissivity. The selection of indicators was made on the basis of scientific literature and technical data related to typical PoDe emissions. As evidenced in BREF (EC, 2003), ammonia is one of the main indicators of PoDe emissions; dimethyldisulphide (DMDS) is an indicator of poultry manure emissions in comparison with other manure generated by other animals (Asdrubali et al., 2005). Moreover, because of their heavy olfactometric impact, two additional sulphur compounds were selected (methylsulphide, and dimethylsulphide, DMS). In the bating phase, Ammonia contribution was not explored because its TP content (< 5%) is much lower than SF content (18%).

Furthermore input materials (TP) were characterized throughout their production: the indicators were detected along the production process, thus enabling the comparison of the final product with the initial conditions.

Methods

Odour emission analyses were performed for:

- TP production, on different type of TP (Poultry manure treated with a patented method and slight modification of it) contained in big bags, just before its use for the tanning test;
- Leather production, Bating phase, on volatile fraction of process wastewater samples (Bating floats), using different types of TP.

The experimental methodology, together with measurement methods used for emission indicators, are summarized in Table 1. First and Second generation TP were prepared by slightly changing the treatment recipe (AMEK, CTI, 2002), in order to select proper TP. Bating agents were tested in 2 different runs: a first run where SF was compared with W (a test without bating agent) and A (first generation TP); a second run where SP was compared with P (second generation TP).

To allow gas monitoring during TP production, a probe consisting of a Teflon piezometer (1,5" diameter) was inserted and left inside different big bags. The probe was closed at the bottom and equipped with a "T" and laterally perforated with small holes. Measurements of the selected indicators were made by gas-chromatograph (GC)coupled with the mass spectrometer (MS) in order to separate the analytes to be characterized, while MS could identify them (GCMS System Mass Agilent CG coupled to MS 5975C MSD, Agilent Technologies, Milan, Italy). Ammonia was detected by a spectrophotometrical method.

For bating floats, the extraction of volatile substances from the aqueous sample was carried out by means of two techniques: in the first run Purge & Trap (8 ml sample were flushed by means of inert gas (He) flow -purging, which was then conveyed into a concentration trap; from there the substances were injected into the GC-MS system using thermal desorption) . In the second run, Head Space (performed with HS autosampler, three grams of float samples were placed in a 10 mL vial heated at 60°C for 1800 s). In both cases, volatile compounds were identified and semi-quantified by same GCMS System Mass.

Table 1. Outline of matrices analysed (TP and bating floats) and measurement methods used for emission indicators.

TP production		***Leather Production: Bating Phase***	***Measurement Methods foremission indicators***
		Bating Floats	
TP 1st generation (A)		W: Without any bating agent SF: Standard Formulation (Biozym MC/N) A: TP 1st generation	Purge & Trap GC-MS
Start	End		
TP 2nd generation (P)		SF: Standard Formulation (Biozym MC/N) P: TP 2nd generation	Head Space GC-MS
Start	End		

Results and discussion

During TP production, the results of emission indicators show a significant reduction in all parameter concentrations, demonstrating a reduction of odour emission in final TP (start-end). In particular, the "emissions" of DMS were reduced by 89% v/v, while concentrations of the DMDS and methanethiol were both reduced by about 99% v/v. The goal of reducing ammonia g emission by 80% compared with initial conditions was achieved.

With reference to bating float characterization, the chromatogram graphs related to the first run are reported in Fig. 1, which represents the overlapping chromatograms: W (1foro-black), SF (2fori-red), A (5fori-blue). The detected substances, corresponding to the chromatographic peaks, were identified by comparing their fragmentations with those stored in the N.I.S.T. library. Among the detected substances the ones of interest were: the carbonyl sulfide (COS), the methanethiol (CH_3SH), dimethyl disulphide (CH_3SSCH_3), and dimethyl trisulphide (CH_3SSSCH_3). The peak areas are directly proportional to substance concentration; therefore, as a first approach, a comparison of odour impact of the three floating baths can be schematized with the peak area ratio. Taking into reference SF, W presented the following ratio: 47%; 25%; ND respectively for CH_3SH, CH_3SSCH_3, CH_3SSSCH_3. Similarly, A presented the following ratio: 259%; 463%; 222% respectively for CH_3SH, CH_3SSCH_3, CH_3SSSCH_3.

The chromatograms related to the second run are reported in Fig. 2, which represents the HS-GCMS chromatograms of bating floats: SF (M1, red), P (P1, green). The chromatograms of the two samples showed peaks with similar heights, indicating similar concentrations for volatile compounds in the two samples SF and P.

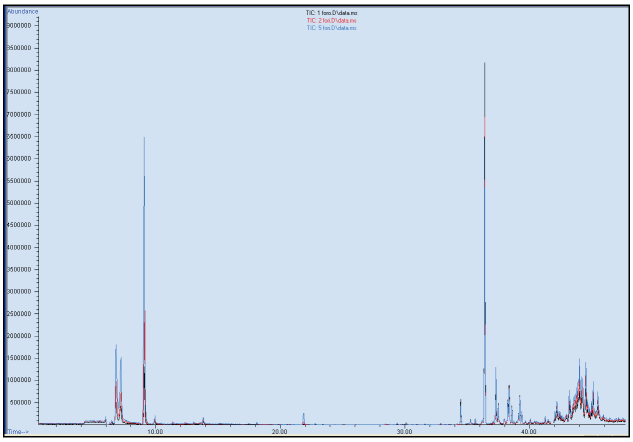

Fig. 1. Representative HS-GCMS chromatogram of overlapping chromatograms W (1foro-black), SF (2fori-red), A (5fori-blue).

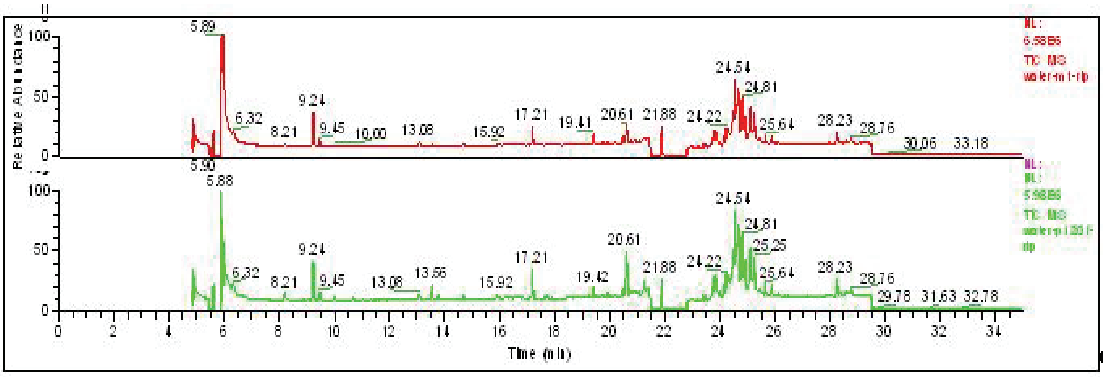

Fig. 2. Representative HS-GCMS chromatograms of bating floats: SF (M1, red), P (P1, green).

The assessment of odour impact modifications was made by technicians and process developers as far as bating process conditions compared with standard process (SF), they are summarized as follows:

- the W test showed foul smells during the bating process as well as bad quality in the final tanned leather;
- the A test showed foul smells during the bating process, but good quality of tanned leather;
- the P test showed very similar smells to SF during bating process and good quality of tanned leather;
- the A and P tests had no odour impact on finished leather, just as SF.

Only second generation TP can assure odour conditions similar to a standard process; nevertheless, all bating agents based on PoDe had no odour impact on finished leather and do not influence them.

PoDe treatment, which is necessary to assure final product sanitation, is a key factor to produce a TP suitable for its use as bating agent in leather manufacturing.

At the moment, according to tanning experts, the results of these activities indicate the reduction of olfactive impact in the use of TP in comparison with first generation TP. In addition they do not show a change in bating phase odour impact taking into reference SF with the use of second generation TP. These results, together with the positive effects on leather structure and cleaning surface, indicate that second generation TP is suitable for tannery

Concluding remarks

The strategy adopted for the control of odor aspects connected with the use of poultry dejections PoDe in the bating phase to replace standard products (chemical formulations containing proteolytic enzymes as well) was useful to select the proper optimized TP and its process production. In fact, second generation TP affords a reduced olfactive impact in comparison with first generation TP samples, and has a very similar impact compared to SF. In addition, TP performs well as a bating agent, in terms of leather structure and cleaning surface. All poultry manure samples had no impact on finished leather (as confirmed by their historical use).

The selected measurement system checking TP production and bating phases in leather production have led to analytical results in agreement with subjective assessment by the experts and are, therefore, indicative of actual indoor conditions.

Keywords: bating phase, leather production, odour impact, poultry dejections

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ADVANCED TOOLS FOR THE MONITORING AND CONTROL OF INDOOR AIR QUALITY AND COMFORT

Extended abstract

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Background

New and refurbished buildings in Europe have to meet requirements concerning thermal insulation and air tightness, as well as primary energy demand for heating, illumination, ventilation and air conditioning. In future net zero energy buildings will be the state of the art. The refurbishing to an energy efficient standard leads to tight buildings (whole envelope: windows, walls etc.) and affects the indoor climate. In case of refurbishing the inhabitants or users are not adapted to this new situation. Therefore the air exchange rates could be lower than required if no mechanical ventilation is installed or the system performance is not optimized. Then, in trying to increase the energy performance of buildings, the indoor environment quality is often degraded due to the lack of exchange with the outdoor environment.

People in Europe spend more than 90% of their time indoors (living, working and transportation). In more than 40 % of the enclosed spaces, people suffer from health- and comfortable related complains and illness. Already in 1984 the WHO reported an "increased frequency in buildings with indoor climate problems". The complexity of the problem and the fact of building related symptom clusters were later described as "Sick Building Syndrome" (EPA, 2009). Major symptoms of Sick Building Syndrome observed are allergy, lethargy, headaches, dry eyes, throat and skin. Office indoor air may also be associated with productivity and sick leave of the office occupants (Mendell, 2007). Improving the health and comfort of the European population in those spaces consequently create a huge potential of economic and societal benefits, manifested in increased productivity, reduced sick leave and medical costs, but also by the prevention of potential liabilities. The FP7 European project called Cetieb (Cost-Effective Tools for Better Indoor Environment in Retrofitted Energy Efficient Buildings – www.cetieb.eu) is moving towards this objective. The modular system for the monitoring has been developed in order to measure several parameters such as VOC (Volatile Organic Compound), RGB (Red, Green and Blue) luminance and CO_2. In addition, the system includes the measurement of environmental variables as the thermo-hygrometric comfort using an innovative sensor for retrieving the PMV index (Predicted Mean Vote). The control of the air quality relies on active systems for actuating the mechanical ventilation, with or without bio-filters, starting from monitored variables. Moreover, the development of passive technologies for the control of indoor environments completes the tools set with the use of photo-catalytic plasters for the air cleaning or light materials with low thermal conductivity. The aim of the paper is to present the main research lines of the CETIEB (begin October 2011 - end September 2014) project in this context with a focus on the innovative aspects of the expected results.

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Objectives

The main objective of the project is to develop and integrate innovative solutions for better monitoring the indoor environment quality and to investigate active and passive systems for improving it. The focus lies on cost-effective solutions to ensure a wide application of the developed systems:

- Development of monitoring systems (wireless and/or partly wired) to detect indoor environmental comfort and health parameters. A modular version will be developed to allow end users a quick check of the indoor air quality.
- Development of control systems to optimize the indoor environment quality and energy efficiency. Measures are innovative passive plaster materials using photo catalytic and phase change materials, plant based bio-filters, and active air flow controlling components. Provision of alarm values for action, if automatic control is not sufficient.
- Modeling of indoor environments for the assessment and validation of monitored data to optimize the control parameters and systems.

Monitoring and measurement tools

The CETIEB project is aimed to deliver a cost efficient wireless or partly wired system especially designed for monitoring indoor environment parameters. The monitoring and measurement technologies developed within the project will be a step forward in terms of: (i) provision of cost-effective and simple to use monitoring systems that allow for monitoring of a large variety of indoor environmental factors; (ii) provision of advanced sensor technologies to better measure and assess indoor environment factors with respect to human health and well-being; (iii) Provision of data collection and analysis software that could be used to better monitor, assess, evaluate and control the indoor environment.

Short and long-term monitoring systems require the application of specific sensors. Although a lot of commercial sensors for determining air quality and comfort are available, there is a demand to develop sufficient sensors that are optimised for the monitoring task. This could be with respect to cost-effectiveness or higher accuracy, precision or reliability. Such sensor technologies could be either integrated into the portable wireless monitoring system or could be integrated into active control systems for permanently improving the indoor environment. Several types of sensors are being developed within the project, e.g. VOC (with medium and high sensitivity), CO_2, thermal image sensors (infrared sensors for multi-point temperature analysis), and indoor light spectrum.

1. Detection of VOC

One key challenge within the project is the detection and monitoring of Volatile Organic Compounds (VOC) for the assessment of health related parameters. Actually, there is an increasing demand to obtain more spectral information in many gas sensing applications, particularly with regard to the analysis of multi-component mixtures, reducing cross-sensitivities between adjacent and overlapping absorption bands and to lower detection limits. Infrared absorption spectroscopy as a broadband and selective measuring principle potentially fills this gap. Based on substance-specific absorption spectra the discrimination between the components of a mixture and a quantitative measurement of their concentrations is possible. In particular the wavelength ranges of 3 – 5 µm and 8 – 12 µm (mid and long wave infrared) are of interest. The hybrid integration of a bulk micro machined high finesse Fabry-Perot Filter and a pyroelectric detector results in a very compact spectrometer module. Existing instrument designs can be easily adapted to such a tuneable detector. InfraTec has developed such devices for the spectral range of 3 – 5 µm and 8 – 11 µm (Ebermann at al., 2010).

As a VOC representative acetaldehyde (CH_3CHO, peak absorption at 3.65 µm) was measured in nitrogen in the concentration range from 0 to 25 ppm (Fig. 1). The achieved resolution is better than 5 ppm. From literature the maximum values of single VOCs like acetic acid (CH_3COOH) could be up to 2.3 ppm (5698 $\mu g/m^3$) in new showcases or up to 1.9 ppm in storage cabinets (average 4.7 mg/m^3). Therefore the real-time detection of single VOCs is visible if the detection range could be further improved.

2. Illumination

The region of light the eye can see (visible region) consists of light with a wavelength between approximately 380 nm to 780 nm. The obvious way to measure this would be with a spectrophotometer, which measures the light intensity in function of the wavelength at intervals of e.g. 5 nm.

An alternative way is the use of a so called RGB sensor. These sensors are silicon based photo-sensors measuring radiation from 300 nm to 1100 nm overlapping the photonic response of the human eye. The unwanted radiation (IR and UV) needs to be filtered. In addition, Red, Green and Blue filters based on the colour matching functions defined by the CIE are reproducing the RGB values as if they were observed by the human eye. Now, instead of hundreds of values coming from the measurement of the spectrum by a spectrophotometer, only four values are given by the sensor: clear (only filtered for IR and UV), Red, Green and Blue. These values can be transformed into XYZ values in the CIE colour space. Obviously, the filters of the sensors do not match completely the colour matching functions of the CIE and need to be calibrated. Within the CETIEB project such a low-cost sensor solution for light intensity and light spectra was realized. The sensor has been developed to determine the Colour or Correlated Colour Temperature of 'white light' with the objective to simulate the natural colour temperature of daylight in function of the time of the day and the latitude of the location. It can be integrated in the monitoring system described above, in turn driving the illumination system. This low cost RGB based colour sensor consists of a packaged optical sensor (TAOS TCS3414CS), diffuser, IR filter and housing. The sensor has been tested providing RGB and total light values when requested to the monitoring software on the PC. These are the necessary values to determine the total illumination level (lux) and the colour temperature of the light.

3. Comfort measurement

Another innovation of the CETIEB project is the development of a low-cost infrared system for real-time measurement of human thermal comfort performed by Università Politecnica delle Marche. The monitoring device, including a set of sensors in a bulk unit, can be installed on the ceiling of the occupied room. The system measures on indoor surfaces and environment to derive comfort parameters (as Predicted Mean Vote – PMV) for several positions in the space. Since the measurement is not a single-point one and is not only based on temperature, the HVAC control strategy can be improved which offers potentials of energy savings. PMV is the average comfort vote, using a seven-point thermal sensation scale, predicted by a theoretical index for a large group of subjects when exposed to particular environmental conditions. As indicated in Eq. 1 the PMV is affected both by environmental parameters (air temperature t_a, relative humidity RH, mean radiant temperature t_r, air velocity v_a) and subjective parameters such as the metabolic rate M and the clothing insulation I_{cl}.

$$PMV = f(t_a, RH, t_r, v_a, M, I_{cl}) \qquad (1)$$

Mean Radiant Temperature (MRT, t_r) appears to be one of the most influential parameters in order to provide a good estimation of PMV (metabolic rate and insulation can be set constant). Therefore a measurement system for a good estimation of this parameter is needed. The system is adopted to provide real-time measurement of thermal images of the indoor environment and derive comfort parameters. Basics of the system are shown in (Revel et al., 2012). Advanced signal processing algorithms allow the calculation of thermal comfort parameters by taking into account all sources and thermal loads in the room (Fig. 2).

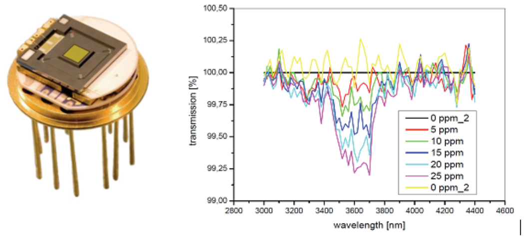

Fig. 1. Sensor developed (left) and measurement of acetaldehyde in N_2 from 0 to 25 ppm in 5 ppm steps (right)

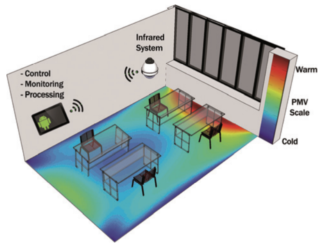

Fig. 2. Principle sketch of thermal comfort measurement system scenario

The thermal image sensors find several fields of applications, from industrial to sanitary, public and residential, where providing an adequate comfort condition to occupants is essential. The system could be of special interest also for museums and cultural heritage buildings with respect to energy savings and protection purposes.

Active and passive methods for indoor environment improvement

1. Ventilation

Ventilation has important energy consequences. In case heating or cooling is required, the energy penalty is the most important reason to minimise the amount of ventilation. In most climates, the supply of outdoor air has an influence on the energy use for heating, cooling, humidification and dehumidification. In case of additional energy use from fans or HVAC (Heating, Ventilation, and Air Conditioning), this will result in additional outdoor pollution. However, ventilation can also reduce the energy need, e.g. in case of an efficient strategy of night-time ventilation/cooling. In a study (JRC, 2003) on ventilation and its effects on energy and indoor air quality (IAQ), the Joint Research Centre estimated that ventilation can constitute up to 50% of energy use in buildings. Considering energy-efficiency isolated, natural ventilation is often a preferred strategy compared to mechanical or fan-forced ventilation (JRC, 2007). According to Seppänen (1998), the developing technologies of natural ventilation and "free cooling" can improve energy efficiency for a given IAQ up to 60%. The main innovation of the active system will be to enable controlled natural ventilation and thus the conditions for drastically improved IAQ and optimal air flow control in buildings. Combined, the two benefits of improved energy efficiency and controlled natural ventilation will effectively decouple the negative correlation between thermal properties and IAQ. In addition, the HVAC control system under development includes a control loop which takes in account not only the merely air temperature as comfort parameter, but the PMV, which, as explained above, is an index obtained from six different variables of the environment and of the occupant.

2. Thermal insulation

Another goal of the project is the development of mineral-based thermal insulating lightweight mortars by the use of phase change materials (PCM) in combination with expanded perlite. With the addition of PCM, the heat capacity of mortars will be increased and walls will adsorb or release energy (heat) from the indoor environment creating much easier a comfortable environment for humans. It is expected that due to expanded perlite and the decreased variation between maximum and minimum indoor temperature, smaller weight percentages of PCMs will be needed to keep the temperature in a range of 24-26 °C than the 20-40 % reported in the literature leading to a cost effective multifunctional (and also machine processable) building material.

3. Photocatalytic plaster

In the photo-catalytic plaster the ability of titania TiO_2 to degrade harmful substances will be utilized. To reduce the high costs of the catalyst it will be combined by a special procedure with perlite microspheres which enhance the effect by scattering the light. Various tests have been performed to find the most promising compositions. Measurements on the plaster layer were performed with NOx as test analysis, whilst measurements with VOC are still on-going. A mortar containing a new modified TiO_2 catalyst which can be activated already by light in the visible region is under investigation.

Improved assessment, modeling and simulation

Standards for energy efficient buildings lead to new thermal indoor environment conditions compared to the building standards nowadays. Because of the high insulated outside walls and windows, there will be inside surface temperatures which are closely to the indoor air temperature. In front of the cold surfaces there will be no cold airflow anywhere. Because of the reduced heating loads of energy efficient buildings often heating systems with low system temperatures like floor heating systems are installed. High air tightness of new and refurbished buildings limits the natural air exchange of the room to a minimum near zero. Natural ventilation by manually opening windows highly depends on the users of the room as well as on the physical parameters wind and temperature difference between inside and outside. Thus a minimum air flow rate for the hygienic air exchange cannot be guaranteed.

Investigations regarding the air flow pattern in such rooms have to be done. In a first step the simulation of this new situation is a good tool to know more about the new indoor air flow pattern. To determine the distribution of air pollutants inside a full 3D-Simulation has to be done. Normally only thermal comfort parameters are investigated by such 3D-simulations. New in this project is the full integration of air pollutants including sources and sinks into normal 3D-room-simulations. These models could be used for a combined simulation of thermal and hygienic comfort.

Concluding remarks

This paper presents a set of tools developed with the CETIEB project for an improved building retrofit which aims at optimal living environments with the lower energy consumption. This requires monitoring technologies which are modular and able to measure all possible parameters to evaluate the indoor air quality and comfort. Data retrieved are used from one side to assess the environment (before and after the retrofit) and from the other side to actuate a better control of the ventilation systems. This control is performed by innovative algorithms able to balance natural and mechanical ventilation, indoor air quality and thermal comfort with a consequent energy saving. Moreover the main objective of the project is supported by the introduction of new materials with increased performances such as bio-filter, photo-catalytic plasters and light-weight insulating mortars which make the envelope as an acting system to ensure better indoor air quality and thermal response. The development is at the final stage and three systems integrating the tools are being installed in real cases to demonstrate the feasibility.

Keywords: Indoor Environment, measurement, thermal comfort, thermal insulating mortar, VOC sensor.

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SOURCE APPORTIONMENT STUDY BASED ON SELECTIVE WIND DIRECTION SAMPLING

Extended abstract

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Background

In order to decrease the concentration and toxicological impact of atmospheric pollutants, it is important to assess not only the total amount of pollutants in a certain area, but also the contribution made by the several emission sources. To this aim, source apportionment analysis should be applied. Several approaches are possible for performing source apportionment studies: collecting samples from different sites, located in zones affected by different pollutant fallouts, sampling at only one site and correlating the results with the meteorological parameters or using samplers coupled with a wind select sensor, in order to sample only the air masses influenced by specific emission sources. The first and second approaches require a large amount of samples and environmental data. On the other hand, the third approach allows a predefined selection of samples, influenced by specific sources, even if they are collected at the same site. For this reason a smaller number of samples should be sufficient to define the contribution of the sources. For this purpose, the sampling site must be located in an area which is upwind or, alternatively, downwind of the principal emission sources identified.

Polycyclic aromatic hydrocarbons (PAHs), among the several pollutants which are present in airborne particulate matter, can be used to assess the origin of the PM. In spite of the fact that PAHs are produced by many sources, their concentration and relative distribution depend on the specific emission source (Zhang et al. 2010). Nevertheless PAHs are affected by atmospheric removal and transformation processes, which can modify their relative distribution greatly (Galarneau, 2008). PAHs are present in the atmosphere in the gaseous phase or sorbed to particulates. The phase distribution of PAHs in the atmosphere is important in determining their fate because of the difference in rates of chemical reactions and transport between the two phases. In general, PAHs having two to three rings (naphthalene, acenaphthene, acenaphthylene, anthracene, fluorene, phenanthrene) are present in air predominantly in the vapor phase. PAHs that have four rings (fluoranthene, pyrene, chrysene, benz[a]anthracene) exist both in the vapor and particulate phase, and PAHs having five or more rings (benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, benzo[a]pyrene, dibenz[a,h]anthracene, and indeno[1,2,3-c,d]pyrene) are found predominantly in the particle phase (ATSDR 1995). One problem in the application of source apportionment methods based on PAH concentration derives from the semi-volatility of PAH. Consequently, these methods, when applied only to particle phase PAH, tend to show compounds of comparable volatility as associated with one another as they will vary temporally in a similar manner. This, however, simply reflects their physico-chemical properties rather than a common source (Mari et al. 2010). Nevertheless in this study, only PAHs found predominantly in the particle phase were determined and this problem should be overcome.

The aim of this paper is to assess the potential of the use of particulate samplers coupled with a wind sensor in source apportionment studies. This approach has been applied in an area influenced by three main emission sources i.e., an urban area, a medium-sized Municipal Solid Waste Incinerator (MSWI) and a motorway. To obtain this, PAHs and PM_{10} contribution made by these sources has been determined. The aim of this study is not to undertake a quantitative analysis of PAHs in atmosphere but to assess the differences between air masses sampled at the same

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site; atmospheric removal and transformation processes should affect similarly the two air masses and it is thus not a problem to reach the purpose of the study. Furthermore this study aims to determine the input of specific local sources. Atmospheric removal and transformation processes should little affect concentration and relative distribution of PAHs emitted by local sources, since the short distance between the source and the sampling site.

Methods

The sampling site (43°59' N, 12°39'E) is located in a city park, on a 60 m ASL hill ridge, in the southwestern suburban area of the medium-sized tourist costal town of Riccione (RN) (35 000 inhabitants). The two principal wind directions are southwest and northeast (land and sea breeze), roughly perpendicular to the coast line. Consequently the site is alternatively downwind of the costal urban area and of the hinterland, which is mainly characterized by the presence of a Municipal Solid Waste Incinerator (MSWI) and a motorway. The industrial plant is 2 km away from the sampling site; it is authorized to burn 140 000 t of urban and hospital solid waste per year (maximum 1000 t/ year of the latter), and the emission stack is 40 m tall. The main wind direction in the area matches to the site-incinerator axis. The A14 motorway is about 600 m away and runs roughly 30 m below the sampling site. It is used by an average of 60 000 vehicles per day.

Two medium volume samplers (Skypost PM, TCR TECORA), equipped with a PM_{10} sampling head, were used. Each sampler operated at the flow rate of 38.33 L/min. The samplers were coupled with a wind direction sensor, which allows the turning on and off of the instrument depending on wind direction. The first sampler (C1) collected PM_{10} coming from inland, that was thus influenced by the incinerator and the motorway. The sampler switched on when it was downwind of the incinerator ±60° (120 degree window). The second sampler (C2) collected PM_{10} coming from the coast, that was thus influenced by the urban area. The sampler turned on when it was downwind of the coast ±90° (180 degree window).

Two sampling campaigns were performed, the first one in the autumn (from 26th October to 30th November 2009) and the second one in the spring (from 17th May to 20th June 2010). Overall, 32 samples were collected (20 in the autumn and 16 in the spring).Each sampling lasted 72 hours, so 2 samples a week were collected. In order to assess differences between midweek (m) and weekend (w) days, the first weekly sampling began on Monday, at 12:00 a.m. and finished on Thursday, at 12:00 a.m. The second one began on Friday at 00:01 a.m., and finished on Sunday at 11:59 p.m.PM_{10} samples were collected on quartz fiber filters (SKC, 47 mm diameter). To determine the ambient concentration of PM_{10}, reference methods was the European Standard EN 12341. In this study, 4, 5, 6 rings compounds of the US EPA PAHs priority pollutants list were determined: Fluoranthene (Flu), Pyrene (Pir), Benz[a]anthracene (B(a)A), Chrysene (Cri), Benzo[b]fluoranthene (B(b)F), Benzo[k]fluoranthene (B(k)F), Benzo[a]pyrene (B(a)P), Dibenz[a,h]anthracene (D(a,h)A), Benzo[ghi]perylene (B(g,h,i)P) and Indeno[1,2,3-cd]pyrene (I(1,2,3)P). They were determined by HPLC with a fluorimetric detector.

Results and discussion

PM_{10} air concentrations (Table 1) show typical values of a medium polluted suburban area. In the spring, the PM_{10} air concentration is always lower than 19 μg/m^3, while in the autumn, values of particulate matter concentration range from 9.1 μg/m^3 to 67.7 μg/m^3. In Table 1 meteorological parameters and ozone concentration are also reported. Seasonal variation must be partially ascribed to the different mixing layer height. From the data, it can be inferred that the study area is generally characterized by low speed winds, i.e. light and gentle breeze; during no sampling, winds reached moderate breeze speed (> 5.5 m/s).

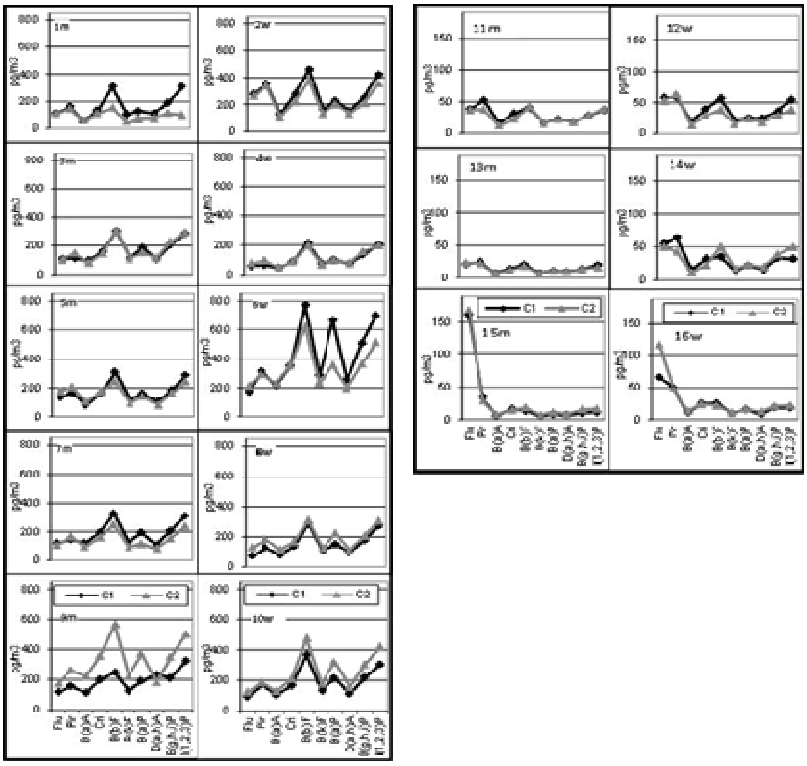
By comparing PM_{10} concentration in the air masses coming from the inland (C1) and from the coast (C2), differences below 10% are observed for 3m, 5m, 10w, and 11m samples. These samplings coincide with more instable weather conditions i.e. higher wind speed, about 3 m/s or more, and heavy rain. These conditions led to a greater atmospheric mixing, which tends to cancel the differences between the two air masses. 4w, 6w and 12w samplings are some exceptions. However, for 4w sampling, the particulate concentrations are very low; so, even if the relative difference between the two concentrations is quite high, the absolute difference is low. On the other hand, 6w and 12w samples show similar PM_{10} concentration, even if they were collected on stable weather days. PM_{10} concentration in air masses coming from the coast is usually greater. No particular trend capable of distinguishing midweek samples from weekend ones has been registered. Particulate PAHs air concentrations are reported in Table 1. Autumn period values are one order of magnitude greater than spring period ones. This is due to the lower mixing layer height and to PAHs chemical stability in atmosphere in the presence of other background parameters: photochemical oxidation, reactive pollutants (such as O_3), temperature. All these parameters contribute to a lower concentration in spring period. In the autumn period, PAHs concentrations in air masses coming from the inland (C1) and from the coast (C2) show differences lower than 10% for 3m, 4w, and 5m samples. The coincidence with atmospheric instability is still greater than for PM_{10} concentration. In this case, 10w sampling is an exception. The difference between the air masses is quite high, even if the meteorological conditions were unstable. On these days, the mixing layer was on the average 260 m high, while during the 3m, 4w and 5m samplings it was more than 300 m high. Thus, this parameter also affects mixing conditions. In the spring period, the differences between the two air masses are usually lower. This is combined with a very high mixing layer height, as reported above. For 12w and 16w samples, the difference between the concentrations in the two air masses is greater than 10%. On these days, wind speed was lower. The residual standard deviation (RSD) of PAH concentrations in the two air masses has been determined for each sampling. Pearson's product moment correlation analysis has been applied in order to evaluate the relationship between the above mentioned RSD and meteorological parameters. The results show a significant inverse correlation ($p=0.05$) between RSD of PAH concentrations and mixing-H and wind speed. These data confirm that an higher mixing layer height and a faster wind speed lead to a greater atmospheric mixing, which determines the disappearance of possible differences between the two air masses. The effect of the rain is lower ($r=-0.42$, $p=0.11$). However, by considering only autumn samples, the effect of this parameter increases ($r=-0.67$, $p=0.03$).

Table 1. PM$_{10}$ air concentration, meteorological parameters and O$_3$ concentration during the autumn and spring sampling campaigns

		PM$_{10}$ C1 μg/m^3	***PM$_{10}$ C2 μg/m^3***	***∑PAHs C1, ng/m^3***	***∑PAHs C2 ng/m^3***	***Mixing -H (m)^a***	***Wind speed (m/s)^a***	***Rainfall (mm)^a***	***Temperature °C***	***Visible radiation (W/m^2)^a***	***O$_3$ (ug/m^3)^a***
FALL	1m	57.7	67.7	1.61	0.99	260	2.36	0	13.16	124.139	32.754
	2w	44.6	26.2	2.62	2.22	210	2.46	0.2	9.33	107.194	48.376
	3m	14.2	15.0	1.67	1.67	370	4.48	8.6	9.38	43.262	39.979
	4w	12.5	9.1	1.07	1.11	350	3.27	13.6	10.42	75.231	44.793
	5m	19.7	20.6	1.70	1.62	310	3.26	19.6	9.55	83.193	36.099
	6w	54.9	54.4	4.23	3.36	160	1.79	0.2	10.16	56.312	30.757
	7m	29.2	46.4	1.84	1.45	110	0.89	1.6	10.61	38.205	8.1292
	8w	36.9	47.2	1.51	1.87	170	1.64	0.2	10.48	37.120	14.557
	9m	32.2	41.7	1.91	3.20	140	1.54	0.4	9.39	33.928	17.394
	10w	18.2	20.3	1.88	2.50	260	3.59	6	11.55	58.526	44.201
	Average	32.0	34.8	2.00	2.00	230	2.53	5.0	10.4	65.7	31.704
SPRING	11m	18.1	18.7	0.30	0.27	410	2.90	7.8	15.11	211.693	76.332
	12w	12.3	13.7	0.39	0.32	430	2.14	0	16.42	245.453	80.863
	13m	14.4	17.8	0.15	0.14	500	2.60	1.6	18.29	232.959	86.603
	14w	9.2	13.5	0.32	0.33	410	2.30	0	18.55	311.324	88.725
	15m	11.7	15.8	0.27	0.30	440	2.39	19.8	22.9	261.635	74.26
	16w	11.7	14.6	0.25	0.31	450	2.26	19.4	18.87	189.967	73.031
	Average	12.9	15.7	0.28	0.28	440	2.43	8.1	18.4	242.2	79.969

[a] *Values provided by Arpa Emilia Romagna.*

Distribution profiles for each sample are reported in Fig.s 1. They are usually similar in the two air masses. For the autumn period, not only do the 3m, 4w and 5m samples have similar total PAHs concentration in the two air masses, but the congener profiles are almost the same also. This is also true for 2w samples. Other autumn samples show greater differences. For the 1m, 6w, and 7m samples, PAHs concentration is greater in air masses coming from the inland. Specifically, the concentration increases especially for I(1,2,3)P, B(b)F and B(g,h,i)P. BghiP and I(1,2,3)P are components of vehicular fuels and BbF is usually associated with heavy-duty diesel vehicles emissions. Therefore a high concentration of these reflects the contribution of PAHs from vehicular emissions (Bourotte et al. 2005). Their higher concentration in air masses coming from the inland may be due to the contribution of the motorway. For the other samples, the total PAHs concentration is greater in the air masses coming from the coast and every congener shows this trend. Particular differences which could distinguish midweek samples from weekend ones have not been registered. For the spring period, 11m, 13m, and 15m samples show very similar profiles in the two air masses. For 12w samples, the concentration of five- and six-ring compounds is greater in the air masses coming from the inland, while for 16w samples, Flu concentration is greater in air masses coming from the coast. For 14w samples, even if total PAHs concentration is very similar in the two air masses, the profiles are different. Four-ring compound concentration is greater in air masses coming from the inland, while the concentrations of five- and six-ring compounds are greater in air masses coming from the coast. Wind speed on these days is one of the lowest observed. Only during 12w and 16w samplings is the wind speed lower. Comparing the two sampling campaigns, considerable differences can be observed. The profile of autumn samples is very similar to what is typically registered in urban areas, where the main PAHs source is vehicular traffic (Bourotte et al., 2005). In the spring, distribution profiles are rather different; in particular, relative Flu and Pir concentrations are greater. This happens especially during two samplings (15m and 16w), when the concentration of these compounds accounts for more than 50% of the total mixture. Transport and partitioning of PAHs in the environment are determined to a large extent by physicochemical properties. The high Flu and Pir contribution on some days can be due to the different physicochemical proprieties of these compounds compared to the other determined (ATSDR 1995). Nevertheless, the effect of a specific source cannot be excludes, since these compounds era fingerprints of several emission sources. The sampling site is located in a suburban area, near various farmlands. Especially in the spring, the open-air burning of agricultural debris and weeds is common. Flu and Pir are the compounds most emitted from this combustion process (Hays et al. 2005). Other studies report that these compounds are markers of incineration process (Bourotte et al. 2005). But since both air masses show a high Flu and Pir concentration, the additional source is not likely a point one. Moreover the higher concentration of these compounds only in the spring period is difficult to explain. Flu and Pyr are markers of other emission sources: diesel emission, coal combustion, natural gas, oil burning and petrol powered vehicles (Bourotte et al. 2005). Diesel emission and petrol vehicles are characterized also by other markers (Bourotte et al. 2005) which do not increase their concentration as Flu and Pir. Coal combustion source is not present in the study area, while natural gas is a spread fuel for domestic heating, but this is not a source which can be found in the spring period. Therefore the last sources should be excluded



(a) **(b)**

Fig. 1. Distribution profiles of PAHs for each sample during autumn campaign (a) and spring campaign (b)

Concluding remarks

The sampling technique may be a valid support in source apportionment studies. However, meteorological and territorial conditions could affect the results. The technique seems suitable for areas characterized by moderate winds and with two prevailing directions, as in the case of costal zones.

The two sampled air masses monitored in this study often proved very similar, as far as the analyzed compounds are concerned. Results confirm that the study area does generally not seem characterized by a dominant source, as the incinerator, but by a widespread contamination due especially to vehicular traffic

Keywords: Municipal Solid Waste Incinerator, Polycyclic aromatic hydrocarbons (PAHs), PM_{10}, Selective sampling device, Source apportionment

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ASSESSING CO_2 EMISSIONS OF REGIONAL POLICY PROGRAMMES: AN APPLICATION OF CO2MPARE TO EMILIA - ROMAGNA 2007 - 2013 Operative Regional Program

Extended abstract

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Background

CO2MPARE is a model designed to support regional governments in the implementation of low-carbon policies, through the quantification of the effects of the various project interventions funded and defined in the operational programs for regional development. As it is well known, one of the main objectives of the "Climate and Energy 2020" package is the reduction of emissions of greenhouse gases. The EU policy on climate change in fact defines a target of reducing greenhouse gas emissions by 20% in 2020 (compared to 1990 levels) and 80-95% in 2050. As a consequence, in order to achieve these objectives, it is required that the intensity of greenhouse gas emissions into the atmosphere by the socio-economic and production activities is reduced considerably and in a short time. In addition to particular technical and political tools specifically dedicated to this (such as, for example, the Emission Trading System and the Directive on energy performance of buildings), the European Commission is now seeking to adopt, and include, climatic and environmental considerations and evaluations of policy instruments even within plans, such as the regional operational programs, so that EU policy could be internally consistent with respect to the overall objectives for contrasting climate change (CO2MPARE, 2013a,b,c). For example, within its actions of financing of regional public investment, with specific targets on agriculture, business, environmental protection and so on, the EU is trying to include emission budgets within the procedure of approval of individual Regional Operational Programs (ROP). The choice of particular alternative options may in fact have very different consequences depending on the individual areas of development, such as industrial growth or job creation in agriculture. Depending on the various types of specific investment, greenhouse gas emissions into the atmosphere may vary significantly. In this context it can be used "CO2MPARE", a computational model aimed at assessing and quantifying the emissions of the main greenhouse gas, carbon dioxide (CO_2). This model allows comparing different programmatic alternatives in the regions of the European Union. In practice this is an advanced decision support operating tool designed, on behalf of the European Commission - Directorate General for Regional Policy, by a consortium of 6 European partners (Energy research Centre of the Netherlands - ECN, ENEA, Energies Demain, University College of London, ENVIROS and CRES). ARPA Emilia-Romagna has supported the consortium in the test phase of the model CO2MPARE applying it to the evaluation of the 2007-2013 ROP of Emilia-Romagna, quantifying the various programming scenarios and their resulting impact in terms of CO_2 emissions. With the model it was possible to compare the emissions of several alternative scenarios in order to identify the best performing program even from the perspective of CO_2 emissions.

Functionality

The CO2MPARE model starting from the individual measures financed by an operational program allows quantitatively assessing the resulting emissions of carbon dioxide. Each program is based on funding allocations

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related to the main themes, sub-themes and operational actions. The CO2MPARE user must first of all include in the model the distribution of financial resources from economic budget allocations of funding. In practice, each regional program contains themes, structured in measures, in turn structured in more different actions that in the model are represented by a set of "Standardized Investment Components" (SICs) that are common across all regions. In the model these SIC are predefined by default, but thanks to the possibility to modify the specific calculation parameters within each SIC, these are then changeable by the user in such a way that the evaluation of the specific program may be significantly adapted to the regional characteristics, and therefore the model can provide better and more reliable and informative results. On the basis of the input of the economic characteristics and physical properties of these SIC, the model then calculates indicators, the physical quantities and related emissions of carbon dioxide for each individual activity. Emissions are then added together to get the total emissive aggregates, of each main topic and therefore complete program. The model allows preparing different versions of a ROP (for example, with different funding schemes within the same total budget) by comparing them with each other in terms of CO_2 emissions.

The alternative within the model the alternative versions (actual or potential) of a program are called "scenarios". In the last instance it is therefore possible to compare the results of two or more scenarios to choose the best one and/or to build other better scenarios on the base of the results of output. To properly configure the scenarios, the user needs to have a good knowledge of the financial model of the operational program to assess the type of projects funded (Fig. 1). From the results it is possible to: (i) identify investments that give rise to higher CO_2 emissions, both in the construction phase and during the operational management of the works over years;(ii) verify the results of the investment programs in physical terms (for example, length of the roads built, surface of buildings, renewable power plants installed capacity etc.); (iii) evaluate the effect of eco-criteria to be prescribed in funding programs (e.g. the criterion of funding only buildings **with high levels of energy performance**)

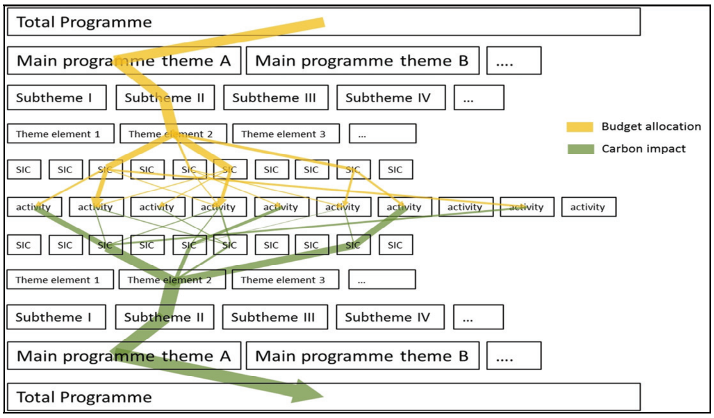


Fig. 1. Steps of disaggregation of financial resources and aggregation of impacts in terms of CO_2 emission that form the general principle of the model CO2MPARE

Multi-regional applications and intended users

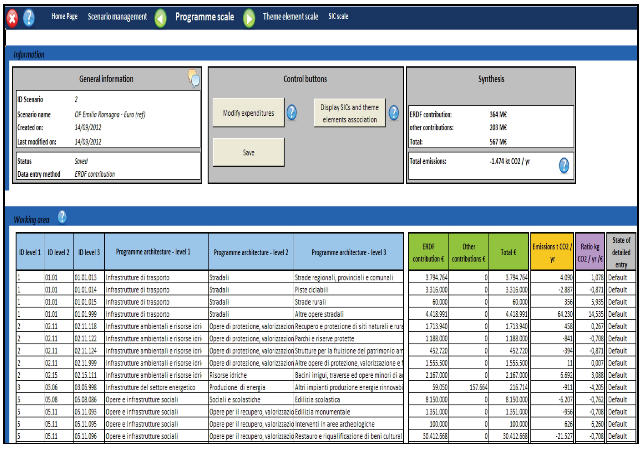
CO2MPARE, through the simple insertion of financial data as only input, enables regional authorities to evaluate their own programs (ex-ante, in-progress, ex-post) and to assess their consequences in terms of physical outputs and related CO_2 emissions. Depending on the region in which one evaluates the operational programs, the technological indices used are different and the evaluation of the program thus leads to different results. These results, however, are comparable between them thanks to the use of the same conceptual system, structured with the same SIC. For example, a building built from scratch in Sweden or Italy cannot have the same energy performance, and therefore has different carbon emissions, but the use of the model CO2MPARE allows comparing the performance of ROPs in the two regions. However, it is also important to remind that CO2MPARE is not born to compare ROPs of different regions but for the comparison within the same ROP of different financial allocations, and thus of different types of "themes and actions", that is for comparing different scenarios of the same ROP. Each region should independently define its own calibration of the technological indices.

To take these issues into account, the chain of calculation adopted in the model uses two types of parameters (called “ratios”): (i) Global-RATIOS, which are independent of geographic detail; it is assumed that they will always remain the same, regardless of the region in which one adopts and evaluates the operational program (e.g. the carbon dioxide emission factor for the raw material "steel", measured in tons of CO_2 emissions per ton of used steel); (ii) Regional-RATIOS, which vary from one region to another (e.g. the cost of construction of a building in €/ m^2); (iii) Initially, the model offers options with default values for both the Global and Regional RATIOS. It is however strongly advisable to adjust the default RATIOS values in order to better adapt to the regional characteristics. This process of regionalization requires technically trained staff with a good knowledge of Life Cycle Analysis (LCA) and data collection. After regionalization, the model is fully operational, and can be easily used by management authorities, policy makers, environmental agencies etc. in the preparation of operational programs. To best meet these various needs of users, two different modes of use of the model are available:

- a "basic mode" for users who exclusively want to analyze and compare the effect of different investment schemes about the impact of a carbon ROP, without going into management and redefinition of the coefficients of the scientific-technical life cycles materials and operability or useful life of the works realized;
- an "expert mode", which allows users to drill the calibration of the model and the ROP on the basis of technical more reliable and responsive scientific coefficients to the degree of local technology.

Examples of application in Emilia-Romagna

The model CO2MPARE has been used for the Strategic Environmental Assessment (SEA) of the 2007-2013 ROP of Emilia-Romagna. The model was produced in 2012, during the final management of the program, and has been used to evaluate on-going and ex-post performances, offering the opportunity to calibrate data and indices (RATIOS) pre-structured by default at the regional level. The use of the model has led to the identification of an "allocation of funds" into the different categories of expenditure provided for by the EU. A "man month work" was needed to verify the distribution of funds, to identify the progress, and place them in the appropriate items of the model. This distribution of funds has constituted the first scenario on which to run the algorithms (SIC) and the components of the model CO2MPARE. The model runs on Excel and provides results in both tabular form and in graphs. The tables allow a direct quantitative estimate, can be exported, and of course managed by the user (typically an expert of regional institutions, or an expert of the scientific community as a consultant of the institution). Graphics are useful to have a quick summary view readable by policy makers, in the different technical phases of design evaluation and / or the performance of the ROP. As an example below are shown some Tables and Figures taken from the SEA (Strategic Environmental Assessment) report of the 2007-2013 ROP (Arpa Emilia-Romagna., 2011, 2012). As it can be seen the model CO2MPARE allows a clear emissive comparison between different investment alternatives. The reading of graphs and tables in the experience made on the SEA of the POR 2007-2013, implied a joint analysis between the experts who had entered the financial data and other experts who had expertise in the thematic "emissivity" inherent the actions financed, that are the material projects put in place, and experts from various fields involved in the actions of financing, such as roads and viability sector rather than the public housing sector (Regione Emilia-Romagna, 2007, 2013). The comparison over the period of life-supported interventions shows that the greenhouse gas emissions of the evaluated alternatives are negative, that is, the overall impact of the interventions financed under the ROP translates into a certain amount of carbon dioxide emissions avoided in Emilia-Romagna. It is therefore important to point out two important considerations: (1) Any type of development program leads to additional emissions; (2) These additional emissions are not quantitatively univocally imposed, but can be modulated (decreased and/or increased) depending on the type of actions that are financed, that is the type of works and their energetic performance. The use of CO2MPARE, and its design methodological peculiarity composed of flexible output to the client (decision maker) conducts, however, the decision maker to a third consideration, which is derived from the graphs in a visual way, and from the tables in math mode; (3) The emissions are not consistently negative, but they compensate themselves in the phase of “management of the works", so you do have to end the lives of themselves, not only a compensation with respect to the additional emissions created during the construction phase of the works themselves, but, applying criteria of energy efficiency, there is a reduction in emissions compared to works not "energetically efficient." In fact, if on the one hand the actions of building construction have a positive contribution, on the other hand they are largely offset, mainly due to financing for energy efficiency. The model then quantifies and shows neutralizing activity "carbon-positive" with other activities “carbon-negative”: the budget is more than positive, in the sense that the ROP saves and thus avoids more CO_2 than it generates. Table 1 shows how CO2MPARE, applied in Emilia-Romagna in the experimental stage, has allowed to evaluate, at a reduced cost, different alternative financial scenarios, all contained in the envelopes of the ROP in force, different both for developmental effects that in the estimation of emissions-related effects.



General information

ID Scenario 2
Scenario name OP Emilia Romagna - Euro (ref)
Created on: 14/09/2012
Last modified on: 14/09/2012
Status Saved
Data entry method ERDF contribution

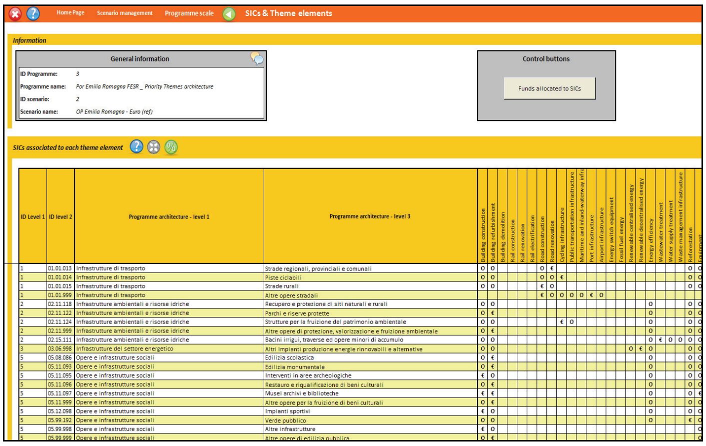
Control buttons

Synthesis

ERDF contribution: 364 M€
other contributions: 203 M€
Total: 567 M€
Total emissions: -1.474 kt CO2 / yr

ID level 1	ID level 2	ID level 3	Programme architecture - level 1	Programme architecture - level 2	Programme architecture - level 3	ERDF contribution €	Other contributions €	Total €	Emissions t CO2 / yr	Ratio kg CO2 / yr /€	State of detailed entry
1	01.01	01.01.013	Infrastrutture di trasporto	Stradali	Strade regionali, provinciali e comunali	3.794.764	0	3.794.764	4.090	1,078	Default
1	01.01	01.01.014	Infrastrutture di trasporto	Stradali	Piste ciclabili	3.316.000	0	3.316.000	-2.887	-0,871	Default
1	01.01	01.01.015	Infrastrutture di trasporto	Stradali	Strade rurali	60.000	0	60.000	356	5,935	Default
1	01.01	01.01.999	Infrastrutture di trasporto	Stradali	Altre opere stradali	4.418.991	0	4.418.991	64.230	14,535	Default
2	02.11	02.11.118	Infrastrutture ambientali e risorse idri	Opere di protezione, valorizzazion	Recupero e protezione di siti naturali e rura	1.713.940	0	1.713.940	458	0,267	Default
2	02.11	02.11.122	Infrastrutture ambientali e risorse idri	Opere di protezione, valorizzazion	Parchi e riserve protette	1.188.000	0	1.188.000	-841	-0,708	Default
2	02.11	02.11.124	Infrastrutture ambientali e risorse idri	Opere di protezione, valorizzazion	Strutture per la fruizione del patrimonio am	452.720	0	452.720	-394	-0,871	Default
2	02.11	02.11.999	Infrastrutture ambientali e risorse idri	Opere di protezione, valorizzazion	Altre opere di protezione, valorizzazione e f	1.555.500	0	1.555.500	11	0,007	Default
2	02.15	02.15.111	Infrastrutture ambientali e risorse idri	Risorse idriche	Bacini irrigui, traverse ed opere minori di a	2.167.000	0	2.167.000	6.692	3,088	Default
3	03.06	03.06.998	Infrastrutture del settore energetico	Produzione di energia	Altri impianti produzione energie rinnovabi	59.050	157.664	216.714	-911	-4,205	Default
5	05.08	05.08.086	Opere e infrastrutture sociali	Sociali e scolastiche	Edilizia scolastica	8.150.000	0	8.150.000	-6.207	-0,762	Default
5	05.11	05.11.093	Opere e infrastrutture sociali	Opere per il recupero, valorizzazio	Edilizia monumentale	1.351.000	0	1.351.000	-956	-0,708	Default
5	05.11	05.11.095	Opere e infrastrutture sociali	Opere per il recupero, valorizzazio	Interventi in aree archeologiche	100.000	0	100.000	626	6,260	Default
5	05.11	05.11.096	Opere e infrastrutture sociali	Opere per il recupero, valorizzazio	Restauro e riqualificazione di beni cultural	30.412.668	0	30.412.668	-21.527	-0,708	Default

Fig. 2. Screen example of input / output of the ROP Emilia-Romagna 2007-2013



General information

ID Programme: 3
Programme name: Por Emilia Romagna FESR _ Priority Themes architecture
ID scenario: 2
Scenario name: OP Emilia Romagna - Euro (ref)

Control buttons

ID Level 1	ID level 2	Programme architecture - level 1	Programme architecture - level 3	Building construction	Building refurbishment	Building demolition	Rail construction	Rail renovation	Rail electrification	Road construction	Road renovation	Cycling infrastructure	Public transportation infrastructure	Maritime and inland-waterway infra	Port infrastructure	Airport infrastructure	Energy switch equipment	Fossil fuel energy	Renewable centralised energy	Renewable decentralised energy	Energy efficiency	Wastewater treatment	Water supply treatment	Waste management infrastructure	Reforestation	Equipment
1	01.01.013	Infrastrutture di trasporto	Strade regionali, provinciali e comunali	0	0					0	€														0	0
1	01.01.014	Infrastrutture di trasporto	Piste ciclabili	0	0					0	0	€													0	0
1	01.01.015	Infrastrutture di trasporto	Strade rurali	0	0					€	0														0	0
1	01.01.999	Infrastrutture di trasporto	Altre opere stradali							€	0	0	0	0	€	0										
2	02.11.118	Infrastrutture ambientali e risorse idriche	Recupero e protezione di siti naturali e rurali	0	0																0				0	0
2	02.11.122	Infrastrutture ambientali e risorse idriche	Parchi e riserve protette	0	€																0				0	0
2	02.11.124	Infrastrutture ambientali e risorse idriche	Strutture per la fruizione del patrimonio ambientale	0	0							€	0								0				0	0
2	02.11.999	Infrastrutture ambientali e risorse idriche	Altre opere di protezione, valorizzazione e fruizione ambientale	0	€																0				0	0
2	02.15.111	Infrastrutture ambientali e risorse idriche	Bacini irrigui, traverse ed opere minori di accumulo	0	0																0	€	0	0	0	0
3	03.06.998	Infrastrutture del settore energetico	Altri impianti produzione energie rinnovabili e alternative	0	0														0	€	0				0	0
5	05.08.086	Opere e infrastrutture sociali	Edilizia scolastica	0	€																0				0	0
5	05.11.093	Opere e infrastrutture sociali	Edilizia monumentale	0	€																0				0	0
5	05.11.095	Opere e infrastrutture sociali	Interventi in aree archeologiche	€	0																0				0	0
5	05.11.096	Opere e infrastrutture sociali	Restauro e riqualificazione di beni culturali	0	€																0				0	0
5	05.11.097	Opere e infrastrutture sociali	Musei archivi e biblioteche	€	€																0				0	€
5	05.11.999	Opere e infrastrutture sociali	Altre opere per la fruizione di beni culturali	0	€																0				0	0
5	05.12.098	Opere e infrastrutture sociali	Impianti sportivi	€	0																0				0	0
5	05.99.192	Opere e infrastrutture sociali	Verde pubblico	0	0																0				€	0
5	05.99.998	Opere e infrastrutture sociali	Altre infrastrutture	€	0																					0
5	05.99.999	Opere e infrastrutture sociali	Altre opere di edilizia pubblica	0	€																					0

Fig. 3. Input example of financial contributions programmed disaggregated into SICs. (On rows there are the actions of the ROP, while on the columns the SIC (quantified as a percentage% respect to the budget allocated to each action)

Table 1. Example Table about comparison of alternative funding in Emilia-Romagna for 2007-2013 ROP

	Original financial plan		***Alternative financial editing***		
AXES	Total costs (€)	Weight of the total (%)	Total costs (€)	Weight of the total (%)	Variations (€)
1 - Industrial research and technology transfer	114,328.164	32.96%	119,328.164	30.54%	5,000.000
2 - Entrepreneurial development and innovation	69,591.056	20.06%	91,680.706	23.46%	22,089.650
3 – Energetic environmental improvement and sustainable development	79,532.635	22.93%	79,532.635	20.93%	0
4 - Development and qualification of the cultural and environmental heritage	69,591.056	20,06%	84,591.056	21.65%	15,000.000
5 - Technical assistance	13,876.788	4.00%	15,630.523	4.00%	1,753.735
TOTAL	346,919.699	100.00%	390,763.084	100.00%	43,843.385

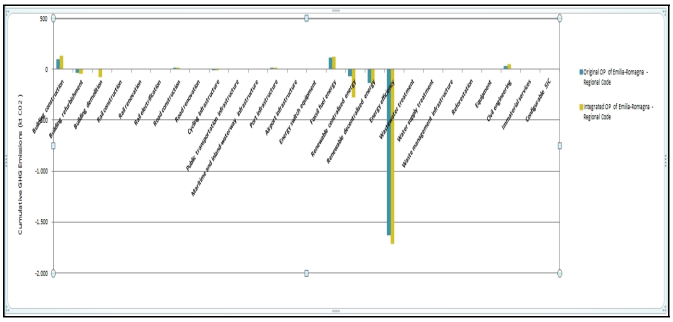


Fig. 4. Comparison of CO_2 emissions cumulated and caused by two alternative scenarios of the ROP of Emilia-Romagna 2007-2013 (Arpa Emilia-Romagna, 2011, 2012).

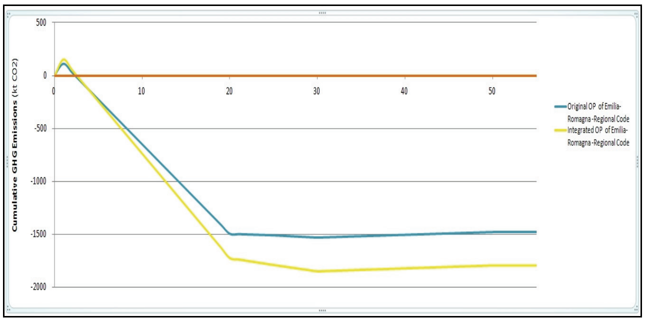


Fig. 5. Comparison of CO_2 emissions, cumulated over the period of life of the interventions efficiency (Arpa Emilia-Romagna, 2011, 2012).

Figs. 4 and 5 also show how a region can allocate funding in measures particularly negative (additional emissions), but can also, at the same time compensate with the positive effects (reduction of emissions) up to a total compensation. This assessment process, put in place with the model CO2MPARE allows the decision maker to implement alternately sustainable development actions, even within economic contingencies, such as those derived from the current crisis, financially supporting energy-intensive sectors (emissive), provided they are accompanied by other funding to sectors with high emissions reduction potential.

Concluding remarks and key success factors

The model CO2MPARE has several features that make it a very interesting tool for the management authorities, environmental agencies and all other involved parties in regional development policymaking. The model provides information on the carbon emission effect of a program at various levels of detail and in the various phases (ex-ante, in-progress, ex-post). It is fast and easy to use, operate in the basic mode only requires the input of planned financial contributions and their disassembly in percentage of standardized investment components (SIC). Currently the model is being used for the preparation of the ROP of Emilia-Romagna Region 2014-2020.

Keywords: CO_2 model, emissions of carbon dioxide, operational program assessment

Acknowledgements

The model (software) CO2MPARE together with all related deepening documents are freely available online at the link: http://ec.europa.eu/regional_policy/newsroom/detail.cfm?id=673&LAN=EN

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FINE AND COARSE FRACTIONS IN THE DESCRIPTION OF THE ATMOSPHERIC AEROSOL BEHAVIOR

Extended abstract

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Background

From the health stand point atmospheric Particulate Matter (PM) is regulated on mass basis through PM_{10} and $PM_{2.5}$ conventions by the Directive 2008/50/EC. The Directive recognizes the negative impact on human health due to fine PM ($PM_{2.5}$) and points out how the approach to be pursued should aim at a general reduction of $PM_{2.5}$ concentrations in urban background. The Directive prescribes that Member States shall take the measures necessary to guarantee the fulfillment of such limit. Setting up a policy of particulate matter (PM) reduction necessarily involves a good level of knowledge of what components sum up to yield PM_{10} measurements.

As reported in literature (Almeida et al., 2005) the fine mode of PM is dominated by both primary anthropogenic pollution from combustion processes and gas-particle partitioning, while the coarse mode is mainly related to wind erosion, mineral dust emission and long-range transport from desert area (natural events). In particular, episodes of coarse dust transport from Sahel towards Europe across the Atlantic Ocean occur in February and March, whereas from Sahara over the Mediterranean basin in summer.

PM_{10} daily - average ponderal values are inadequate to investigate the occurrence of fine / coarse episodes and consequently do not give significant information on its source apportionment. The separation of coarse and fine fractions and their chemical characterization (Avino et al., 2002; Avino et al., 2006; Movassaghi et al., 2008; Avino et al., 2008) do not satisfactorily describe atmospheric PM pollution if data averaging times greatly exceed the time scale of the dynamic of the boundary layer (about one hour time scale).

For this reason an integrated approach using average PM_{10} and $PM_{2.5}$ mass concentration data and time resolved size spectrum analysis was developed and applied to analyze an intense episode of PM pollution occurred in Rome in the period 2005 - 2012.

Objectives

The purpose of this study is to address the relevance of aerosol size distribution measurements concerning the health protection standpoint and to show how such kind of data could be supportive to source apportionment studies, especially identifying the long-range transport of polluted air masses widely reported affecting surface PM_{10} and $PM_{2.5}$ levels measurements. A methodology has been adopted, based on size and time resolved measurements of atmospheric aerosol. Aerosol size spectrum analysis can help to individuate long-range transport episodes of polluted air masses by means of local surface size distribution measurements. The analysis of aerosol spectra and the study of the temporal evolution of the size fraction correlation has been applied to different acute PM_{10} pollution episodes. It will be shown that some episodes involve coarse PM advection, while other episodes will be due to the inflow of two different air masses, one transporting coarse dust and the other fine PM.

Outline of the work

The approach adopted relies on the analysis of the aerosol aerodynamic-diameter spectra to highlight the

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contribution of long-range transport of polluted air masses. To this purpose, the temporal evolution of the correlation of different size fractions has been studied. The study was carried out in Rome.

Different applications are discussed involving long range transport over Italy of coarse desert dust and of fine PM. The transition from highly correlated size fraction to sharp drop of correlations is suggestive of the inflow of polluted air masses. The enrichment either of the coarse or of the fine fractions allows to make hypotheses as to the origins of the polluted air masses.

Methods

Aerodynamic size distributions of atmospheric aerosol were measured by means of a TSI Aerodynamic Particle Sizer 3321 (APS) (Febo et al., 2010). Simultaneously, particle size distribution measurements were also carried out through a Scanning Mobility Particle Sizer (SMPS 3936, TSI Inc., Shoreview, MN, USA) spectrometer (size range 3.5 - 117 nm; 5 min resolution time) (Avino et al., 2011) and a Fast Mobility Particle Sizer (FMPS 3091, TSI Inc.) spectrometer (range 5.6 to 560 nm; 1 - s time resolution) (Manigrasso and Avino, 2012).

Natural radioactivity measurements are used to interpret the meteorological atmospheric variations. In fact, radioactivity measurements are extensively using as a proxy of the Planetary Boundary Layer (PBL) evolution. As fully described in different papers (Avino et al., 2003; Manigrasso et al., 2012), the variations of Radon emission rate can be considered negligible in the time scale of some days and the space scale of some kilometers. Then, its temporal pattern of variation is determined by the Planetary Boundary Layer (PBL) vertical extension and degree of remixing.

Results and discussion

A straightforward way to highlight the concept of the natural radioactivity as tracer of the low boundary layer and index of the remixing properties of the atmosphere, fundamental basis of this work, is to apply it to interpret the temporal trend of ground level ozone concentration for the following reasons: a) the emission source of Radon is at ground level; b) on the contrary, it is the upper atmosphere that is to be considered as an O_3 reservoir.

In Fig. 1 we report a typical trend of ozone and of natural radioactivity during winter season. When ground level ozone formation due to photochemical processes is negligible (as is the case for the period shown in Fig. 1) the ground based temporal trend of O_3 concentration is completely determined by its vertical transfer from the upper layer and by its removal processes (e.g., NO titration), that are particularly effective at surface level. Then in conditions of intense vertical mass transfer we observe the maximum O_3 surface concentrations, because it is efficiently transferred from the upper layer to ground level (Avino and Manigrasso, 2008). On the contrary, obviously, Radon concentration is at minimum levels, due to the intense vertical remixing (Fig. 1). When the atmosphere gets stabilized, as occurs in the late evening and during nocturnal hours, O_3 transfer is inhibited. Consequently, its surface concentration in urban polluted areas quickly decreases, due to O_3 removal processes.

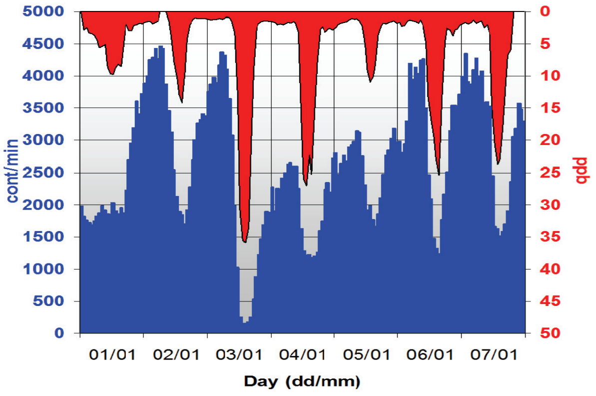

Fig. 1. Temporal trend of variation of ozone (red) and natural radioactivity (blue)

Clarified the validity of Radon as a qualitative descriptor of the vertical degree of remixing of the lower troposphere, we would like to discuss how helpful these concepts are to understand Particular Matter (PM) evolution. To this purpose we describe the temporal evolution of different aerosol size fractions (Fig. 2) over a long period from November 30th to January 11th. In the period considered, if we compare the size channels representative of the fine mode (0.28-0.5 µm) with the other size fractions, passing from the smaller to the greater one, we can see that differences progressively appear. This occurs until the comparison is made between the 0.28 - 0.5 µm and the 3 - 5 µm size fraction, one representative of the fine and the other of the coarse modes of PM. We can see that their trends are basically independent one from the other, as we would expect in the case of local PM sources. The reason is that their sources are completely different. Fine mode aerosol is due to primary anthropogenic combustion sources and to secondary processes, whereas coarse mode PM derives from natural sources (e.g. sea salt aerosol, dust resuspension, etc.).

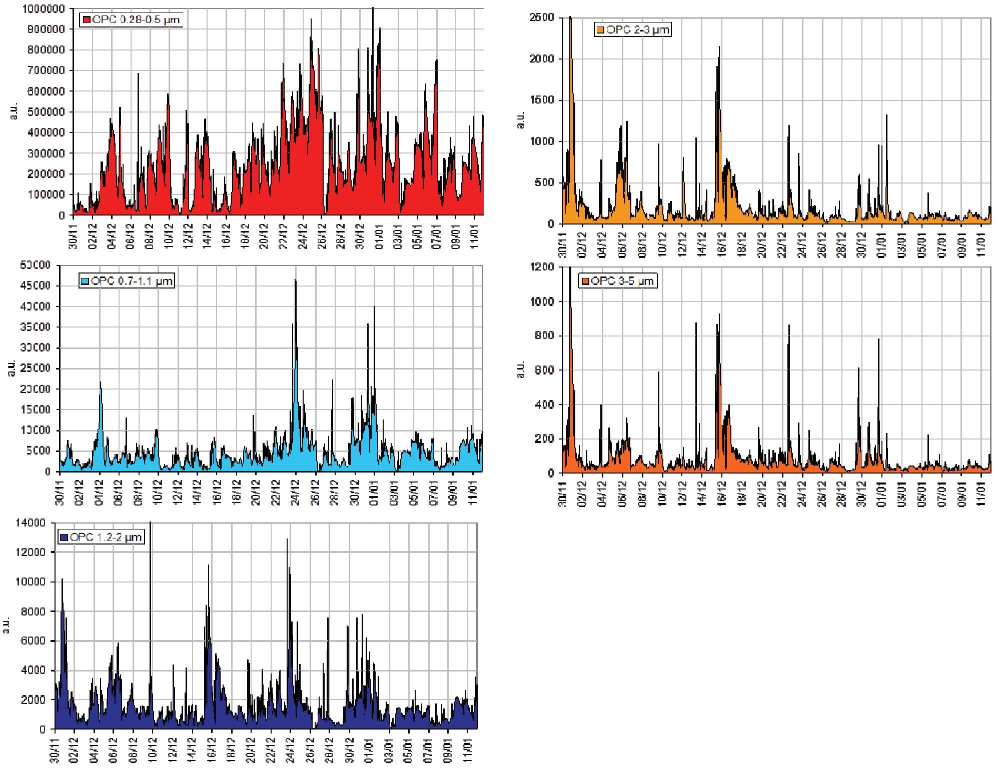

Fig. 2. Temporal trend of different aerosol size fractions

In Fig. 3 we show the temporal trends of the 0.28 - 0.5 µm size channel (representative of the fine mode PM), and of natural radioactivity. As expected, the temporal modulation of the fine mode PM is dominated by the temporal modulation of PBL. In fact, the highest levels of fine mode aerosol are in correspondence with the lowest PBL mixing heights (high values of Radon concentrations). It is fundamental to observe that when radioactivity level is very low (greater dilution), fine mode PM concentration is very low as well.

The crucial point is that if the level of natural radioactivity is low, then the contribution to fine PM due to local sources must be negligible. On this fundamental point relies the interpretation of the Fig. 4. During the transition from June 29th to June 30th a clear drop of nocturnal natural radioactivity was measured (Fig. 4) and simultaneously the fine mode markedly increased. Such apparent contradiction (i.e. the degree of dilution of the low atmosphere increases and the fine PM concentration increases too), is explained admitting a remote source of fine PM, very likely transported through the inflow of new air masses. When radioactivity drops, fine PM surface concentration increases instead of decreasing: this is a consequence of the increased vertical transport with fine PM rich streams sinking from the higher atmospheric layers. Thus, natural radioactivity measurements give a key to interpret the variations of the aerosol size distribution shape, allowing to discern whether such variations are due to the changing contribution of local sources or to long range transport phenomena. In both cases aerosol size fractions with very close values of aerodynamic diameters, cease to covariate and then appear poorly correlated. In fact, basically very close aerodynamic diameters are highly correlated.

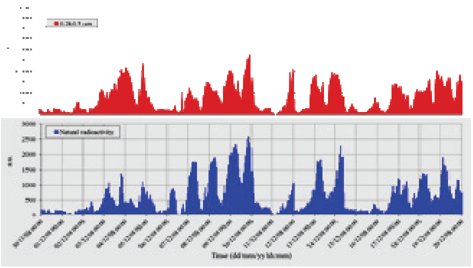

Fig. 3. Temporal trend of variation 0.28-0.5 µm (optical diameter) aerosol size fraction and of natural radioactivity

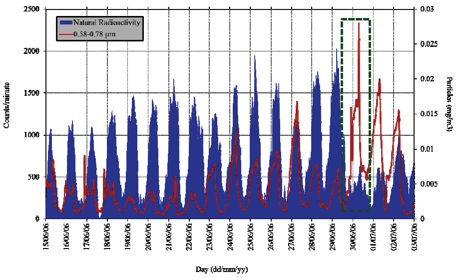

Fig. 4. Daily trends of fine (0.58-0.78 µm) mode fraction and of natural radioactivity (June 15th-July 02nd,Fonte Nuova site).

Finally, an important point to be clarified regards the method validation. Chemical analysis is missing in our data because the aim of our work is to emphasize how size and time resolved aerosol measurements can be used as qualitative support to source apportionment studies. Nevertheless, chemical analysis referring to the period studied is well-described in literature (Saharan dust intrusions in the Rome atmosphere). Marked increments of crustal matter (calculated as sum of Al, Si, Fe, K, Ca, Mg and Na oxides) can be noted in the two investigated periods, June 20th-23rd and 27th-29th. It is worth observing that, in the transition from June 29th to 30th, the daily average value of secondary inorganic PM_{10} increases of about 75 %: the aerosol episode behind such occurrence finds full explanation in Fig. 4, thanks to the temporal analysis of aerosol size distributions (diagnostic role of particle size).

Concluding remarks

The methodology adopted can be of useful support to qualitative source apportionment studies for recognizing the contribution of remote sources; simultaneously, it is quite easy and rapid to apply since it based only on continuous measurements of both aerosol size spectra and natural radioactivity.

Keywords: aerosol size distribution, fine/coarse fraction, particulate matter, Planetary Boundary Layer, source apportionment.

Acknowledgements

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CONTRIBUTION TO THE KNOWLEDGE OF AIR QUALITY IN A HIGHLY INDUSTRIALIZED SITE (TARANTO CITY, ITALY), BY BIOMONITORING TECHNIQUES

Extended abstract

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Background

The city of Taranto (Southern Italy), close between large industrial plants is considered among the Italian cities most at risk of pollution, due of increased release of toxic substances in the environment. Monitoring of air quality, therefore, represents a problem of primary importance.

Traditional techniques are based on the use of monitoring stations and physical chemical methods.

The use of bioindicators is of considerable interest because it allows measurements on a large scale, relatively quickly at low cost. In particular, the use of mosses has gone increasingly spreading in monitoring high-risk areas for the environmental capacity to absorb atmospheric pollutants and provide integrated responses on the air quality, although there are critical issues regarding different storage capacity of the species used and the influence of environmental factors.

Mosses are used to study pollution in the surroundings of particular industrial plants (e.g., thermal power plants, steel works, metal smelters, cement works etc.) and their use in metal pollution monitoring was of significant importance, and subject of several, though limited, reviews (Fernandez et al., 2007).

These organisms are used as bioindicators and bioaccumulators. In the later case, the most commonly used biomonitoring techniques are of two types: active, taking advantage of carpets of mosses transplanted or using moss bags and passive ones that rely on indigenous/native peoples.

The first allow to obtain information concerning the effects of pollutants on the ground assessing the air quality as a whole, even in areas lacking or deficient in mosses. The majority of investigations have utilised epiphytic mosses as *Hypnum cupressiforme, Hylocomium splendents* and *Pleurozium schereberi*; these were widely used in Europe due their abundant (Gerold et al., 2000; Oniawa, 2001).

Among the pollutants, "heavy metals" are of particular interest (Schilling and Lehman, 2002) whose presence in particulate atmospheric is the result of complex interactions between natural and anthropogenic factors.

This paper illustrates the use of mosses in the monitoring of air quality in a highly contaminated industrial site.The obtained results, using mosses as biomonitors of trace metals, were compared with the data of atmospheric distribution of particulate matter (ISPESL, 2006).

Objectives

The purpose of this study was to evaluate the atmospheric deposition of heavy metals by native species, *Hypnum cupressiforme and Pleurochaeta squarrosa*, in four stations in Taranto area applying both active and passive biomonitoring techniques, to include the area of Taranto in a national network of biomonitoring.

The metals analyzed were chosen in relation to toxicity and specific situations of industrial pollution and vehicular traffic. It was set up a "network of biomonitoring" using mosses collected in contaminated areas.

The analyses were carried out in several seasons and in different environmental conditions.

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Methods

The *Hypnum cupressiforme* for the preparation of moss bags and for active sampling, was collected in the woods Orimini (Martina Franca, Taranto), an area chosen because of funds not subject to obvious contamination. The carpets of moss were collected from the trunk of most trees and in different parts of the logs. In the laboratory, the mats of moss were subjected to a coarse cleaning and washing were performed seven successive period of ten minutes each, in order to enhance removal of metals, and especially metals associated with atmospheric particles. Finally, the washed material was dried in air. The development of moss bags was, made using pieces of nylon mesh particle 10x10 cm, with mesh 2.1 mm, previously conditioned with a solution of HNO_3 10%, closed with a nylon thread to form spherical bags having diameter of 3-4 cm; in each bag was placed a quantity of moss equal to 400 mg. The moss bags were placed in four sampling stations of Taranto city (Fig. 1): Villa Peripato (city center), Piazza Garibaldi Square (city center), Tamburi district, Paolo VI district at a height of 1,5-2 m from the ground. They were attached using nylon thread in support present in the monitoring stations placed in the sampling stations; before each exposure moss bags was carefully moistened with distilled water. The exposure period was six weeks and were carried out two rounds of exposure in two different seasonal periods: spring and summer. After exposure the moss bags were collected and placed in polyethylene containers. In the laboratory *H. cupressioforme* was removed from the bag and placed in a crystallizer and dried at 45 ° C for 48 hours in an oven thermostat. In addition, a sample portion was dried at 105 ° C to assess the loss of water.

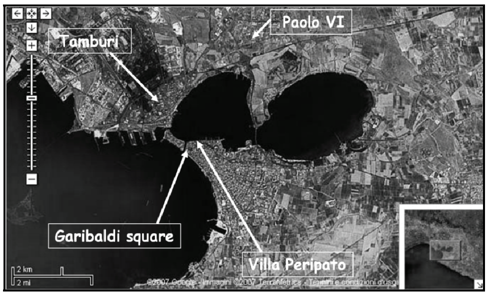

Fig. 1. Map of sampling area

The tissues were then ground in a centrifugal ball mill and stored in polyethylene containers, previously conditioned with 10% $HN0_3$ until mineralization in a microwave oven. For the determination of metals 0.25 g of each sample were then taken to the mineralization (2.5 ml of 30% H_2O_2 and 5 ml of concentrated HNO_3) with microwave model MARS X (CEM Corporation). The digestion of the soil was performed by placing 0.25 g of sample in Teflon containers (PTFE), in which were later added 9 ml 70% HNO3 and 3 ml HF 50%. The determination of mercury was performed using automated mercury analyzer (Advanced Mercury Analyzer AMA 254). For quantification of Cd, Cu, Zn, As, Pb, Ni, V, Pt, Pd, Cr, Mn, Al and Fe was used ICP-MS. For passive sampling *H. cupressiforme* and *P. Squarrosa* species were used. Only Villa Peripato has been select as station of sampling because results to be the more one contaminated by heavy metals by previous studies (Buonocore et al., 2010). In the laboratory to obtain a sample of moss as homogeneous as possible we chose to take only the apical part (1-1.5 cm), green or yellow-green probably corresponding to the biomass produced during the last two years, until obtain at least 3 grams of sample. The analyses did not reveal any correlation between the analyzed metals and Al, so it not was necessary to apply the fix from contamination by soil.

Results and discussion

The moss bags analysis shows that in all stations there was an increased level of metals in *Hypnum cupressiforme* compared to blank. In particular levels of Ni are about ten times higher than the blank, those of Cd, As, V approximately six times; the levels of Zn, Hg, Al, Cr, Cu m, Fe and Mn are increased by three times while the Pb twice.

High concentrations of metals were found in urban zone (Villa Peripato and Tamburi stations); the first levels of concentration for metals follow the order: Al>Fe>Mn>Zn>Cu>Pb>V>Cr>Ni>Cd>As>Pd>Hg. The highest concentrations of Cd, Ni, Al, Cr, As, Mn, V were found mainly in the sampling station of Villa Peripato while in the station of Tamburi district (near the industrial area) higher levels of Hg, Zn, Cr and Cu were found. In the summer, values of concentration of metals were reported even higher and levels follow more or less the same trend that you had in spring: Al>Fe>Mn>Zn>Pb>Cu>V>Cr>Ni>As>Cd>Pd>Hg.

Particularly in the station Tamburi were found higher concentrations of Zn>Cr>Fe>Mn>Pb and V. In the station of Villa Peripato and Tamburi district were found higher values of Al, Hg while V and Pb have the same concentrations in the stations of Villa Peripato, Piazza Garibaldi and Tamburi district. Regarding Cd, there was a decrease of concentrations at all stations, this could be justified by the fact that during the summer the source linked to the traffic impact is a lesser extent than the industry, as a result of repayment of the population in places tourism.

For Zn was found the same behavior except the Tamburi district station, located near the industrial zone, where it was observed an opposite situation.

Analytical results show that the most contaminated areas are to be urban areas where there is the influence of industrial pollution, vehicle traffic and harbor activities. In the station of Paolo VI, located to the northeast of the industrial area of Taranto, these contributions are approximately the same order of magnitude of other stations, although the concentration levels are lower because, due to the wind direction, remains on the edge of the polluted area for much of the year.

Rainfall in spring was higher than in the summer and this has negatively affected the uptake of metals sampling in the summer, promoting leaching. The obtained results with the active biomonitoring (moss-bags) using the moss *H. cupressiforme*, show that the most contaminated station is found to be Villa Peripato followed from the Tamburi district. In the second experiment, therefore, it was decided to carry out the passive biomonitoring only in the most contaminated area (Villa Peripato) using the same species of moss grown naturally (*Hypnum cupressiforme*).

The obtained data show that the epiphytic moss, in the passive sampling, has a higher bioaccumulation capability than that obtained in the active sampling with moss bags. For both types of biomonitoring, however, the order of the bioaccumulation levels of metals is the same: Al> Fe> Mn> Zn> Cu> Pb> V> Cr> Ni> Cd> As> Pd> Hg. A further comparison was carried out between the *H. cupressiforme* and an another species of epiphytic moss present in the selected station (*P. squarrosa*).

The purpose was to compare the bioaccumulation capability between the two species of mosses. The sampling was carried out in two different seasons (spring and summer). For example, in Fig. 2, it are shown the results obtained: both species of mosses have a good bioaccumulation capability.

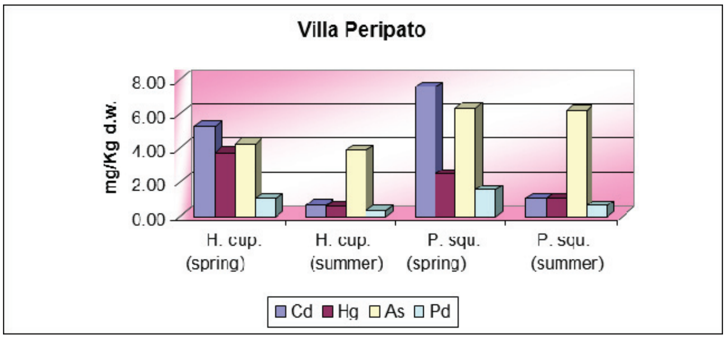

Fig 2. Comparison in passive biomonitoring between *H. cupressiforme* and *P. squarrosa* for Cd, Hg, As, Pd

As regards the following metals: Ni, Zn, Ál, Cu, Pb, Cr and Hg result bioaccumulated in greater measure from the *H. cupressiforme* while Pd, As, Fe, Mn, Cd, V bioaccumulated mostly from the kind *P. squarrosa.*

This data are comparable with obtained data in active biomonitoring, in both cases Villa Peripato results to be the most contaminated area from heavy metals. Furthermore, data from ISPESL (National Institute for Prevention and Safety at Work) referring that concentrations of PM_{10} (mg/m^3) detected by automatic monitoring systems of atmospheric pollution in Taranto area, show that Villa Peripato station is the most contaminated site in comparison to the Tamburi and Paolo VI stations.

Statistical analysis

The results of active biomonitoring were statistically processed, by testing the linearity of Pearson coefficient; analysis was performed ($p < 0.05$) between the concentrations of metals in samples of *Hypnum cupressiforme* in both samples for the four monitoring stations.

Moreover, experimental data were processed by multivariate statistical analysis using the program STATISTICA (StatSoft Inc., Tulsa, OK, USA). The cluster analysis (HCA) was applied to a given set of four samples and 13 variables (Hg, Cd, Cu, Zn, As, Pb, Ni, V, Pd, Cr, Mn, Al and Fe). Tables 1 show the correlations between metals in the four stations sampled in spring and summer respectively.

The high correlation coefficient between the elements shows their common origin: V, Pb and Cd originating from petroleum refining processes, the same is true for As, Mn and Fe that may result from emissions from iron and steel center.

These metals are associated not only to particulate air pollution arising from industrial activities, but also arise in relation to vehicular traffic. Through dendrograms reveals that stations Garibaldi Square and Paolo VI district are correlated, in both samples, having similar levels of concentration and lower than the other two stations.

In fact in the spring sampling station of Villa Peripato is the most polluted sampling while in summer the same situation occurs for the station of Tamburi district. Marked correlations are significant at $p < 0.05$

Table 1. Pearson product moment correlation coefficients between metal levels in sampling stations during spring and summer period in active biomonitoring

	Cd	Hg	Ni	Zn	Al	As	Cr	Cu	Fe	Mn	Pb	Pd	V
Cd	1												
Hg	0.05	1											
Ni	0.45	-0.75	1										
Zn	0.34	0	0.58	1					a) Spring sampling				
Al	0.79	-0.55	0.89	0.44	1								
As	0.46	-0.85	0.95	0.3	0.9								
Cr	0.26	-0.56	0.91	0.83	0.68	0.73	1						
Cu	0.23	0.35	-0.57	-0.79	-0.18	-0.32	-0.84	1					
Fe	0.88	0.15	0.52	0.74	0.71	0.37	0.53	-0.19	1				
Mn	0.98	-0.12	0.51	0.22	0.85	0.58	0.25	0.28	0.78	1			
Pb	0.91	-0.11	0.7	0.68	0.88	0.61	0.63	-0.2	0.96	0.87	1		
Pd	0.45	-0.41	0.19	-0.57	0.48	0.48	-0.24	0.67	-0.02	0.61	0.17	1	
V	0.96	-0.22	0.69	0.44	0.93	0.69	0.49	0.02	0.86	0.97	0.95	0.46	1
Cd	1												
Hg	-0.47	1											
Ni	0.29	0.57	1							b) Summer sampling			
Zn	0.46	0.21	0.9	1									
Al	0.07	0.84	0.79	0.46	1								
As	0.72	0.05	0.84	0.94	0.46	1							
Cr	0.81	0.09	0.79	0.8	0.58	0.95	1						
Cu	0.58	0.29	0.16	-0.13	0.61	0.11	0.43	1					
Fe	0.59	0.16	0.9	0.98	0.51	0.99	0.9	0.03	1				
Mn	0.87	-0.22	0.66	0.84	0.25	0.96	0.92	0.11	0.91	1			
Pb	0.83	-0.09	0.75	0.87	0.37	0.99	0.96	0.17	0.94	0.99	1		
Pd	0.64	0.32	0.59	0.39	0.76	0.61	0.83	0.86	0.54	0.56	0.63	1	
V	0.87	0	0.71	0.74	0.52	0.92	0.99	0.46	0.85	0.93	0.95	0.83	1

Concluding remarks

The results obtained using *Hypnum cupressiforme* and *Pleurochaete squarrosa* as biomonitors for heavy metals are comparable with the data of atmospheric distribution of particulate supplied by ISPESL data. Heavy metals are good environmental indicators because they do not undergone degradation processes, are readily ascertainable from the analytical point of view and can be considered as typical tracers of contamination of the process of air pollution.

Moss-monitoring using *Hypnum cupressiforme* and *Pleurochaete squarrosa,* offers a more cost-efficient method with less available technology. It also allows to identify problem areas and local sources of emission. As a consequence it is recommended for ecological monitoring at a national and local scale. Both the active and passive biomonitoring, show good results for the determination of metal contamination in the atmosphere. The techniques are readily reproducible and low cost and can be used now commonly in other parts of the world. The active biomonitoring has as advantage, compared to the passive, the possibility of being able to be applied anywhere you want. For passive monitoring it is necessary that the moss is present in the chosen area. It is not always possible, however, find mosses growing in industrial areas. However, overall, the data obtained are in agreement with the literature for various Italian and European cities. This study provides a methodological approach that can monitor the environmental quality of areas at risk by entering the city of Taranto in a national network of biomonitoring.

Keywords: air pollution, biomonitoring, bryophyte, heavy metals, mosses.

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2005:2012 AIR QUALITY IN APULIAN URBAN AREAS

Extended abstract

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Background

Apulia is a 19,362 km^2 region in the south-east of Italy developing about 800 km of coastline, surrounded by the Adriatic Sea in the northeast and by the Ionian Sea in the south. Its territory is quite low with mountains only per 1.5 %, level ground per 54 % and hills per 44 %. It is divided into six provinces: Bari, Brindisi, Lecce, Foggia, Taranto and Bat (Barletta, Andria, Trani), the latest one including ten Municipalities. Two relevant industrial areas (Brindisi and Taranto) and several cities of medium-large dimension characterize the territory.

Bari is the capital of the Region and its most populated town, with over 300,000 inhabitants. Its urban centre is characterized by high vehicular traffic, while in its industrial area activities in the mechanical sector take place. Lecce and Foggia are service industry towns, with small artisan areas. Due to the numerous and high impact industrial activities (steel production, metallurgical, chemical, petrochemical, cement – producing and coal power plants), Taranto and Brindisi are included in the so - called *areas at high risk of environmental crisis* of the Region. In particular, Taranto hosts a heavy industrial district unfavorably positioned towards nearby residential areas, including the largest steel factory in Europe (ILVA), an oil refinery (ENI) and a kiln factory (CEMENTIR).

At the aim of improving air quality, during the last decade European emission mitigation policies have been following a multi - pollutant approach implementing various legal instruments. Also at regional level, air quality strategies were actuated to ensure good life quality to citizen, especially the ones living close to industrial areas and exposed to pollutants high levels.

The aim of this paper is to evaluate pollutants concentration from 2005 to 2012 in Apulian urban areas, in order to estimate PM_{10}, benzene and dioxide nitrogen trends and efficiency of environmental regional policies. In industrial area of Taranto, special attention will be turned to benzo (a) pyrene.

It must be pointed out that trend detection can be considered a key aspect of understanding the state of air quality on the basis of past data (Blanchard, 1999; Klemm and Lange, 1999). It also aids the development of air pollution control policy and provides a reference for making further evaluations.

Exposure to pollutants such as benzene, nitrogen dioxides and particulate matter is associated with increased mortality and hospital admissions due to health outcomes such as respiratory and cardiovascular diseases (Pope and Dockery, 2006). Benzo (a) pirene is classified in Group 1 by IARC as carcinogenic for human; cancers associated with exposure to PAHs - containing mixtures in humans were predominantly lung and skin cancers, following inhalation and dermal exposure, respectively (USEPA, 2010).

The pollution criticals of particular sites in Apulia Region were already evaluated in some other studies; Amodio et al. (2008) performed a statistical analysis on Taranto city highlighting an important contribution of industrial facilities on the air quality, especially in terms of concentrations of micro pollutants such as PAHs and metals. Caselli (Caselli et al., 2010) evaluated BTEX pollution in urban areas of Bari, confirming the presence of a single source, the vehicular traffic, having a strong impact on air quality. Mangia et al. (2011) analyzed sixteen years of air quality data (NO_2, SO_2 and TPS) in Brindisi area, revealing the influence of industrial area and of harbor on pollution levels and high correlation between pollution levels and wind blowing from eastern sectors.

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Methods

Apulian air quality monitoring network consists of 88 sampling sites located in urban, suburban and rural areas. Continuous monitoring stations are equipped with data analyzers connected to a data acquisition system. Data validation is carried out in order to provide accurate and reliable data.

Spatially representative sampling sites with consistent time series were chosen to evaluate pollution trend in Apulia over the last decade. Different kinds of sampling sites were considered: four traffic stations in urban site (Bari – Via Caldarola – lat 41.1135 long 16.3888; Brindisi – Via Taranto – lat 40.6342 long 17.9478; Taranto – Via Alto Adige – lat 40.4605 long 17.2636; Lecce – Via Garigliano – lat 40.3644 long 18.1743), one industrial station (Taranto – Via Machiavelli - lat 40.4886 long 17.2258) and one background station (Taranto – Talsano – lat 40.4119 long 17.2839). Foggia was not considered in this paper because of the lack of data; in fact air monitoring was carried out for just few years at the beginning of 2000 and then stopped. Monitoring started again in 2012 in a new site by the Regional Agency for Environmental Protection and Prevention (ARPA) will allow to produce a consistent time series in the future.

PM_{10} daily concentration was monitored by two different kind of instruments, both based on ß attenuation method: SWAM 5a monitors (FAI Instruments s.r.l. Rome, Italy) and MP101M (Environnement S. A., Poissy Cedex, France). NO_2 was monitored by 200 series (Teledyne - API San Diego, USA), an automatic instrument based on chemiluminescence detection principle which produces hourly values.

Benzene was monitored by automatic instruments based on gas chromatography technique with a built - in pre - concentration system. Hydrocarbons are pre-concentrated, desorbed thermally and separated in column. Analysis is performed by a photo ionization detector. B(a)P determination was carried out on PM_{10} filters collected in the three Taranto sites, according to UNI EN 15549:2008 by a DFS High Resolution GC/MS system (Thermo Fisher, Bremen, Germany).

Results and discussion

Fig. 1 shows annual mean concentration trends of benzene, NO_2 and PM_{10} from 2005 to 2012 in traffic sampling sites.

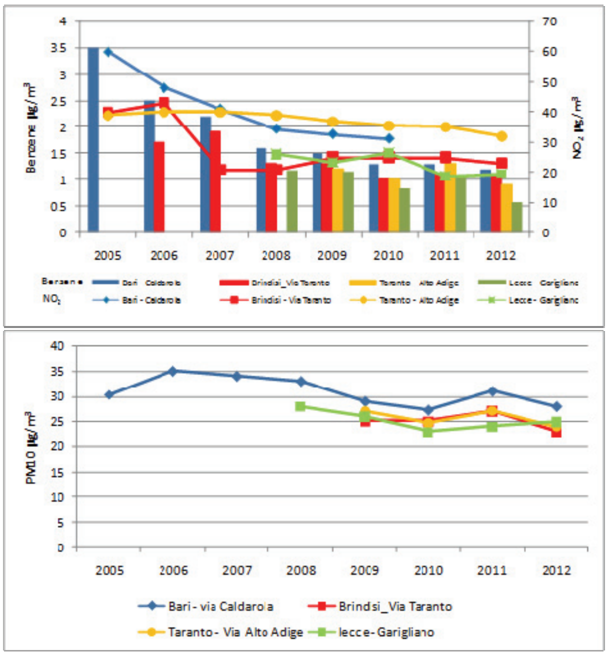

Fig.1. Benzene, NO_2 and PM10 trends from 2005 to 2012

Benzene concentrations from 2005 to 2012 decreased by 65 per cent in Bari, by 35 per cent in Brindisi, by 40 per cent in Lecce and by 10 per cent in Taranto. The reductions at these urban locations are mainly the result of regulations which lowered the benzene content of gasoline and regulations aimed at improving the emission performance of on-road vehicles. A similar trend, even if less pronounced, was observed for NO_2.

The reason of this smaller reduction could be found in the failure of European policies for emission reduction from light-duty diesel vehicles based on the increasing stringency of emission limits (the so-called Euro standard), that did not result in an equivalent reduction of on-road NOX emissions. In fact, average NO_X diesel vehicles emissions exceed limits up to a factor of 14 (Weiss et al., 2012).

Table 1. Daily threshold overcoming number in traffic stations

	2005	*2006*	*2007*	*2008*	*2009*	*2010*	*2011*	*2012*
Bari - Via Caldarola	n.a.	54	42	38	16	9	28	13
Brindisi - Via Taranto	n.a.	n.a.	n.a.	n.a.	n.a.	12	10	0
Lecce - Garigliano	n.a.	n.a.	n.a.	30	17	11	10	3
Taranto - Via Alto Adige	n.a.	n.a.	n.a.	n.a.	13	6	9	2

Fig. 2 shows PM_{10} and benzo (a) pyrene trends from 2009 to 2012 in three different stations at Taranto municipality. PM_{10} annual means follow the same trend of concentrations and do not change significantly during this period; even if no annual threshold overcoming is recorded at any of these stations, industrial site “Machiavelli” has steadily highest values because of its proximity to industrial area.

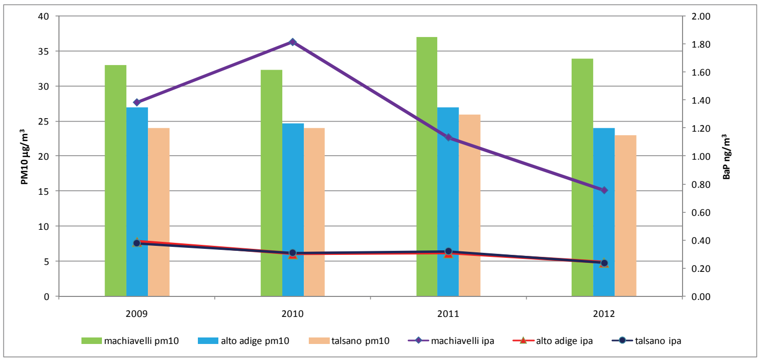

Fig. 2. PM_{10} vs. BaP in Taranto city from 2009 to 2012

More significant differences are recorded for benzo (a) pyrene levels. As for PM_{10}, “Machiavelli” concentrations are constantly higher than other sites, but a well-rendered decrease was observed for this pollutant from 2010 and, for the first time since the monitoring start, in 2012 B(a)P annual mean was lower than the 1 ng/m3 objective value. The reason of decrease could be found in Air Quality Recovery Plan for Taranto Area (Regione Puglia, 2012) enacted by Apulian Government in 2012. Because of the close correlation between unfavorable wind conditions and pollutant transport from industrial site to the adjacent urban area, in the so-called wind days the Plan requires the industries to put into effect mitigation measures such as emission reduction from point and diffuse sources. Therefore, B(a)P seems to show a strong correlation with emission sources.

Concluding remarks

On the basis of an 8 - year investigation on air quality, a benzene and NO_2 concentration decrease in Apulian urban areas was found with no exceedances of annual mean limit values. PM_{10} instead showed no significant difference over the years and within different areas, its levels depending on large contribution of regional background and long range transport.

A different scenario was observed in the Taranto area where in the industrial site “Machiavelli” PM_{10} levels are higher than in urban and background sites, with annual mean concentrations remaining unvaried among different years. Benzo (a) pyrene, instead, showed an evident decrease from 2010 to 2012 and appears to be a good indicator evaluating industrial emission variations.

Keywords: air quality, Apulia, benzo(a)pyrene, Taranto, Trend.

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INTEGRATED TECHNOLOGIES FOR SEDIMENT TREATMENT

Extended abstract

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Background

The management of sediment in aquatic ecosystem has been an important issue for water managers throughout history. The changing nature of sediment issues, due to increasing human populations, the increasing prevalence of man and recognition of the important role of sediment in the transport and fate of contaminants has meant that sediment management today faces many complex technical and environmental challenges. Sediment management is complex, involving a careful balance of science, policy and economics. So, there is not a single correct way to address a problem, but, rather, the approach should be driven by the ecological, political and economic goals of interested parties.

When sediments are managed to achieve ecological goals (i.e. reclamation of the seabed next to former industrial areas), the main focus is on sediment contamination analysis, removal and treatment or disposal, thus involving sediment quality more than quantity. Trevi SpA, together with the Department of Industrial Engineering (DIN) of Bologna University designed, realized and tested a new dredging prototypal device, called Sludge Buster (SB), that has been designed for application where excavation accuracy and environmental impact minimization have particular relevance (i.e. contaminated sites).

On the other hand, when sediments are managed to achieve socioeconomic goals (like navigational dredging or flood defense), the focus is on managing sediment quantity, because it is the presence or absence of sediment that is affecting final objective (for example, excess sediments in navigation channels) However, uncontaminated sediments have some ecosystems implications in terms of turbidity and/or habitat loss. In these cases, the movement of sediments is a given (if permitted), involving also management of removal, placement, disposal and/or treatment options. Trevi SpA, together with DIN designed, realized and a first commissioned a prototypal Pneumatic Flow Mixing (PFM) method plant. PFM method is a process for sediments transport and on-line consolidation (Oota et al., 2009).

Objectives

Sediment removal activities carried out with usual machineries (such as mechanical or hydraulic dredges) generate significant problems, especially in contaminated sites, due to the mechanical and/or hydraulic action of the dredge which involves the re-suspension of a considerable part of the dredged material. Moreover, the action of such devices does not allow to reach high performance in terms of precision dredging. Finally, also the working depth range is limited. Therefore, design specifications for an innovative technology for dredging of sediments, particularly those contaminated, should be (1) no moving submarine mechanical devices, (2) minimization of turbidity generated by the dredging device, (3) high accuracy in sediment removal and (4) adaptability to different depths (operational flexibility). SB was developed to reach these objectives. A first prototype was tested to verify its functional characteristics.

A new approach is needed to optimize sediment management after dredging, in particular regarding to sediment transport, which is often seen as a separated phase of the sediment reuse cycle. Instead of moving the dredged material and storing it for an indefinite time waiting for the follow-up treatments, you can think of to take advantage from this movement to perform some additional treatment on the sediment. PFM method was developed

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to allow sediment transport and on-line stabilization by injection of binder trough transport line. A first prototype plant was designed by use of software simulator.

Outline of the work

This work is divided in two main parts:

- The first part covers design process and experimental test results on first SB prototype. Based on results, a new industrial prototype was designed and realized.
- The second part covers design process of PFM prototypal plant. In particular, the paper shows critical aspects in PFM plant design.

Methods

A jet pump is a device that transfers momentum from a high velocity primary jet flow to a secondary flow. It is geometrically simple since it consists of four main components: nozzle, suction chamber, mixing throat and diffuser. The absence of moving mechanical parts eliminates operational problems associated with bearings, seals and lubrication. Moreover, when applied in sediment removal from backdrop, turbidity and, generally, environmental impact are minimized. Jet pump has been used in the field of sediment management since '70 (McNair, 1976), especially for sand by-passing plant. DIN developed an innovative plant for draught maintain characterized by the fact that the main element, called "ejector", is a fixed open jet pump (i.e. without closed suction chamber and mixing throat) with a converging instead of a diffuser. First experimental plant was designed, realized and tested (Amati and Saccani, 2005) in Riccione, Italy, showing good results in terms of efficiency and economic. A second industrial scaled up and fully automatized plant has been installed in Portoverde, Italy, and is still under experimental investigation regarding management costs that, however, seems to be an order of magnitude lower than dredge ones. Since the fixed ejectors plant demonstrates to reach the goals (1) and (2), Trevi and DIN decided to adapt this technology to a mobile device, which is the SB.

PFM can be classified as a premixing treatment method where dredged sediment and binder are carried out in a transfer or discharge pipeline (Oota et al., 2009). The materials in the pipeline are mixed by the effect of turbulent flow caused by pneumatic conveying transport conditions. In the PFM method dredged sediment is discharged on a screening and then in a hopper, where water can be added. The sediment is pumped into the transport pipeline until compressed air is injected. Pneumatic conveying is designed to obtain a plug flow transport: plug flow increases turbulence, thus allowing mixing between sediment and binder, that is usually cement. Depending on plant size, about 50-100 m are needed to fully develop plug flow into the pipeline. So, cement injection is placed at a distance L_1 from air injection. A minimum length L_2 before treated sediment discharge from pipeline is needed too, in order to guarantee cement and sediment mixing. Plug flow has also the skill of reducing pressure loss into the pipeline if compared with sediment transport at full pipe with the same velocity (about 8-10 m/s), that is the parameter that affects transport mixing capacity. Pneumatic conveying design is a central issue in PFM design process. Over the years DIN developed a fluid-dynamic software simulator, called TPSimWin, able to foresee pneumatic conveying parameters that produce a certain transport behavior (Saccani, 2005). TPSimWin has been used in PFM prototype plant design process. Moreover, sediment density control is an important issue in PFM method. Sediment density must be controlled to keep constant as possible the mass ratio w/c between sediment water content w and cement c, since this parameter affects sediment strength and treatment cost.

Results and discussion

An SB prototype has been designed in 2008, then realized and tested in 2009. First experimental campaign was conducted with the final aim of optimize hydraulic section and to determine SB behavior as a function of different geometrical parameters, that are nozzle diameter d and distance L between nozzle output and converging inlet.

Both delivery flow and mixture ratio (that is the mass ratio between solid and water inside the discharged mixture) were estimated on the basis of previous experience (Amati and Saccani, 2005). So, D was chosen to guarantee an output SB velocity higher than saltation velocity, thus avoiding discharge clogging.

Since D is a fixed parameter, dimensionless geometrical parameters d' and L' were defined as d'=d/D and L'=L/D. SB was tested on a drainage canal: sediment composition was about 80-85% of silt and clay and about 12-14% of sand. SB was trained by a boat which was connected to a winch, located at the shore. Boat (and thus SB) velocity may be regulated on five level, from about 6 to 29 cm/s. Test were carried on both in static condition (motionless SB placed on the riverbed) and in dynamic condition (boat and SB trained by the winch).

Pressure of primary flow was measured at the nozzle inlet as well as pressure of delivery flow at the convergent outlet. Primary and delivery mass flow were measured too, thus computing secondary mass flow as the difference between delivery and primary ones.

Then, flow ratio Q was defined as the ratio between secondary and primary mass flow, while head ratio H was defined as the ratio between delivery flow pressure at the converging and primary flow pressure at the nozzle.

Finally, SB efficiency η was defined as η=Q×H, according to general jet pump definition. Fig. 1a and Fig. 1b show experimental results obtained during stationary tests.

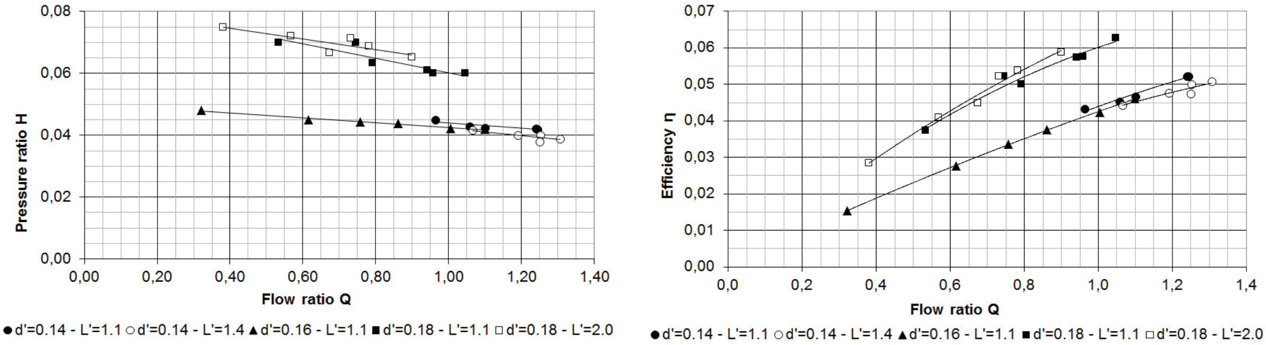

Fig. 1. (a) Head ratio H as a function of flow ratio Q for different SB configuration (d' and L'), (b) Efficiency η as a function of flow ratio Q for different SB configuration (d' and L'). Both curves from stationary tests.

Fig.s 1a and 1b shows that an higher nozzle diameter d lowers SB suction capacity (measured by flow ratio Q). On the other hand, an higher nozzle diameter d allows to reach higher pressure at the converging outlet, thus increasing sediment transport length. So, depending on specific application, it is possible to adapt SB for working with high solid mixture ratio, but with low SB discharge pipe length, rather than covering long distances from SB and discharge point or booster, but with low solid mixture ratio. The results are in line with the theoretical provisions for the behavior of the jet pump (McNair, 1976). Fig. 5 shows how, in the investigated range of flow ratio Q, a diameter nozzle d increasing corresponds to an increasing in terms of SB efficiency η. Fig.s 1a and 1b also shows that distance between nozzle and converging L should not have relevant influence in the investigated range of flow ratio Q in term of both head ratio H and SB efficiency η. Furthermore, results shown in Fig.s 1a and 1b are in line with passed DIN experiences (Amati and Saccani, 2005). The results obtained under dynamic conditions are corresponding to those carried out in static conditions. The only difference involves SB velocity management. In fact, it is important to move the SB with a velocity that is compatible with SB suction capacity. If velocity is too high, SB removes from the bottom a quantity of sediment greater than that which can "eat".

On the basis of the experimental results, a new prototype of SB has been designed and realized in 2011. SB suction device is connected to a self-propelled amphibious track (designed by Soilmec, that is an enterprise of Trevi group) served by a service platform placed on the track (alternatively, it may be placed on a support boat or directly on shore, if possible). This solution allows to high excavation precision with regard to the previous prototype. Precision may be increased by integrating the system with a GPS control system. Moreover, the suction chamber inlet can be equipped with a rotating screening or a reel. The new SB prototype suction capacity is about 160 m^3/h (can be higher or lower depending on sediment characteristics and nozzles size d) and it is able to dredge an area of about 200 cm per 20 cm.

First step of PFM plant design process is pneumatic conveying dimensioning. If a linear development (abscissa x) of the plant is considered, it can be stated that pressure p varies linearly along the pipeline. Air expansion due to pressure variation along the pipeline varies plug velocity V_p from start to end of sediment pneumatic conveying. Consider now the air expansion as an isothermal process. Thus, air density ρ_a varies along the transport only because of head loss $\Delta p = p_2 - p_1$. Head loss Δp can be expressed as a function of plug mean velocity V_{pm} by Eq. 1, where λ_s is the friction loss, that is a function of Reynolds number and relative pipe roughness, ρ_s is sediment density, Q_s is volumetric sediment flow and d_e is the equivalent diameter.

$$\Delta p = \frac{2}{\pi} \lambda_s \frac{L_1 + L_2}{d_e^3} \rho_s Q_s V_{pm} \qquad (1)$$

Plug mean velocity V_{pm} is a fundamental parameter. Low V_{pm} allows to maintain low head loss Δp and increases residence time of the cement inside the pipeline. On the other hand, low V_{pm} reduces mixing efficacy with regard to the homogenization process of sediment and cement which is favored by turbulent flow.

Moreover, if V_{pm} is too low, it can promote unmixing phenomena of the solid fraction, starting from the coarse one, with resulting in deposition of material and the risk of interruption of transportation due to clogging.

Otherwise, a high V_{pm} reduces the risk of duct clogging, but at the same time reduces the residence time of the cement and increases the head loss Δp, with a consequent increase of the difference between the initial and the final plug velocity V_p.

The simulation software TPSimWin was used to analyze and evaluate the effects of pneumatic conveying development. PFM plant was modeled with a first pipeline of length L_1 and diameter d_1 and second pipeline of length L_2 and diameter d_2, where d_2 is higher than d_1 to take into account air expansion.

Between L_1 and L_2 it was inserted an expansion chamber, where cement is injected, characterized by a negligible length L_3 if compared with L_1 and L_2, but with a diameter size d_3 higher than d_1 and d_2. Fig. 2a shows results for a 10 m^3/h plant.

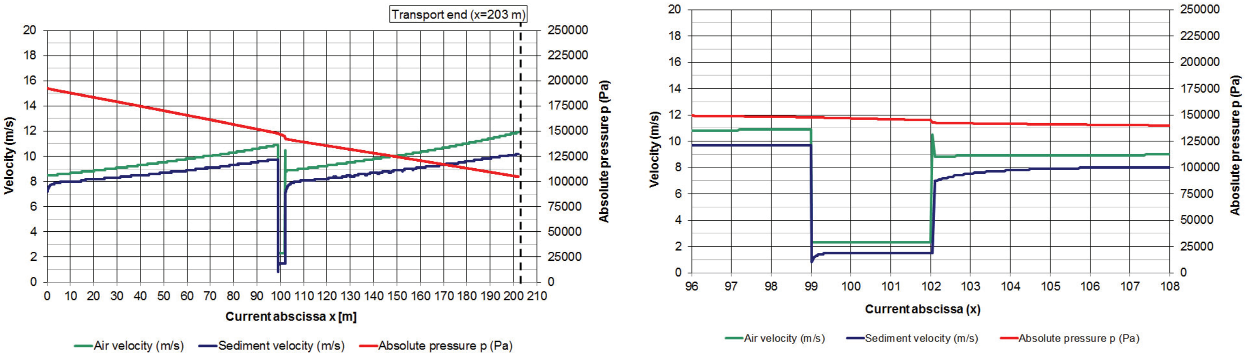

Fig. 2. (a) TPSimWin simulation result: air and sediment velocity and absolute pressure as a function of pneumatic conveying pipeline length, (b) TPSimWin simulation result for the expansion chamber: air and sediment velocity and absolute pressure as a function of pneumatic conveying pipeline length.

Sediment plug does not have the same velocity of air. This occurs because of the permeability of the liquid phase: the air flows at an increased velocity because permeate through water plug. If expansion chamber sediment velocity is not taken into account, a plug mean velocity of about 9 m/s is reached with an initial pressure p_2 equal to 1.9 bar. Furthermore, TPSimWin simulation shows the benefits of the expansion chamber, positioned between x=100 m and x=103m (Fig. 2b). In this section of the pipeline, plug transport, initially decelerates strongly from a velocity of about 10 m/s to about 1 m/s. Then, sediment reaches a regime velocity inside the chamber of about 1.5 m/s and, therefore, accelerates abruptly at the entrance of the next line from 1.5 m/s to 7.0 m/s. Thus, the expansion chamber favors the mixing between sediment and cement (which is injected into the chamber) through a lowering of the velocity which increases the length of the plug due to braking and mixing of different plugs. Moreover, deceleration increases the residence time of the sediment inside expansion chamber. With regard to sediment density control, a novel patent-pending measurement system has been developed and tested. This system will allow to decrease installation costs (with regard to measurement system like γ ray density meter) without decreasing measurement accuracy. A first PFM test facility was designed and realized in 2012. Plant size was scaled-up from 10 m^3/h to 2 m^3/h in order to allow better experimental field management (by reducing plant size it is possible to reduce pipeline whole length) and to contain costs. On the other hand, the plant has all the components of an industrial one, including a monitoring and automatic regulation system managed by a PLC. PFM plant is able to transport sediment up to 1,600-1,800 kg/m^3 of density. First commissioning finished at the end of 2012 and showed promising results in terms of cement and sediment mixing.

Concluding remarks

Sediment removal, placement, disposal and treatment are critical aspects of aquatic ecosystem management and restoration. Trevi and DIN developed, realized and tested two new different technology that can be interesting both in terms of economic and environmental impact reduction in the sediment management field. The Sludge Buster is a self-propelled amphibious track able to treat up to 160 m^3/h of sediment and it was designed to allow very accurate operations removals of sediment, thus being of particular interest in contaminated site application. The Pneumatic Flow Mixing scaled up industrial plant size is about 2 m^3/h. It is able to made a premixing treatment of dredged sediment by injecting cement while sediment are carried out in a transfer or discharge pipeline.

Keywords: Pneumatic flow mixing, sediment removal, sediment stabilization, sediment treatment, sludge buster.

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RESTORATION OF A POLLUTED INDUSTRIAL SITE IN ORDER TO CONNECT URBAN DEVELOPMENT AND NATURAL AREAS PROTECTION

Extended abstract

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Background

The presence of polluted areas, which often are abandoned and degraded, inside a town can represent a great element of discontinuity for the urban development; a work of restoration of a polluted site in a urban area has to cope with this problem. The present paper describes the restoration of the industrial site of the steelworks "Acciaierie e Ferriere Pugliesi (AFP)" located in the town of Giovinazzo, province of Bari, in the south of Italy, Apulia region.

The AFP was founded between 1923 and 1924 to produce steel; the factory was extended during the years 1932 and 1933 to build the rolling mill, the steelwork and later the foundry, the engineering workshop and a section to produce farming equipment (Pugliese, 1998). During the Second World War the factory was occupied by the British armed force and it was used only to produce military weapons and equipment. At the end of the war the steelworks was reorganized and the plant for the production of the steel was modernized with the presence of special cooking chambers; the factory produced steel pipes, rails and shapes for rail equipment, especially for the East market. During these years, thanks to the AFP, Giovinazzo became one of the most industrialized towns of south of Italy (Pugliese, 1998) (Fig. 1).

Fig. 1. Historical image of the steelworks ex AFP (Giovinazzolive.it)

The steelworks was closed in 1979 because of the great crisis of the steel industry, started during the seventies. Currently, the site of the steelworks includes buildings occupied by small companies and unused buildings.

The interest of the present work is not only due to the importance of a polluted industrial site, one of the largest of the south of Italy, but also to its location. The site of the ex AFP is next to *Lama Castello*, which is a slightly incised valley typical of the Apulia region; this karst valley acts as water flow channel only during and immediately after heavy rainstorms and it reaches the shoreline. Even if the Lama Castello is protected by the regional landscape planning, it is actually in condition of degradation and abandonment because of the presence of

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wastes and steel slag which create a great embankment in the lower part of it. Furthermore, the south part of the site of the ex AFP is close to a great residential area planned in the general town plan, called C3. The residential area includes private and public residential buildings and a great green area corresponding to Lama Castello. The site of the planned residential area is separated by the site of the ex AFP by the railway from Bari to Bologna; the presence of the railway and of the polluted site represent an important separation of the residential area from the rest of the town; the presence of the polluted area of the ex AFP also can represent a danger for people health. Therefore, design for the intervention of restoration and of removal of pollution of the area of ex AFP in Giovinazzo also includes the area of Lama Castello and the area of the planned residential district.

The work also aims to regenerate the area of Lama Castello and to create a green course connecting the residential area to the town and to the sea in order to ascribe to the ex AFP the role of sewing up s parts of the urban context with different characteristic. The work of restoration of the area of the ex AFP is also connected with the Strategic Environmental Assessment of the plan for the residential area of the C3.

Objectives

The main objective of this work is to make people understand the importance of a connection between the restoration of a polluted site located inside a urban area and the needs of the town planning, in order to change an empty and insignificant space in a considerable place which can be able to connect different areas in a homogeneous way. In particular the present work is aimed at:

- Analyzing the pollution in the area of the ex AFP, of Lama Castello and the planned residential area C3;
- Designing e realizing intervention of restoration of the polluted areas;
- Regenerating the natural area of Lama Castello;
- Creating a green way connecting the planned residential area, to the town and to the sea through the Lama Castello.

The work of restoration and regeneration will be led together with the studies of the Strategic Environmental Assessment of the plan for the residential area of the C3, in order to integrate the analysis of the pollution with the studies on the environmental impacts of the implementation of the plan.

Outline of the work

The work is divided in three main parts (Fig. 2):

- The **Area A**, which is the area of the steelworks ex AFP. The area is about 98.000 square meters; the unused industrial building occupies an area of 30.500 square meters, whereas the buildings occupied by small companies occupy an area of 13.000 square meters. There are also 54.500 square meters occupied by service roads, wastes and steel slag. The project includes surveys and analysis of the pollution, emergency safety measures (MISE) and permanent safety measures (MISP) (D.Lgs, 2006). It also includes safety measures for the operability of the small companies working in the area of the ex AFP.
- The **Area B** is the area of the Lama Castello included between the railway and the road to Bari. The area is of about 14.00 square meters. The project of the Lama Castello consists of surveys and analysis of the pollution and of permanent safety measures (MISP). The work also includes interventions of regeneration of the lama (Fig. 3)
- The **Area C** is planned as residential area by the general town planning of Giovinazzo for an extension of about 223.200 square meters; the area also includes a part of the Lama Castello. The project consists of surveys and analysis aimed to know if the area is polluted in order to exclude danger for the health of resident people.

Fig. 2. Image of the project area

Fig. 3. Image of Lama Castello with the steelwork in the background

Methods

This paper presents a best practice in the restoration of polluted industrial sites connecting both the needs of removing pollution and the regeneration of a natural area and the urban development.

This is the reason why this paper talks not only about the techniques for the restoration of a polluted site, but also about the other measures affected to preserve the natural area of the Lama Castello and to solve the problem of the non-connection of the area C3 with the rest of the town caused by the presence of the railway and of the polluted site of the ex AFP. In such a project it is very important to work with people who live or work in the interested area or near it. So, one of the first action conducted during the project has been a number of meetings aimed to involve people. The citizens have been involved in two public meetings organized with the help of a city committee, the *Osservatorio per la legalità e per la difesa del bene comune* of the town of Giovinazzo.

The aim of the meetings was to explain the project and the main problems of the interested areas, and collect ideas for the restoration, regeneration and reuse of the area of the ex AFP. Each meeting consisted in a power point to explain the project and a question time to give people the opportunity to communicate ideas for the project or to ask question about the risks for their health due to the pollution of the area. Furthermore, one of the main problems of this project was that the industrial area of the ex AFP is actually in part occupied by small companies working in the industrial buildings; so it could be interference between the activities of restoration of the area and the activities of the companies. Each meeting consisted in a power point to explain the project and a question time, in order to give people the opportunity to communicate ideas for the project or to ask questions about the risks for their health due to the pollution of the area. Furthermore, one of the main problems of this project is that the industrial area of the ex AFP is actually in part occupied by small companies working in the industrial buildings and this could represent interference between the activities of restoration of the area and the activities of the companies.

In order to solve this problem the project includes safety measures for the operability of the small companies working in the area of the ex AFP. These measures have been agreed with the companies themselves in two different technical meetings aimed to establish the areas to be used only for the restoration interventions and the areas to be used by the companies, especially with reference to the interior road access. The result of the two meetings has been the plan of the safety measures for the operability of the small companies working in the area of the ex AFP (Fig. 4).

Fig. 4. The illustration of the safety measures for the operability of the small companies defined during the meetings

The presence of the natural area of Lama Castello nearest to the ex AFP was to be faced with particular regard because of its importance for the flora and fauna and its actual state of degradation. Furthermore, the restoration and regeneration of Lama Castello was to be conducted together with the activities of the planned residential area C3, because some soil analysis implemented in 2005 gave the result that the area was polluted with understandable risks for the health of residents. Besides, the presence of the ex AFP and the railway represented a great separation of the area C3 from the rest of the town. The plan for the area C3 was very old so that any Strategic Environmental Assessment has been assessed. The correct methodology has been suggested so to conduct together the analysis of the pollution in the area and the studies for the Strategic Environmental Assessment of the plan of the C3 in order to examine all the possible interaction of the plan with the environmental components and with the health of people.

The consideration of the need to reduce the environmental impacts due to the transportation of people living in the area of C3 suggested the need to create pedestrian paths and cycle lanes connecting it to the rest of the town; therefore the regeneration of Lama Castello could be the only way to create a connection with the town, such a green way from the area of the C3 to the town and to the sea.

Results and discussion

A good relationship with the small companies working in the area of the ex AFP has been started up. In a short time the operation of the emergency safety measures and of the safety measures for the operability of the companies will start; meanwhile the companies continue to work in their industrial buildings.

A collaboration with the owners of the industrial building began during the activity of the project, aimed to define together the appropriate future use of the area in order to combine the economic interest of the property with the needs of giving to the ex AFP the role of connection element between the protection of the natural area of Lama Castello and the development of the residential area C3.

The analysis of steel slag, which create a great embankment in the lower part of Lama Castello, define it "non-hazardous waste" - CER code 100903 "furnace slag". This suggests that the wastes can be removed to regenerate the course of the valley. Besides, the Strategic Environmental Assessment indicates that the lama can be a green course connecting the area of C3 with the town and with the sea.

There is also a web site of the project, always updated at the same speed of the activities, where people can be informed about the progress of the activities (Fig. 5).

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Fig. 5. The web site of the project

Concluding remarks

The project will end in 2014 and it will give to the citizens of Giovinazzo not only a place with no pollution, but also a central crux connecting the new residential area of the C3 to the sea by means of pedestrian paths and cycle lanes in the regenerated Lama Castello.

Keywords: natural areas, regeneration, restoration, , steelworks, urban development.maximum five, alphabetically

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CONTAMINATED SITES: ASSESSMENT OF VOLATILE ORGANIC COMPOUNDS (VOCs) IN OUTDOOR AND INDOOR AIR

Extended abstract

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Background

VOC migration from contaminated surface soil, subsurface soil and/or groundwater to outdoor and/or indoor air can deteriorate air quality in both residential/recreational areas and industrial/commercial sites. The high conservatism of predictive models used to assess the health risk associated to this exposure pathway is now well known. When the health risk results not acceptable or the site specific target levels are exceeded, soil gas and/or indoor/outdoor air sampling can be planned to verify the modeling results and monitor the actual exposure of population and workers to migrated VOCs. The Legislative Decree n. 152/2006 (transposing, inter alia, VOC Solvents Emissions Directive, 1999/13/EC), as "any organic compound having at 293,15 K a vapor pressure of 0,01 kPa or more, or having a corresponding volatility under the particular conditions of use". The World Health Organization (WHO) categorizes indoor organic pollutants depending on their boiling point (BP) (WHO, 1989) as:

- Very Volatile (gaseous) Organic Compound – VVOC: BP from < 0 °C to 50 - 100 °C,
- Volatile Organic Compounds – VOC: BP from 50-100 °C to 240-260 °C,
- Semi Volatile Organic Compounds - SVOC: BP from 240-260 °C to 380 - 400 °C
- Organic compound associated with particulate matter or Particulate Organic Matter – POM: BP > 380 °C

In this work VOC means any VVOC, VOC and SVOC as defined by the WHO.

Objectives

This paper presents the content of a protocol nearing completion for the national contaminated site Porto Marghera (Venice, Italy) to verify by air monitoring the acceptability of VOC levels indoor/outdoor or to confirm the human health risk assessed by the predictive models applied for the inhalation exposure pathway. The measured concentrations will be used to decide if a remediation, an interim or abiding mitigation action is required to protect the area goers or resident depending on the area use and, for industrial sites, also on the eventual overlapping of occupational and environmental exposure. This last aspect related to worker tasks has been so far generally neglected in the current practice. The inappropriateness of the proposed procedure to assess the occupational exposure of the workers assigned to remediation activities must be highlighted.

Outline of the work

The present work is so structured: (i) the overall procedure developed to decide the protective actions to be taken (or not) is described (Fig.1); (ii) then the criteria to define the acceptable or reference values in air (CR_{air}) to compare with the measured ones are reported (Fig.2); (iii) finally air monitoring strategies are outlined.

Methods

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When a VOC contaminates the unsaturated soil or groundwater, the Legislative Decree n.152/2006 requires a comparison between its concentrations measured in the contaminated matrix and the corresponding screening levels or CSCs (STEP 1). If the CSC is not exceeded no action is required, while if the CSC is exceeded the site is deemed potentially contaminated.. If the risk is acceptable or the measured values are not greater than CSR, no action is required. Otherwise the following options are available (STEP 3): • *Option A*: Action on environmental media. • *Option B:* Soil gas measurements. Then the risk assessment must be worked out again using the measured values as input for it, to calculate the risk (R') or the risk threshold value in the unsaturated soil or groundwater from soil-gas (CSR') and the eventual exceedance of the acceptable risk or of the same CSR' must be verified. If R' or CSR' are not exceeded no action is needed, otherwise Option A or Option C should be selected. • *Option C:* Air monitoring. Modes to proceed according to the residential/recreational or industrial/commercial use of the site are illustrated below. For residential/recreational sites compare the measured values with the acceptable or reference value (CR_{air}). If CR_{air} is not exceeded no action on the contaminated environmental media is required. For industrial/commercial sites two options are available distinguishing between exposed workers and not exposed workers according to their tasks.To manage the health risk for the occupationally exposed workers, the following options are available: • *Option D:* as like as for residential/recreational sites compare the measured values with the acceptable one (CR_{air}). If CR_{air} is exceeded an action on the contaminated environmental media is required. • *Option E:* to manage the health risk for the occupationally exposed workers fulfill the legislative decree n.81/2008 (directive 98/24/EC transposition) duties verifying the compliance with OELs by monitoring workplace atmosphere, considering the suggestions of the National guidance document for worker protection from carcinogens and mutagens (Italian Technical Coordination of the Regions and Autonomous Provinces for Occupational Safety, 2002) where exposure to carcinogens occurs.

To manage the health risk for the occupationally not exposed workers, the following options are available: • *Option F*: Put into effect the Option D that is carry out air monitoring and compare the measured values with the acceptable or reference value (CR_{air}). If CR_{air} is exceeded an action on the contaminated environmental media is required. • *Option G:* The employer includes among the occupational hazards VOCs emitted from the contaminated soil or groundwater and fulfils the Legislative Decree n. 81/2008 duties. Particularly he reviews the occupational risk assessment attributing an additional risk to the involved tasks and verifies the compliance with OELs considering the suggestions of the above cited National guidance document where exposure to carcinogens occurs.

Acceptable or reference values for VOCs in air (CR_{air})

The criteria to define the acceptable or reference values to compare with the measured ones reported below apply with some necessary distinctions for residential/recreational or industrial/commercial sites. The CRs_{air} are deemed valid for both indoor and outdoor air. They in effect provide a basis for protecting public health from adverse effects of air pollutants and WHO Air quality guidelines do not differentiate between indoor and outdoor air exposure because the site of exposure does not directly affect the exposure–response relationship (WHO, 2000). The criteria (Fig. 2) provide the following steps:

Step 1: CR_{air} coincides with national or international limit/target/guideline value, when available. The Legislative Decree n. 155/2010, national transposition of the directive 2008/50/EC on ambient air quality and cleaner air for Europe, in order to protect human health, regulates only benzene among the soil pollutant listed by the Legislative Decree n. 152/2006. For other pollutants, it is possible to refer to WHO Air quality guidelines. Particularly some VOCs of concern for soil are addressed by the Air quality guidelines for Europe (styrene, toluene, 1,2-dichloroethane, dichloromethane, vinyl chloride) (WHO, 2000) and by the guidelines for indoor air quality (trichloroethylene, tetrachloroethylene) (WHO, 2010). WHO guideline values for 1,2-dichloroethane, dichloromethane and tetrachloroethylene are at present based on noncarcinogenic effects while they are all classified as carcinogens both by the UE (cat. 1B or 2) and the IARC (Group 2A or 2B). Then in specific cases (e.g. in the presence of human sensible targets) the opportunity to take into account the carcinogenic effects of these pollutants should be assessed. In these cases the next steps (2 or 3) are appropriate.

Step 2: The CR_{air} coincides with the background level when available. Background levels shall be measured where the pollution level is not dominated by a single source (industry, traffic or residential heating), but is influenced by the integrated contribution from all sources upwind of the station. The position of the background measurement stations shall be locally assessed depending on the site context (rural, urban, industrial area), according to the criteria laid down by the Legislative Decree n. 155/2010. Air quality data collected by the monitoring network managed by public or private entities and compliant with regulatory requirements are published by the ISPRA, National Institute for the Environmental Protection and Research (ex APAT) (ISPRA/BRACE, 2011).

Step 3: The CR_{air} is calculated applying the risk assessment procedure in backward mode that is setting the acceptable level for the human health risk and selecting the most conservative value between the ones calculated for carcinogenic and noncarcinogenic effects (Eq. 1-2):

$$CR_{air}\left[\frac{\mu g}{m^3}\right] = \frac{TR}{EM \cdot SF_{inhal}} \times 10^3 \textit{ for carcinogenic effects} \tag{1}$$

$$CR_{air}\left[\frac{\mu g}{m^3}\right] = \frac{THQ \cdot RfD_{inhal}}{EM} \times 10^3 \textit{ for non carcinogenic effects} \tag{2}$$

where: TR is the acceptable value for the individual risk from carcinogenic substances; SF_{inhal} is the inhalation Slope Factor value for the pollutant of concern; THQ is the acceptable value for the individual non carcinogenic risk (Target Hazard Quotient); RfD_{inhal} is the inhalation Reference Dose value for the contaminant of concern; EM is the effective Exposure.

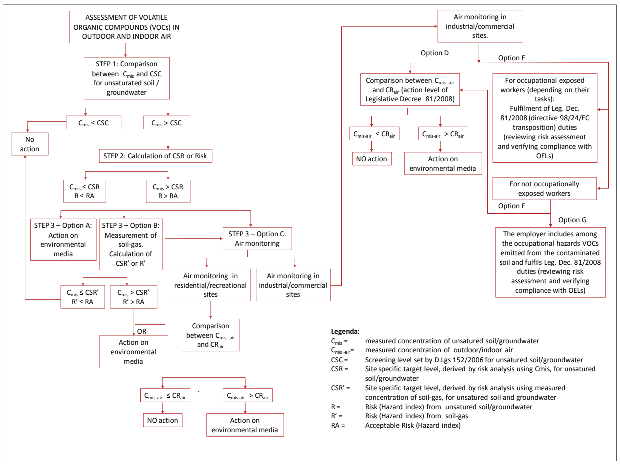

Fig. 1. Procedure flow sheet for VOCs assessment

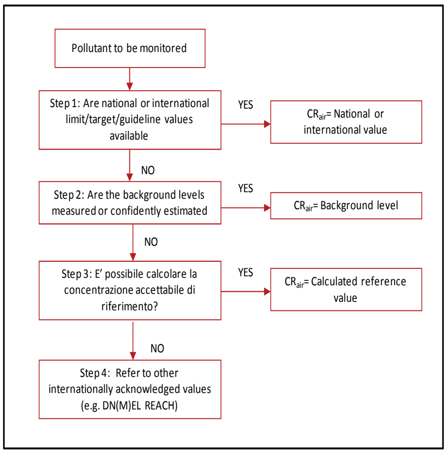

Fig. 2. Procedure to define the CR_{air}

Rate defined as the quantity of inhaled air per body weight unit, estimated by the following expression (APAT, 2008)(Eq. 3):

$$EM\left[\frac{m^3}{kg \times day}\right] = \frac{B_{air} \times EF_d \times EF \times ED}{BW \times AT \times 365\,\frac{days}{year}} \qquad (3)$$

The Legislative Decree n.152/2006 sets acceptable values for the individual carcinogenic risk ($TR=10^{-6}$), the the cumulative carcinogenic risk ($TR_{CUM} = 10^{-5}$) and the individual and cumulative risk for noncarcinogens ($THQ = THQ_{CUM} = 1$). Table 1 contains the definition and default values of the parameters to be used for EM and then CR_{air} calculations (APAT, 2008). The Age Dependent Adjustment Factor (ADAF) has also been introduced for carcinogens that act via a mutagenic mode of action (USEPA, 2005; USEPA, 2011). The site-specificity of the exposure factors to derive contextualized target values is anyhow recommended.

Table 1. Default exposure factors for CR_{air} calculation

Exposure Factor (EF)		***Symbol***	***Unit***	***Residential***		***Industrial***
				Adult	***Child***	***Adult***
Body Weight		BW	Kg	70	15	70
Average exposure Time to carcinogens		AT_c	years	70	70	70
Average exposure Time to noncarcinogens		AT_n	years	ED	ED	ED
Exposure Duration		ED	years	24	6	25
Exposure Frequency		EF	days/year	350	350	250
daily Exposure Frequency		EF_d	hours/day	24	24	6
Outdoor/Indoor inhalation rate by Activity Level	Sedentary/Passive	B_{air} (B_o/B_i)	m^3/hour	0.90	0.70	0.90
	Moderate Intensity			1.50	1.00	1.50
	High Intensity			2.50	1.90	2.50
Age Dependent Adjustment Factor		ADAF	(adim)	1	3-10(*)	1

(*) ADAFs of 10 and 3 are recommended for children ages: birth - <2 years and 2 - < 16 years respectively, when there is exposure during those years and available data are insufficient to derive chemical-specific adjustment factors (USEPA, 2011)

Step 4: When the CR_{air} is not calculable as the pollutant is not carcinogenic by inhalation, an inhalation RfD (for noncancerogenic effects) is not available and neither the background level can be measured or confidently estimated, other internationally acknowledged values can be used. For example the Derived No (Minimum) Effect Level DN(M)EL estimated for the specific target, long term, systemic (or local when more precautionary) effects, by entities subjected to REACH, when available (ECHA/CHEM, 2013).

Results and discussion

The environmental investigation is aimed at assessing the actual inhalation exposure of targets to VOCs migrated from a contaminated unsaturated and/or saturated soil, to decide if a remediation and/or mitigation action is required. An overall strategy shall be developed to allow the collection of samples being representative of the actual exposure of the area goers by both spatial and temporal points of view. For indoor air the monitoring strategy can be developed referring to the National Institute of Health indications (ISS, 2013). For outdoor air references are available in the Legislative Decree n.155/2010 and for workplaces in the Legislative Decree n.81/2008. Some indications considering the exposure to VOCs derives from soil contamination and referring to industrial sites, are reported below.

Sampling techniques. Indoor/outdoor air according to specific technical EN standards can be monitored by:

- Personal sampling: the equipment is placed on the employee and samples air in the breathing zone;
- Static sampling: the equipment is placed in a fixed location in the area of concern.

In the cases of our concern personal sampling may be complex, especially in residential sites. Then, even if personal samplers are not excluded, the following indications refer to environmental sampling.

Spatial distribution of sample points. For outdoor air at least on sample per homogeneously polluted area should be planned. In general a point is representative of an area surface of no more than 2500 m^2 (50 m x 50 m) (APAT, 2008). Where the site is contaminated by hydrocarbons, for which notable concentration gradients are expected, a lower distance (e.g. 10-20 m) is advisable. To define homogeneously polluted areas is possible to refer to the criteria for site area division laid down in the national guidelines (APAT, 2008). The sampling devices shall be located where the exposure (detected contamination and target presence) is maximum or where there are environment or population peculiarities. At least one sampling device shall be placed away from the influence of local emissions. To characterize indoor air a sample per each room is not generally needed and a representative room on the ground floor or basement if present, where the exposure is maximum, can be identified.

Sample and monitoring duration. Each sample shall go on for a time equal to the daily exposure frequency (EF_d in Table. 1) associated to the selected CR_{air} value. Generally: • in residential sites the sample duration should be 24 hours; • in recreational sites the sample duration should be decided case-by-case in function of the actual exposure duration. In the absence of site-specific information sampling should conservatively continue for 24 hours; • in industrial/commercial sites sample duration shall comply with EN 689/1997 standard indications for the determination of shift values, except for specific conditions to be case-by-case assessed.

The measurements to determine the environmental concentration should go on for 5-14 days (ISS, 2013). Measurement campaigns should be at least one during summer and one during winter to appraise seasonal variations related to meteorological conditions and/or cycles of activity (domestic heating, traffic intensity, etc.). On the basis of the initial measurement results the monitoring plan should be updated. The duration shall be associated to the selected CR_{air} value, representative of all the possible exposure conditions and particularly of the worst ones.

Concluding remarks

This paper illustrates the main features of a protocol nearing completion for the national site Porto Marghera (Venice, Italy). Where a risk to human health by inhalation of VOCs from contaminated soil was estimated using conservative predictive models, the protocol provides a tool to assess the actual exposure of area goers or resident by air monitoring and ultimately to decide if a remediation, an interim or abiding mitigation action is needed to protect these exposed targets. An overall procedure has been developed including some options about the protective actions to be taken (or not) according to the area use and the eventual overlapping of occupational and environmental exposure. The criteria to define the acceptable or reference values for VOCs in indoor and outdoor air (CR_{air}) have also been determined to allow the comparison with the measured values. Air monitoring strategies have finally been outlined differentiating outdoor from indoor environments.

Keywords: Contaminated sites, Health risk assessment, Inhalation exposure, Volatile Organic Compounds (VOCs).

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INDUSTRIAL SYMBIOSIS AND PRODUCTIVE AREAS

Extended abstract

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Background

Green economy is becoming an important sector in many developed economies and it can be considered a perspective for the characterization of the economical systems of emerging areas and of those economies looking for their place in the context of economic globalization. There are many definitions of green economy, one of the most comprehensive is provided by UNEP, the UN agency that deals with environment, "UNEP defines green economy as One That results in improved human well-being and social equity, while significantly reducing environmental risks and ecological scarcities"(UNEP, 2011). In the in-depth report carried out by UNEP there is also a realistic estimate of the costs associated with the large-scale implementation of green economy. In the estimation of the international agency, the sectors and investments needed to convert the world economy are the following: a total of 2% of GDP per year, equal to a total amount of $ 1.300 billion. In a more analytical way, in the different sectors, the estimation are the following: agriculture (108 bn), construction (134 bn); renewable sources (360 bn), fishing (110 bn), forests (15 bn), industrial (75 bn) , tourism (135 bn), mobility (190 bn), waste (110 mld) water sector (€ 110 bn).

The guiding principles of green economy in the study accomplished by UNEP are summarized as below: sustainable development, equity, quality of life, respect of the limits, inclusion, responsibility, resilience, efficiency, solidarity between generations. All these principles are also values, which will closely link economic action and social impact of the strategies and policies adopted by policy makers and governments. The economic sectors where the impact of green economy may be decisive, according to Tim Jackson, are listed below: building renovation, technologies based on renewable sources, redesign of the networks of public utilities, infrastructures for public transport, public areas (pedestrian zones , green spaces, libraries, etc.)., safeguarding and development of the ecosystem (Jackson, 2011). According to data jointly provided by ILO (International Labour Office, Geneva) and UNEP, an ecological conversion could create up to 60 million new jobs in the world. Data compiled by the EU suggest that, in Europe, a 17% reduction in the consumption of resources would lead to an increase in GDP of 3.3% and an increase in employees between 1.4 and 2.8 million people. The relevance of these estimates is indubitable, especially in the current economic crisis which produces continuous loss of jobs in traditional industrial sectors.

The close relationship between economy, employment and social progress is the basis of the strategic policies of the European Union in Europe2020. Not by chance the keywords of the policies in the coming years will be sustainability, inclusiveness and intelligence. From an operational point of view, this means betting on a society based on the respect for the environment, innovation and new technologies, on equal opportunities for the different segments of citizens Europe is composed of. Also in Italy, now aware of the challenge represented by green economy, we have tried to translate the opportunities and potential into concrete projects that can be realistically pursued. The "Roadmap for the green economy" presented each year at Ecomondo (www.ecomondo.com) shows many productive areas to invest in: eco-innovation, eco-efficiency, recycling and renewability of materials, efficiency and energy conservation, development of renewable energy sources, environmental protection and enhancement of ecosystem services, development of eco-agricultural sectors, development of sustainable mobility. With the green economy, ecology and economy go hand in hand with each other.

Objectives and methods

An attempt to apply the principles of green economy in the relevant sectors of European economies has been achieved through the development of eco-industrial parks and through the promotion of projects based on the principles of territorial marketing and, more specifically, on green marketing aimed at promoting the local development. The characteristics of eco-industrial parks can be summarized as below: planning of exchanges of resources between the businesses settled in the industrial park, integrated system for the minimization of the use of energy and raw material in the industrial park, integrated system for the minimization of waste material, construction of environmentally, socially and economically sustainable relationships between the businesses settled in area, integration among all the activities in the area and among those and the environment.

The conditions conducive the development of eco-industrial parks are the following (Franco, 2005):

- economical feasibility: the implementation of an eco-industrial park is subject to the possibility it offers to achieve a reduction of costs and an increase in the margins of incomes;
- public policy: public policy can encourage the creation of industrial ecosystems;
- organizational relationships: the presence of collaborative exchanges between companies and procedures encouraging participation facilitates the implementation of eco-industrial parks.

Organizational and conceptual models are gradually emerging and they distinguish different types of eco-industrial parks. Indeed, we can identify some main types: *industrial symbiotic system*, aggregation of only industrial assets and activities with relations of exchange of waste-resources and integrated management systems for resources; *mixed system*, aggregation of not only industrial assets but also agricultural, residential and service ones, where the aggregation is based on the recovery and the re-use of resources; *virtual symbiotic system*, network with the exchange of resources between industrial activities not distributed in the territory.

The development of ecoindustrial parks may also represent an original path with an high impact to the theory of Gunter Pauli dealing with Blue Economy. The conceptual proposal of G. Pauli is intended to reproduce in industrial processes the same mechanisms that operate in ecosystems and in the cycles of transformation of energy and natural resources. This principle is defined by G. Pauli biomimicry, in order to emphasize the strict adherence of industrial processes to ecological processes. Closing cycles of the reuse of resources will reset the impacts on the surrounding environment, will increase the energy and environmental efficiency, it will encourage the research and development of new and improved technologies based on knowledge and innovation processes. Finally, there will be positive effects on economy, on jobs, on new businesses. Ultimately it sets in motion a truly virtuous circle able to generate development, knowledge, innovation and wealth on a large scale, especially in those areas of the world that are in search of new projects that can guarantee increased prosperity and quality of life for population (Pauli, 2010).

Today, however, to be active in the green economy and to promote new development models based on sustainability also means ability to make territorial marketing and ability to make green marketing of local production systems, taking into account that we are in a context of strong global competition between different areas of the world. The periodic survey carried out by the strategic consulting firm Ernst & Young's highlights the distinctive factors of competitiveness of our continent. The key levers in Europe should be, according to these analysis, the green and digital economy, a fair level of taxation, city attractions through the development of infrastructure and industrial parks, the presence of qualified human resources and with high levels of skills. These are the factors that can ensure development, competitiveness and ability to attract new businesses.

Other areas of the world can count on low cost of raw materials or low wages. Europe must instead enhance the knowledge and the ability to implement productive activities in a sustainable way. Europe should clearly communicate these values, and distinctive elements making green marketing of territory and of European regions. Making green marketing according to John Grant is to act simultaneously on three levels at least (Grant, 2007):

- the business and markets, where you can start by simply promoting products and green consumption and then generate, over time, a real new demand for green goods and services and finally get to develop real new concepts and entirely innovative areas of green business;
- social identities and brand, where the basis is the credibility of trading partners and it is essential to apply, progressively, the techniques and rules of social media using tools of online marketing such as community of interests and promoting the tribe brands. All these devices appeal to the strong identification of potential consumers and to the connective role of new media;
- product and habits, moving from a simple clarification of the indirect benefits of sustainable consumption, one gradually comes to change the habits of consumption, and finally even to affect the lifestyles and behavior of people. This means to act on the core values, that guide consumer choices addressing towards sustainability.

By this way, the green marketing develops a very wide range of potential, both traditional and innovative ones. The traditional ones are related to products and services such as the followings: improving environmental quality and meeting the consumer needs; know how and actions to operate in the green market; managerial and commercial plans to minimize the environmental impact of productive activities; matching of green demand and green offer; research and development of competences for the promotion of green products and green services; planning of actions to maximize the opportunities of green market and to allow the reaching of environmental goals.

The new areas of activity are related to the close relationship between local development, marketing and promotion of the territory, investment in sustainable productive areas with new and advanced services for businesses (Kotler et al., 1993).

Case studies

How to spread sustainable practices in the Mediterranean productive areas enhancing at the same time the attractiveness of territories by developing strategies for green marketing? These are, very briefly, the objectives of the project MER (Governing Innovative Marketing and Industrial Areas), a project developed within the European Programme MED. This programme aims at stimulating the interregional cooperation between European countries in the Mediterranean area: France, Italy, Spain, Greece, Portugal, Slovenia, Malta, Cyprus. The thematic areas covered by the programme are some of the most important for the economic and social development of the Mediterranean countries: renewable energy, innovation and technology transfer, sustainable mobility, cultural and environmental heritage are some of the main issues experimentation and cooperation initiatives are increasingly occurring. In this context, the project MER is based on the principle that the green promotion of territories and industrial areas is a key value to invest on. MER project will work to make green marketing a tool for integrated governance of industrial areas, contributing to improve the competitiveness and attractiveness of the Med area according to Europe 2020 targets for a sustainable growth.

All the countries participating in the MED Programme take part to the MER project through the following organizations: Province of Bologna (lead partner of the project), Enea (national research body for energy and environment), Informest (Institution for the development of international cooperation of the Regions Friuli Venezia Giulia and Veneto), University of Algarve (Portugal), MIEMA (Malta Intelligent Energy Management Agency), FVMP (Valencian Federation of Municipalities and Provinces, Spain), CEEI Valencia Business and Innovation Centre (Spain), UIRS Urban Planning Institute of the Republic of Slovenia, Anatoliki Development Agency (Greece), Chambers of Commerce of Nice (France).

The keyword of this project is capitalization, considered as the key be able to generate positive impacts in organizations and geographical territories of the countries participating in the project. The capitalization is in fact a multidimensional and complex process that involves several variables.

To capitalize means to extend the impact of innovation to a wider area; to integrate services and create new opportunities and innovation kits with added value and able to enforce the competitiveness of businesses and productive areas; to increase the efficiency of marketing and promotional action accomplished within local territorial sistems. Only to act in an integrated and systemic way on all these variables produces tangible and measurable effects on the scope and the strength of the impact of projects on the local economy and the quality of services provided to businesses.

Expected results and discussion

The expected results of this project are numerous and they affect very significant and diversified issues and areas of intervention, as we can see from the following table:

Table 1. Expected results of the project

Outputs for capitalization	***Aims of MER capitalization***	***Type of activities***
Green marketing: handbook, integrated guidelines, gmk plans, etc	To provide a tool kit for green marketing for clusters and IAs on a greater scale	Networking Replication campaign Local action plans
Web based training platform	Use and diffusion of web based training platform for training activities	Accomplishing of a training package after training need analysis
Marketing tools	To provide more effective guidelines and tools for green marketing	Benchmarking analysis and identification of best practice Design of guidelines
Report on scenario assessment and public participation process	To include environment into territorial marketing strategies and to assess local governance, stakeholders engagement and decision processes	Promotion of tools for the assessment of Territorial scenarios Development of guidelines and training tools
Multipolar Technopolis Interface Structure	Enlarged and enforced territorial/sectorial structure technology hubs	Promotion of the activities and the mission of technopolis; networking
Resource center allowing searching and sharing information and services on innovation and creativity	Promotion of Knowledge economy and enhance the cooperation between public bodies, economic actors and organizations for new territorial development policies	Networking activities Replication campaign Multi-level diffusion
Help Desk network	Qualification of the European MED area as a context conducive to innovation	Tools and policy recommendation to support the diffusion of regional help desk
Brownfield manager For regeneration processes	To define professional competences and expertise suitable to become drivers of sustainable development	Networking activities Stakeholders involvement

On the one hand the project is expected to develop a series of information and analysis activities necessary to identify situations and local contexts that are inevitably very heterogeneous. The laws, the promoting policies and the governance of the structures that deal with supporting the production plants are in fact the result of choices and organizational arrangements that are very different among the countries bordering on the Mediterranean. These actions involve plans and programs which are strongly influenced by the territorial relationships with the economical world, with businesses and they are the result of the history that led to this type of interaction. On the other hand, after these essential study activities, the project aims to identify innovative tools for supporting business, which may represent the actual economic factors for enhancing the economical appeal of a production area. For this reason, special attention is paid to the tools and the plans of operational marketing, web platforms for the deployment of innovative services, to the training and development of skills to promote technologically advanced services in support of business networks.

Within MER there will be the arrangement of both tools to encourage the awareness of good practices developed in the different countries of the Mediterranean addressed to the partners of the project and tools for the network of stakeholders that can be involved in the development of marketing actions and in the design of actions for the governance of production areas. Wide space will be reserved to study visits open to entrepreneurs and experts (or actors belonging to specific areas crucial to the local economy), to the realization of integrated guidelines to develop services and actions for the management of productive areas; to training packages for operators and for economic and institutional actors involved in local development. The project, in its final part, also intends to produce documents commitment for the cooperation for green marketing underwritten by entrepreneurs, local authorities, business associations, research centers and universities. The aim is to clarify and make explicit the commitment of economic actors to act jointly. All these efforts are aimed at developing with determination local marketing strategies and to promote green economy in the European regions participating in this important European initiative.

Concluding remarks

The green marketing applied to productive areas is a still largely unexplored theme. While there are many experiences in the field of marketing for green products and services, there are few proposals for green marketing targeted to whole areas. Anyway the local development and competitiveness of the European countries in the coming years, will depend more and more on the capacity of these areas to offer innovative services to businesses. The European regions of the Mediterranean area can effectively intercept the demand for high quality of life and high environmental quality, that are becoming increasingly important social themes, and they can use these common needs to effectively promote their industrial areas. As in the past there were forms of green supply chain in production, today it is essential to focus on optimizing tangible and intangible exchanges between companies, by applying industrial symbiosis at the national level.

The principles of biomimicry and closing cycles of resource use in the productive areas, may represent factors of innovation, efficiency and can minimize waste and adverse impacts on the environment. Close the circle as nature does can become economically, as well as ecologically, convenient.

Keywords: green marketing, industrial areas, management

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PODEBA: AN INDUSTRIAL SYMBIOSIS CASE

Extended abstract

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Background

Leather processing involves a series of unit operations that can be classified into three groups: i) pre-tanning, to clean the hides or skins; ii) tanning, to permanently stabilize the skin or hide matrix; iii) the post-tanning and finishing operations, in which aesthetic value is added (Palanisamy et al., 2004). At each stage, various chemicals are used. The bating process takes place in the pre-tanning phase. It is the process of removing proteins other than collagen using proteolytic enzymes. The bating enzymes cause physical-chemical changes in the skin (Palanisamy et al., 2004) and remove its coagulable proteins. This process prepares the hide or skin for the tanning phase, which completely stabilizes them, to obtain finished leather products. In the bating stage, proteolytic enzymes or mixtures of enzymes with acid ammonium salts are normally used, to neutralize the fleshed and alkaline hides and to allow enzymes to act. This process has a high environmental impact, because of water consumption and N charge (for wastewater) (Zengin et al., 2002).

Poultry Dejections (PoDe) are the major waste/animal by-product in poultry intensive farming, and their disposal is often a relevant problem. They are composed of organic carbon, nutrients (nitrogen and phosphorus compounds), microorganisms and extracellular enzymes.. Their main use is for soil manuring, often after storage or treatment. And their distribution is based on N dose per hectare, according to Agronomic Use Plan (Water Framework directive 2000/60/EC). Poultry farms are very often intensive and concentrated in restricted areas. Because of farm concentration, often the soil surface needed for their correct distribution becomes a problem. It is therefore important to pursue different PoDe uses in a bioeconomy strategy to overcome this limitation.

The use of PoDe has an historical background thanks to their proteolytic enzyme content which can weaken the three-dimensional structure of derma, breaking elastin and collagen, swelling and preparing de-limed pelts for the tanning phase. This PoDe utilization was abandoned because of its high environmental impact (odour and health aspects). Through a LIFE project, its use as a bating agent has been reintroduced, in a modern and controlled way, overcoming the limitations described above.

LIFE project PODEBA (LIFE10 ENV/IT/365, Use of poultry dejections for the bating phase in the tanning cycle) is demonstrative of an industrial symbiosis case. In fact, the byproducts of agro-industrial production (output) are used, after proper treatment and transformation into Deodorized and sanitized Poultry Manure (DPM), as technical products (input) for the tanning industry (Fig. 1). This results in an increase in the efficiency of the agrifood industry while reducing the environmental impact of the tanning industry. PoDe bio-treatment is aimed both at deodorizing and sanitation and it is performed according to a European patent (AMEK, CTI, 2002).

The development of the project is consistent with European policy and strategies:

- Best Practice under the European Waste Framework Directive (2009)
- Roadmap to a Resource Efficient Europe (2011)

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- DG Enterprise Sustainable Industry-Going for Growth & Resource Efficiency (2011)
- European Climate Knowledge and Innovation Community (2012)
- European Resource Efficiency Platform (2012)
- Directive 96/61/EC, on Integrated Pollution Prevention and Control (IPPC)
- Water Framework Directive 2000/60/EC
- REACH Regulation, EC 1907/2006 (Registration, Evaluation, Authorization and Restriction of Chemical substances; European Community Regulation on chemicals and their safe use)

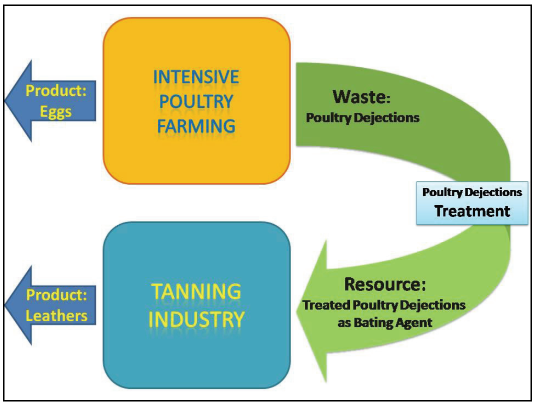

Fig. 1. PODEBA as an industrial symbiosis: transformation of waste from intensive poultry farming into a resource (Poultry manure as bating agent) for tanning industry

Objectives

The activities were focused on the following 4 issues:

- Suitable PoDe to be transformed into bating agents, based on chemical-physical properties required by bating process conditions.
- Suitable PoDe drying management system, chosen among recognized Best Available Technique (BAT).
- PoDe treatment (Manure preparation), already identified in PODEBA project.
- Application of DPM in the bating phase, taking into account odour aspects and final leather characteristics.

Outline of the work

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Methods

The bating process inside rotating drums needs water soluble/dispersible reagents, without the presence of material such as straw pieces which could inflict mechanical damage to pelts during rotation. Therefore, PoDe from laying hens without litter were chosen. PoDe were taken from intensive poultry farms in order to have available amount that are large enough for industrial application and to obtain a standardized final product quality.

The most common PoDe drying systems were investigated in order to obtain a final product for leather processing. In particular, the Manure Drying System (MDS) and the ventilated belt system were tested in PODEBA activities. Both systems are classified as BAT according to BREF (EC, 2003) and they are representative of large(> 100.000 animals) and medium size (30-50.000 animals) intensive poultry farms in Europe. MDS allows drying up to 85% DM, in a tunnel outside poultry housing in 72 hours. A ventilated belt system allows drying up to 60-65% DM, in 6 days time.

As provided for in the project, Bio-Treatment was performed according to the European patented process "A process for maturing and stabilizing biomasses under reduction of smelling emissions" (AMEK, CTI, 2002). It describes a complex product, a natural enzymatic cocktail named Vegetable Active Principles (VAP), prepared from selected plants, picked up in their balsamic period VAPs were developed in order to speed up biooxidation processes, reduce biomasses turning and to maintain N in slow release form. Treatment consists in adding VAPs to dried manure directly inside bioreactors (big bags (1m^3 of size) as they are being filled by conveyor belt, in doses up to 1 kg/m^3. In bioreactors, manure matures at least for 120 days by means of static batch processes in ; at the end the big bags are ready for marketing. Two generations of DPM were produced with a slightly modified VAP recipe, which ensures sanitary conditions (Golfari et al., 2010)

Laboratory tests for the use of DPM as bating agent were carried out in order to check its efficiency in comparison with SF and define the appropriate use condition Biozym MC/N is the most commonly used formulation (SF); it is composed of proteolytic enzymes (0.5-5 % w/w), Ammonium Sulphate (about 60% w/w), Ammonium Chloride, saw dust and other inerts. Another aim of the test was to verify the effect of the bating agent on odour impact both as far as the bating floats and the leather products,. Bating trials were carried out on cow hides which were then treated in order to obtain tight items (for shoes and leather goods) and soft items (upholstery, garments). The bating process variables under investigation were:

- Qx, the quantity (%) of bating agent, depending on bating agent activity; DPM quantity, to use in comparison with SF, was calculated on the basis of DPM enzyme activity, which was assessed by means of the Lohlein-Volhard method (Lohlein-Volhard method, 2001).
- tx: bating process time (min), depending on bating agent efficiency.

Different bating agents were used for this study, in order to investigate olfactory impact as well, as reported in Fig. 2. Also used a bating treatment without agent as reference for odour emissions (to recognize leather emissions) in order to understand the usefulness and the efficiency of the bating agent.

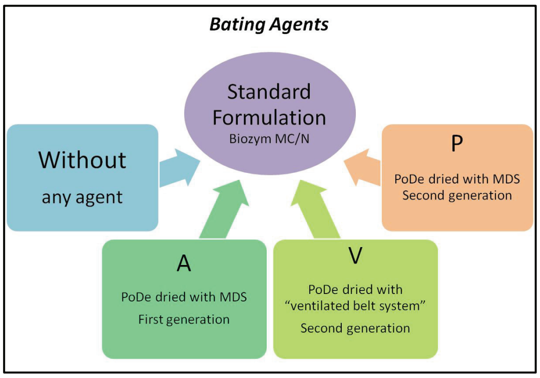

Fig. 2. The different bating agent samples tested. First and second generations differ for VAP recipe.

The effects of the different bating agents were observed by means of selected indicators for final leathers (leather structure and cleaning surface of final product) and odour aspects both for bating phase and final products (Dall'Ara et al., 2012).Technicians and tanning process developers assessed odour impact modifications in bating process conditions and in finished leather . Also measurements were made of the volatile fraction in process wastewater samples and volatile fraction in wet blue leather (leather right after bating and chromium tanning).

Furthermore, leather samples were subjected to different quality control processes according to international standards (EN-ISO) to verify their suitability for use in the manufacture of footwear (breaking strength, tensile strength and breaking elongation).

Results and discussion

The results of laboratory tests are reported in Table 1, where results are related to standard conditions with SF (Biozym MC/N), as shown in Fig. 2.

Table 1. Results of the odour qualitative analyses of a test without bating agent (without), a first generation PoDe sample (A), and two second generation tanning agents (V and P), compared to SF

Trial code	***Odour***			***Final Leathers***	
	Smell during process	Smell on wet blue leather	Smell on finished leather	Leather's structure	Cleaning surface
Without	bad	bad	No	quite harder	less
A	bad	bad	No	similar	similar
V	quite bad	notable	No	similar	similar
P	quite similar	weak	No	very similar	similar

The patented PoDe bio-treatment ensures sanitary conditions (Golfari et al., 2010), but only the new VAP recipe (the one used for the second generation DPM) solved the odour issue and was suitable for the purpose of this project. In fact, the first generation DPM had a reduced odorigen impact in dry conditions but showed a significant odorigen impact under wet conditions (in bating phase with water and delimed pelts). In the second generation, the new bio-treatment recipe allowed to obtain a DPM that was suitable for bating, since the smell developed during the bating process was very weak and it was not a problem for workers. The smell o at the wet blue leather stage was very weak and there was no effect on finished leather. Final leathers were characterized and properties measured: those obtained with DPM showed pleasant appearance, fine-grain and adequate smoothness, softness, flexibility, grain firmness, and fullness. The physical parameters measured in final leathers showed that the recommended values for the manufacture of footwear were achieved. Leather structure, surface cleaning, odours during process, and smell on finished leather were very close to the standard. It is important to emphasize that the use of big bag as bioreactor allows to perform PoDe treatment practically inside the sale packaging, and this makes both marketing and symbiosis easier from a practical point of view.

Nowadays poultry farms are often concentrated in a limited areas and poultry manure is delivered to farmers for free, just to get rid of the dejections. PoDe partial reuse as a resource for tanning industry can solve the problem of waste management and disposal in intensive poultry farming, in the areas where the farms are more concentrated. It also leads to profits and/or to the elimination of costs for poultry farm owners.

Pre-tanning and tanning processes contribute 80-90% of the total pollution in the industry and generate noxious gases, such as hydrogen sulfide and other wastes (Palanisamy et al., 2004). The use of DPM instead of chemical mixture allows to eliminate the need for sodium sulfide and other chemicals during the bating process, thus reducing toxic waste and water pollution.

Implementation of this symbiosis is also a strategy to prevent waste production, to save resources and to reduce environmental impact, consistently with the need of European leather producers to exploit more efficiently their raw materials in order to remain competitive in the global market place. It represents a waste prevention device because PoDe are directly treated and transformed into a technical product right on the farm. It saves resources since each ton of DPM used as bating agent prevents the use of 0.3-0.6 tons of ammonium sulphate. Also wastewater load is reduced during bating phase by using DPM: more than 40% for TKN and ammonia.

The tanning industry aims to achieve environmental protection objectives such as waste reduction, recycling and recuperation of secondary raw materials. Accordingly, EU tanners are adjusting their production towards higher quality output and high fashion content leathers.

Concluding remarks

This paper presents a process which is suitable to transform PoDe (animal by-product) into a technical product (DPM), a bating agent for tanning. This gives rise to a potential case of industrial symbiosis between agro-industry (egg production) and the tanning industry, as developed in a European project carried out in Italy and Spain, countries that represent 90% of the European leather sector. Technical viability was demonstrated for different types of leather (soft and tight items), for different raw materials (hides, skins) and for different articles (shoes, upholstery). Investigations of the economic aspects are in progress.

If this solution were applied it could require large amount of PoDe to be transformed into bating agent, (2-3% of Italian PoDe production). Furthermore, implementing this solution could reduce the environmental impact; by the end of PODEBA project an assessment of the overall impact reduction will be carried out through a LCA analysis.

Keywords: industrial symbiosis, leather, poultry dejections, tannery

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ADAPTING TO CLIMATE CHANGE: BOLOGNA AS A RESILIENT CITY

Extended abstract

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Background

In the last decade, the international community has taken the knowledge that our planet will face serious consequences due to climate change, whether attributable to natural causes, and the action of man. While there is a broad consensus on how fast and how our climate is changing, there is an increasing perception of the impact and this can be seen by the shift of the debate about how society should adapt. Growing awareness promoted by the political and economic institutions for adaptation is controversial in some areas of environmentalism, in fact for some senior figures is interpreted as a tacit admission that efforts to mitigate greenhouse gas emissions are no longer sufficient. However it should be remembered how, less efficient mitigation measures will require more pronounced adaptation actions to be undertaken. Therefore this suggests that policies for mitigation and adaptation must be addressed in concert, by exploiting all possible synergies.

The integration of the two policies was confirmed recently by the *Global Risk Report 2013*, published by the World Economic Forum (WEF), a reference document for global investors on the main risks that may afflict their investment portfolio. In the 2013s report, one of the main risks identified is the "**failure of the system to adapt to climate change**." More then this, if you combine the Global Risk Report with the WEF report "*The Green Investment Report. The ways and means to unlock private finance for green growth*", which indicates an increase in public investment world of 36 billion dollars / year to trigger private investment by enough to contain the critical threshold of 2 ° C global warming, we understand how mitigation and adaptation goes together. Both WEF reports reflect what suggested in 2012 by the EU Climate Change Expert Group, which indicates an increase in the costs of climate change impacts, equivalent to 5% up to 20% of the GDP (or higher) in the long run, parallel with the current trend of increase in global temperature.

The European Environment Agency (EEA) has recently published the "*Climate change, impacts and vulnerability in Europe 2012*" reports, where the evidence of the impacts is well identified. In all European regions have been observed an increase in average temperatures combined with a decrease in rainfall in the southern regions and increased precipitation in Northern Europe. The Greenland ice sheet, sea ice and many glaciers are melting all over Europe, the snowpack has decreased and most of the permafrost soils have warmed. These extreme weather events have generated local urban phenomena such as heat waves, floods and droughts causing a consequent increase in costs in terms of human lives and infrastructure.

While these scenarios show that more elements are needed to understand the role of climate change, the growth of human activity in areas at risk could be a key factor. The Agency predicts that extreme weather events will become more intense and frequent, helping to accentuate the vulnerability of such a situation. The recent weather and climate events have shown clearly and unequivocally the high economic and social costs of such disasters, that are expecting to be even worst in the near future. Estimated losses in 2011 alone, for the floods in Thailand amounted to U.S. $ 30 billion, Hurricane Katrina resulted in damage to the U.S. economy $ 125 billion. It should be remembered that in 2003 the heat wave that struck Europe caused 35 thousand victims, while the 2011 drought that hit the Horn of Africa has resulted in tens of thousands of victims and threatened the survival of 9.5 million people.

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As stated by **Jacqueline McGlade**, Executive Director of the European Environment Agency: "*Climate change is a reality all over the world, and the extent and speed of change is becoming more evident. This means that every part of the economy, including households, needs to adapt and reduce emissions*". However, it should be pointed out that some regions of the world will be less capable of adapting to climate change than others because of economic disparities and the effects of these changes could deepen these inequalities.

The consequences, however, has to be considered not only at the global level, in fact in the report of the EEA is emphasized that a different adaptive capacity because of economic inequalities, there might be even within the EU borders. In order to reconcile the challenge of building climate resilience in a situation of great economic stress, it is therefore necessary to re-evaluate current policies and national strategies. For example, in many countries, national insurance systems and housing policies continue to encourage urbanization of coastal areas prone to flooding or high landslide risk, rather than avoid the risks.

Decide to continue with these policies may be the cause of the creation of pockets of vulnerability to climate risks. A 2007 OECD report analyzes 136 port cities around the world, and highlights how the population exposed to coastal flooding could triple by 2070 and this was due to the combined effects of climate change and urbanization. Another interesting fact that comes from the EU project *Corinne* tells us that between 1990 and 2006 the area of artificial soil of the European Union has grown from 176,000 to 192,000 km ^{2} (1), this is an area like half Germany. In the past sixteen years the consumption of fertile soil was then equal to 970 km ^{2} per year, or 265 acres per day. That is to say, it is an area as large as the historical center of Milan (2). If you were to continue business as usual by 2050 would add other 43,000 km ^{2} of ground cemented, an extension equivalent to the entire Denmark.

Objectives

Looking at the increasing awareness that global temperatures will raise, a mentality "Climate-smart" must be adopted by all levels of decision-making. "Climate-smart" is a term that originated in agriculture, to describe those interventions in the agricultural sector that are able to increase the resilience of adaptive capacity to climate change and at the same time reduce emissions of greenhouse gases.

A mentality "Climate-smart" incorporates the analysis of climate change taking place in the definition of strategies and operational decision-making processes. This approach involves the search for synergies between climate change mitigation and adaptation, wherever is possible.

Outline of the work

As for the energy, this approach has been well described in the position paper of the Alliance to Save Energy "*Energy Efficiency: A Tool for Climate Change Adaptation. An Alliance to Save Energy White Paper* " (February 2012), according to American scholars energy efficiency is the first tool to mitigate the changes taking place, through the reduction of fossil fuel consumption, but at the same time measures for energy demand management are also able to address some of the vulnerabilities of the energy sector in relation to the impacts of changing climate.

For example, we should consider as win-win solution:

(1) The distribution of *energy efficient technologies in end-use efficiency* and *production services*, transmission and distribution can help to counteract the increase in demand and at the same time reduce the production of power in a context of higher temperatures;

(2) *Demand response programs* and *efficiency programs* aimed at the management of energy peak load, that can help to counteract the increase in peak demand due to increased use of air conditioning and to address the uncertainties in the production and consumption of electricity and heating, due to extreme weather conditions, and so far, avoiding the need for construction of new energy facilities;

(3) The manufacturers can design *buildings „future proof"*, ensuring long life characteristics such as orientation and insulation and installing fixtures appropriate for the climate conditions;

(4) Cities can reduce the *environment temperature*, and make buildings more energy efficient, with cool roofs or green,

(5) The construction of *distributed generation*, particularly efficient combined production of heat and electricity (CHP), able to ensure the supply of electricity to large consumers or micro grid because they are less prone to outages due to extreme weather conditions, (6) *efficiency programs in water management* can address climate impacts on water resources and reduce the consumption of energy for pumping and water treatment. Energy efficiency, energy savings and demand reduction programs offer consumers and relatively inexpensive technologies to utilities and programs that allow a reduction in demand and the amount of climate-altering gases emitted.

Methods

The importance to look at adaptation has become fundamental to tackling climate change with an integrated approach, as repeatedly stressed by the Working Group II of the IPCC, which since long time stressed the concept that mitigation and adaptation should be complementary components of a strategy to response to global warming.

Develop an adequate adaptive capacity has become therefore a priority for European policy on climate. The European Commission White Paper "Adapting to climate change: Towards a European framework for action", has traced the path to the definition of the European Strategy for Adaptation which was published last April.

The Strategy will provide a leading role of governments but calls for a strong commitment of the local government and companies, since the impact of the changes are highly local. While some national governments are struggling to make binding commitments, many cities have taken the first steps, creating networks such as the ICLEI Initiative Resilient Cities and the EU Adaptation Strategies for Cities Climate (CITIES ADAPT), to share best practices and to promote bottom-up initiatives. The impacts of climate change will be different in every urban context, and therefore new approaches to local urban planning should include these factors in an appropriate manner.

Results and discussion

A "local tailor made" global response and a mix of real politics it is now necessary for the city to quickly adapt to climate change. The first step of the project BlueAP Bologna Resilient City - led by the Municipality of Bologna - is heading in this direction and proposes the definition of the adaptation plan by 2015. The Plan will be based on an analysis of vulnerability and territorial adaptive capacity - Local Climate Profile - made by ARPA Emilia Romagna. The measures to be implemented will then be identified and shared with the citizens and businesses through a participatory process - implemented by Kyoto Club and Ambiente Italia - which aims to engage the community and to improve the existing resilient capacity, starting the collection of memories and the ancient tradition of Bologna.

For responding to the complex future risks a link with what has already been implemented by Bologna Municipality in the definition of its Sustainable Energy Action Plan - Covenant of Mayors and the Metropolitan Strategic Plan will be take in consideration. This integrated approach shows how the Administration is adopting a "Climate-Smart" strategy in future planning.

Concluding remarks

But the fact remains that today we are facing enormous socio-economic challenges that require immediate attention, with the availability of limited public resources - in particular to finance efforts to prevent the long-term effects of climate change, which, in turn, could seriously affect the global economy. We find ourselves in front of a negative feedback loop daunting.

The logic of risk management tells us that countries should invest today for the protection of critical infrastructures and centers of economic activity for two main reasons: (1) estimates of future climate-related losses and damage are on the increase and these annual measures may (2) create new jobs to boost economic growth in the shortest possible time. The real problem is that investment in strategic infrastructure is easier to list than to do, in spite of the benefits you can have both in the short and long term.

Thus, a new approach, which is based on a meeting of minds in various professions, sectors and geographical areas, and the ability to act decisively in the face of considerable uncertainty about what the best plan of action, could tell. Continuing to hesitate to act today, we will continue to add burdens to the future generations.

Keywords: adaptation, climate change, memory, mitigation, resilience

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