

*Procedia*  
*Environmental*  
*Science,*  
*Engineering and*  
*Management*

**18th International Trade Fair of Material & Energy  
Recovery and Sustainable Development,  
ECOMONDO,  
5th-8th November, 2014, Rimini, Italy**

**Selected papers (1)**



***P* - ESEM**

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*Procedia*  
**Environmental Science,  
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***Procedia***  
**Environmental  
Science,  
Engineering and  
Management**

**Editor-in-Chief:        Maria Gavrilescu**  
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**Guest Editors:         Fabio Fava & Grazia Totaro**

**18th International Trade Fair of Material & Energy Recovery  
and Sustainable Development, ECOMONDO,  
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**Selected papers (1)**

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**In memory of**

**Professor Matei Macoveanu,**  
founder of the school of environmental engineering and management  
at the *Gheorghe Asachi* Technical University of Iasi, Romania

**Professor Iustinian Petrescu**  
founder of the school of environmental science and engineering  
at the *Babes-Bolyai* University Cluj-Napoca, Romania



## Aims and Scope

*Procedia Environmental Science, Engineering and Management (P - ESEM)* is a journal focusing on publishing papers selected from high quality conference proceedings, with emphasis on relevant topics associated to environmental science and engineering, as well as to specific management issues in the area of environmental protection and monitoring.

*P - ESEM* facilitates rapid dissemination of knowledge in the interdisciplinary area of environmental science, engineering and management, so conference delegates can publish their papers in a dedicated issue. This journal will cover a wide range of related topics, such as: environmental chemistry; environmental biology; ecology geoscience; environmental physics; treatment processes of drinking water and wastewater; contaminant transport and environmental modeling; remediation technologies and biotechnologies; environmental evaluations, law and management; human health and ecological risk assessment; environmental sampling; pollution prevention; pollution control and monitoring etc.

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## GUEST EDITORS



**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).

Other projects are 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 René Descartes) in Paris in 2001 and was visiting professor at the Ecole Nationale Supérieure 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.

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Procedia Environmental Science, Engineering and Management 1 (2014) (1) 1-98

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## CONTENTS

<b>WASTE1 - Waste, industrial applied research for sustainable management and the achievement of national and EU objectives as a result of regulatory and technological changes</b>	
<b>SOREME: AN EU LIFE+ PROJECT FOR REDUCING MERCURY EMISSIONS THROUGH THE SORPTION ON A CARBON SORBENT PRODUCED FROM USED TYRES (LIFE 11 ENV/IT/109)</b> Emilia Bramanti, Danilo Mascolo, Alessandro D'Ulivo, Massimo Onor, Simone Scardiglia, Giuseppe Magnani, Patrizia Buttol .....	1
<b>ALTERNATIVE RESIDUAL MUNICIPAL SOLID WASTE MANAGEMENT SCENARIOS IN AREAS WITH DEFICIENCY OR ABSENCE OF INCINERATORS</b> Francesco Di Maria, Caterina Micale, Emanuela Morettini .....	7
<b>OIL CONCENTRATION MEASUREMENT IN METALWORKING FLUIDS BY OPTICAL SPECTROSCOPY</b> Marco Grossi, Bruno Riccò .....	13
<b>INDUSTRIAL SYMBIOSIS IN ITALY AS A TOOL FOR SUSTAINABILITY: CASE STUDY ANALYSIS AND REPLICABILITY</b> Antonella Iacondini, Ugo Mencherini, Luciano Morselli, Fabrizio Passarini, Ivano Vassura .....	19
<b>LANTHANUM UPTAKE BY CLAYS AND ORGANO-CLAYS: EFFECT OF THE POLYMER</b> Elena Maria Iannicelli-Zubiani, Cinzia Cristiani, Giovanni Dotelli, Paola Gallo Stampino, Irene Bengo .....	25

<b>RECYCLING SCENARIOS FOR WASTE CATHODE RAY TUBES</b>	
Laura Rocchetti, Francesco Vegliò, Francesca Beolchini .....	31
<b>WASTE2 - Technical Seminar: Waste, byproduct or end of waste?</b>	
<b>THE DEFINITION OF “BIOMASS” IN EUROPEAN AND ITALIAN LEGISLATION: WHEN IT IS WASTE, BY-PRODUCT OR END-OF-WASTE</b>	
Valeria Briigliadori .....	35
<b>THE “END OF WASTE” CRITERIA FOR SCRAP METAL</b>	
Francesca Sarli .....	41
<b>OROBLU2 - Water resources management in the Mediterranean: problems and experiences</b>	
<b>WATER SAFETY OF IMPROVED SOURCE: THE CASE STUDY OF VILANCULOS (MOZAMBIQUE)</b>	
Andrea Pollmann Gomez, Sabrina Sorlini, Carlo Collivignarelli .....	47
<b>WATER SAFETY PLAN: AN APPROACH TO REDUCE DRINKING WATER CONTAMINATION IN A RURAL AREA OF SENEGAL</b>	
Luca Rondi, Sabrina Sorlini, Maria Cristina Collivignarelli .....	53
<b>OROBLU3 - The management of water in the course of natural or incidental special events and interventions to combat and monitor the spread of contamination</b>	
<b>EXTREME EVENTS MANAGEMENT: IMPORTANCE OF STORMWATER QUALITY MONITORING. PRESENCE OF EMERGING POLLUTANTS IN STORMWATER FROM INDUSTRIAL AREAS</b>	
Sebastiano Carrer, Claudio Carrer, Cristina Nasci .....	59
<b>RISK MANAGEMENT AND EMERGENCY PROCEDURES FOR WATER INFRASTRUCTURES UNDER EXTREME EVENTS: SOME EXPERIENCES</b>	
Alessandro Pagano, Raffaele Giordano, Ivan Portoghese, Michele Vurro, Francesco Campopiano, Andrea Duro, Davide De Battisti, Stefano Pacitti, Girolamo Vitucci .....	65
<b>INNOVATIVE TEXTILE BOOM FILLED UP WITH HIGHLY EXPANDED GRAPHITE FOR DIESEL REMOVAL FROM WATER SURFACE</b>	
Annalisa Pola, Giulio Cesareo, Emanuele Galletta, Daniela De Angelis .....	71
<b>SORPTION OF ORGANIC POLLUTANTS ONTO ZEOLITIC TUFF: ISOSTERIC AND STANDARD ENTHALPY</b>	
Paola Vanore, Elio Coppola, Vincenzo Leone, Pasquale Iovino, Stefano Salvestrini, Sante Capasso .....	77

**AIR1 - Technological innovations and new approaches for the management and control of odor emissions**

**MONITORING ODOUR EMISSIONS FROM WASTEWATER TREATMENT PLANTS BY MEANS OF METHODOLOGIES BASED ON HYDROGEN SULFIDE DISTRIBUTION**

Giancarlo Cecchini, Paolo Cirello, Biagio Eramo ..... 83

**AIR2 - The indoor air quality in Italy: the situation, prospects and controls**

**THE MONITORING OF INDOOR AIR QUALITY AND COMFORT: THE EXPERIENCE OF THE PROJECT CETIEB**

Gian Marco Revel, Marco Arnesano, Filippo Pietroni, Jürgen Frick, Manuela Reichert, Markus Krüger, Katrin Schmitt, Jochen Huber, Martin Ebermann, Luc Pockelé ..... 87

**AIR3 - Carcinogenicity of air pollution: new approaches to the assessment of air quality after delivery of the IARC**

**ASSESSMENT OF REDUCTION STRATEGIES FOR THE MITIGATION OF THE ENVIRONMENTAL IMPACT OF THE PRIMARY PACKAGING WITHIN THE LARGE SCALE RETAIL TRADE**

Giacomo Magnone, Pierantonio De Luca, Antonio Salituro, Maria Gemma Cosenza ..... 93







Procedia Environmental Science, Engineering and Management **1** (2014) (1) 1-4

18th International Trade Fair of Material & Energy Recovery and Sustainable Development,  
ECOMONDO, 5<sup>th</sup>-8<sup>th</sup> November, 2014, Rimini, Italy

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**WASTE1 - Waste, industrial applied research for sustainable management and the  
achievement of national and EU objectives as a result of regulatory  
and technological changes**

**SOREME: AN EU LIFE+ PROJECT FOR REDUCING  
MERCURY EMISSIONS THROUGH THE SORPTION ON A  
CARBON SORBENT PRODUCED  
FROM USED TYRES (LIFE 11 ENV/IT/109)\***

**Emilia Bramanti<sup>1\*\*</sup>, Danilo Mascolo<sup>2</sup>, Alessandro D'Ulivo<sup>1</sup>,  
Massimo Onor<sup>1</sup>, Simone Scardiglia<sup>1</sup>, Giuseppe Magnani<sup>3</sup>,  
Patrizia Buttol<sup>3</sup>**

<sup>1</sup>*National Research Council of Italy, C.N.R., Istituto di Chimica dei Composti Organo Metallici-  
ICCOM-UOS Pisa, Area di Ricerca, Via G. Moruzzi 1, 56124 Pisa (Italy)*

<sup>2</sup>*Confindustria Emilia Romagna, Bologna*

<sup>3</sup>*ENEA, Technical Unit for Faenza Material Technologies, Faenza Research Laboratories,  
Bologna Research Center*

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**Abstract**

In this work we demonstrate the use of an innovative sorbent obtained from a pyrolytic process of wasted tyres as mercury sorbent (named SOREME) at laboratory, semi-industrial and at industrial level. The results showed that SOREME sorbent adsorbs in gas flows more mercury Hg<sup>0</sup> (from 2.5 up to 4 times) than commercial sorbent and is able also to adsorb toxic volatile organic compounds (VOC) coming from the combustion. All the tests of mercury release from exhausted SOREME coming from lab, semi-industrial and industrial tests showed that mercury is more tightly bound to SOREME sorbent than to traditional activated carbon (AC).

*Keywords:* adsorption, BET analysis, mercury, pyrolysis, tyre

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\*\* Corresponding author: e-mail: [bramanti@pi.iccom.cnr.it](mailto:bramanti@pi.iccom.cnr.it); Phone: +39 050 3152293, Fax: +39 050 315 2555

## **1. Introduction**

Mercury is a toxic air pollutant that has attracted significant public health and environmental attention recently. Its emission (approximately 150 tons/y) occurs from anthropogenic sources, power plants, municipal waste incinerators, and other industrial sources in the United States (EPA 1997). Mercury is emitted in two major forms: elemental ( $\text{Hg}^0$ ) and oxidized mercury. Control of  $\text{Hg}^0$  emissions is more difficult due to its high volatility and low solubility. Mercury released to the environment is converted through biological processes into methyl mercury (MeHg), a bio accumulative neurotoxin that even at low levels can cause serious damages in neuronal system, cardiovascular, immune and reproductive systems. Adsorption by high surface area activated carbon is among the most promising technologies for mercury removal.

On the other hand, the disposal of millions of tires generated each year in the world is a big problem for their environmental impact. Pyrolysis appears to be the most viable means of waste tires treatment and has a promising future (Fortuna et al., 1997; Martinez et al., 2013). Basically, pyrolysis involves the decomposition of organic wastes at high temperatures in an inert atmosphere or under vacuum and it offers an environmentally attractive method to decompose a wide range of wastes chemically. The products recovered by a typical pyrolysis process are usually, 33-38 wt % pyrolytic char, 38-55wt % oil and 10-30 wt % gas fractions. The char, the solid residue, can be used either as low-grade reinforcing filler or as activated carbon. The resulting hydrocarbons from thermal treatment (liquid product, tar) can be used directly as fuel or added to petroleum refinery feedstocks.

## **2. Objectives**

This work describes the preliminary results of Life+ ENV/IT/109 SOREME EU project, which aimed at demonstrating the performances of an innovative sorbent obtained from a pyrolytic process of wasted tires as mercury sorbent. In this work we report the results of different tests of mercury absorption at laboratory, semi-industrial and industrial level.

## **3. Material and methods**

The scrap tyre rubber for SOREME project was provided by a company in Lucca (Tuscany, Italy) dedicated to car tyre waste management. The proximate analysis of the tyre rubber performed by thermal analysis (TGA) (see below) was: 9.7 % ash; 3 % moisture; 66.2 % volatiles; 21.1 fixed C (calculated). Commercial products used as mercury sorbent were also investigated as comparison: pure activate carbon (AC) employed by EPENZ&Lorenz (Estonia) and a 70 % calcium carbonate-30 % AC formulated mixture employed by Sercim (Modena, Italy) in crematory plants.

## **4. Experimental**

A demonstrative pyrolytic prototype plant was set up, which allowed a single or two step production of impregnated sorbent. In the optimization step both the single and the two-step procedures were evaluated. Table 1 depicts the optimized process for the production of SOREME sorbent after 28 experiments performed varying different parameters. This process was selected on the basis of an experimental design of the mercury sorption properties of the sorbent described in the Results and Discussion section.

**Table 1.** Optimized SOREME process. Two-step (carbonization+ steam activation)

1) Tyre rubber 7 kg carbonized at T=600 °C for 1.30 h
2) Cooling
3) Activation* with 2 L water at T=600°C 1h
4) Cooling

The sorbent exhausted or not was characterized by the direct mercury analyser (DMA80, FKW), FTIR, TGA, chemical sorption tests (iodide, methylene blue, mercury sorption in gas flow and in solution), BET analysis, SEM, Raman, XRD, ICP-MS and ICP-OES.

## 5. Results and discussion

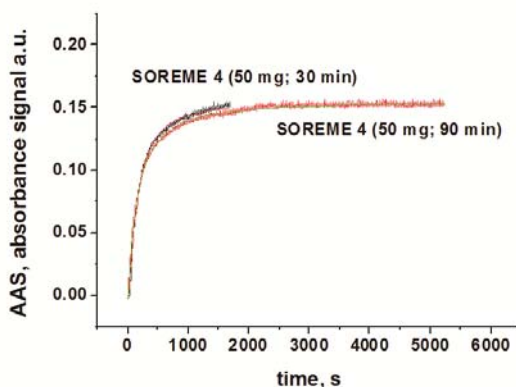
### 5.1. Mercury Adsorption Test of SOREME sorbent at laboratory level

Commercial AC and SOREME sorbent samples were tested for vapor phase elemental mercury uptake at 25°C in a fixed-bed reactor system. A cold vapor atomic absorption spectrometer equipped with an EDL mercury lamp (Perkin Elmer 502) was used to continuously measure the concentration of elemental mercury vapor within a resolution of 0.5 µg/m<sup>3</sup>.

The mercury permeation tube used provides an accurate, stable concentration of Hg<sup>0</sup> at 102 ± 2 ng/min (calibration certificate n.B491 cod. S69H70, Fine). Fig. 1 shows the vapor-phase mercury adsorption breakthrough curves of two representative SOREME samples obtained in the optimized pyrolytic conditions.

From the results obtained we found the sorbent named SOREME 4 had the best mercury sorption capacity, ranging from 0.53 µg/g min of Hg<sup>0</sup> (100 mg sorbent; adsorption time=30 min) up to 1.75 µg/g min (50 mg sorbent; adsorption time=10 min) with an average value of 0.81 ± 0.44 µg/g min.

These results are comparable with the results found by other authors that reported an adsorption capacity of activated carbon from pyrolyzed tyres ranging between 0.52 and 0.95 µg/g min (adsorption test for 360 min with adsorption capacity = 188-342 ng/mg; BET<sub>char</sub>= 60 m<sup>2</sup>/g; BET<sub>AC</sub>=130-432 m<sup>2</sup>/g) (Lehmann et al., 1998; Sun et al., 1997).



**Fig. 1.** Kinetic analysis of Hg<sup>0</sup> adsorption at 25 °C on two SOREME 4 samples obtained in the optimized pyrolytic conditions, by Langmuir kinetic model. Experimental and calculated Hg<sup>0</sup> breakthrough curves are shown. Test time= 30 and 90 min, R<sup>2</sup>>0.996.

In the optimized conditions  $\text{Na}_2\text{S}$  and  $\text{NaOH}$  were not required to obtain the SOREME sorbent with the best performances (Feng et al., 2006). This is likely due to the fact that about 80% of tire rubber sulfur content, in suitable activation conditions, was maintained in the char and can be involved in the chemisorption of mercury.

The resulting carbons exhibited not high specific surface area (around  $100 \text{ m}^2/\text{g}$ ). However, this result is not unexpected as other authors found that the highest  $\text{Hg}^0$  capacities were found for lower surface area ( $< 300 \text{ m}^2/\text{g}$ ).

Desorption tests performed on exhausted SOREME from lab tests showed that mercury is strongly bond to SOREME sorbent: no significant release occurs at  $100^\circ\text{C}$  and only 40-45% is released at  $200^\circ\text{C}$ . The same results were obtained also on exhausted SOREME samples obtained from semi-industrial tests performed at Sercim Crematory chamber.

### 5.2. Semi-industrial tests at Sercim. Comparison of SOREME and commercial sorbent

Several experiments were performed in the Crematory plant of SerCim s.r.l. in Modena. In each experiment one basket loaded with SOREME and one basket loaded with the commercial product were placed *in parallel* through the sampling line of the plant in order have an exact comparison of the two sorbents in each experiment. The commercial sorbent was a mixture of carbonate (70%) and activated carbon (30%) powder. Mercury content in exhausted sorbents was evaluated by DMA80 measurements.

The results showed that SOREME sorbent has better sorption capacities than commercial sorbent with an improvement of its sorption capacity ranging from 2.5 up to 12.2 times. Taking into account that the commercial sorbent employed contains only 30% activated carbon (AC) and 70% sodium bicarbonate in order to neutralize acid emission coming from cremations the sorption capacity of SOREME ranged from 1.1 up to 4.1 times.

All the tests of mercury release form exhausted SOREME coming from lab and semi-industrial tests showed that mercury is more tightly bound to SOREME sorbent than to other commercial ACs. The results show that, also in real conditions, mercury is more strongly adsorbed (chemisorbed) to SOREME4 than to commercial sorbent. The mercury released at  $200^\circ\text{C}$  from SOREME is indeed  $\frac{1}{4}$  than mercury released at the same temperature from commercial sorbent ( $< 5\%$  with respect to  $20\%$ ).

The retention of mercury up to  $200^\circ\text{C}$  gives indications on its disposal as waste. Leaching tests as well showed that no mercury from exhausted SOREME coming from gas or liquid treatment was released in water. This information is fundamental for LCA. SOREME (as well as commercial sorbent) cannot be re-used.

### 5.3. Application of SOREME sorbent in waste incineration cycles

The results showed that also in waste incineration cycles SOREME captures mercury 2.4 times more than AC, in agreement with lab- and semi-industrial tests:  $273 \text{ mg/kg}$  in SOREME with respect to  $113 \text{ mg/kg}$  in AC. Also in waste incineration conditions, mercury is more strongly adsorbed (chemisorbed) to SOREME than to AC.

## 6. Conclusions

Effective mercury sorbent from waste tires can be produced from the pyrolytic process at relatively low temperatures with high yields in char. The sulfur content of tire rubber is kept in char and exploited for mercury chemisorptions using a “green” activation with steam. All the results showed that SOREME sorbent adsorbs in gas flows more mercury  $\text{Hg}^0$  (about 4 times) than commercial sorbent and is able also to adsorb toxic volatile organic compounds

(VOC) coming from the combustion. SOREME is a more hydrophobic material. This is due both to the starting material (rubber) and the controlled operating conditions of its production by pyrolysis. This characteristic may represent an unexpected advantage because, despite its lower surface area determined by BET analysis (100-120 sm/g against 600-800 sm/g of activated carbons) the surface of SOREME particles is less saturated by water vapor and more available for the adsorption/chemisorption of other molecules. This result is fundamental for the future exploitation of SOREME in many industrial cycles.

All these characteristics make the SOREME process a “green”, environmental friendly interface to convert waste tire in evaluable material that can be employed for environmental remediation (char for Hg<sup>0</sup> sorption, the SOREME goal) and, eventually, energy production (tar, a byproduct of SOREME process).

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## **ALTERNATIVE RESIDUAL MUNICIPAL SOLID WASTE MANAGEMENT SCENARIOS IN AREAS WITH DEFICIENCY OR ABSENCE OF INCINERATORS\***

**Francesco Di Maria\*\* , Caterina Micale, Emanuela Morettini**

*LAR Laboratory, Dipartimento di Ingegneria, University of Perugia, via G.Duranti 93,  
06125 Perugia, Italy*

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### **Abstract**

An LCA (Life Cycle Analysis) was realized for different residual waste management scenarios in a given urban area. The analysis was performed by evaluating the environmental impacts and the potential of the conservation of the resources. The results show that the disposal of the residual waste in landfill, even if the waste has been biostabilized before, is always disadvantageous in comparison with the scenarios with energy recovery. The use of Solid Recovered Fuel in the cement plants, in substitution for coal, results to be advantageous. Recycling of metals, coming from mechanical selection, is a significant benefit for the environment.

*Keywords:* energy recovery, incineration, life cycle assessment, landfill, mechanical treatment, residual waste

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### **1. Introduction**

Waste management consists of three main activities: collection, treatment and disposal. Several possible solutions could be exploited for each activity, and also the combinations of them, in order to manage a single ton of Municipal Solid Waste (MSW), could be in great numbers. An efficient Source Segregation (SS) collection can contribute significantly to maximizing waste material recycling, but can represent up to 70% of the entire cost of MSW management (Di Maria and Micale, 2014).

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\*Selection and peer-review under responsibility of the ECOMONDO

\*\*Corresponding author: francesco.dimaria@unipg.it

Despite the recent directives of the European Council (2008/98 / EC) require the maximization of the MSW recovered and recycled, the fraction of the Residual Municipal Solid Waste (RMSW) to manage is still often substantial. The Mechanical-Biological Treatment (MBT) carried out before final disposal in landfill, entails the reduction of the pollutant emissions production (Di Maria et al., 2013) and the volume reduction, but also high energy consumption. The mechanical treatment of the RMSW is useful also for the extraction of recyclable materials mingled with the RMSW, like iron and aluminum.

Several authors have demonstrated that the incineration of the RMSW is more environmentally advantageous than the landfilling, even if this treatment solution involves high investment costs. Also the use of Solid Recovered Fuel (SRF), from mechanical selection in MBT facilities or Mechanical Biological Separation (MBS), could be a good alternative to the use of the coke in the cement plants (Ruth, 1998). The energy substitution plays a relevant role in terms of resource conservation and avoided emissions and strictly depends on the energy mix of the area to which the analysis is referred. Despite the studies about the best solution for waste management are quite numerous, there is a lack of information about the RMSW management strategy. In this study a Life Cycle Analysis (LCA) about the RMSW management options, for an urban area in central Italy with a SS intensity of 25% was carried out.

## **2. Materials and methods**

The present LCA study was performed according to ISO 14040 (2006) methodology and also by following the indications of the ILCD Handbook guidelines (EC, JRC, IES, 2010). The LCA analysis carried out in this study intends to evaluate the more sustainable management solution in terms of environmental impact and can be a valuable contribution to the decision-making of local governments for the achievement of targets set by the European Union. The classic approach "cradle to grave" should be revised. The incoming material, in fact, becomes the waste that can be disposed of or may re-enter several times in the cycle as recycled material, thus avoiding the consumption of primary material.

The replacement of the raw material or energy involves an environmental benefit due to the production process and the material consumption avoided, but at the same time involves environmental loads due to the process of recycling or the energy production itself. The functional unit chosen to perform the LCA analysis is a ton of RMSW and it is also the reference flow used in the analysis. The Life Cycle Inventory (LCI) modeling framework chosen is attributional. The amount of the waste that enters the system and its features are fixed. Only the RMSW mass rate involved in the different treatment processes varies, depending on the scenarios. Fig. 1 describes the different analyzed scenarios. The background of the system is represented by RMSW, energy, ancillary materials and fuels used by the processes.

The energy mix assumed in the analysis is referred to the Italian situation on the basis of the data reported by TERNA (2013). Instead the foreground of the system is represented by the energy produced by incineration and Landfill Gas (LFG) combustion, by the emissions from processes, treatments and energy consumption and by the materials for recycling. The collection model was realized by referring to the collection routes of the reference area of about 24,000 inhabitants with a SS intensity of 25% (Di Maria and Micale, 2013). After collection the RMSW could be directly landfilled or conveyed to incinerator. The model of the landfill was realized by considering an energy recovery of 33-62 kWh/tonne, depending on the biostabilization of the waste before disposal.

Other data of the model are referred to the ELCD database (EC, JRC, IES, 2008). The model elaborated for the incinerator is mainly referred to the Ecoinvent database (Hischier et

al., 2010) but was modified in regard to the mass balance of the outputs and energy production of 500kWh/tonne.

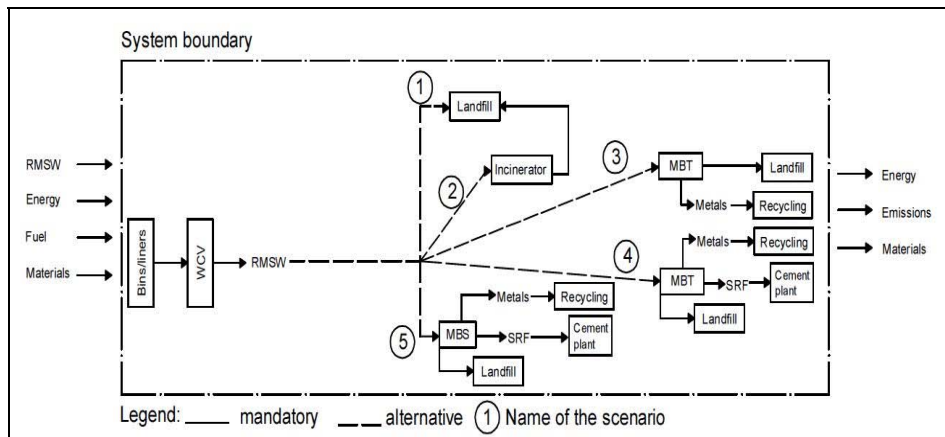


Fig. 1. System boundary

Two types of mechanical and biological treatments were considered in the scenarios: treatments aimed at maximizing the recovery of recyclable materials and bio-stabilization of the waste before landfilling, or treatments aimed at the production of SRF through a first bio-drying and a subsequent refining. Table 1 shows the main features of the treatments. Energy consumption of the treatments, mass balances and the production of LFG were defined on the basis of previous studies (Di Maria et al., 2013).

The model used for the co-combustion in cement plants, in substitution for coke, has been specially created by considering the combustion of each fraction present in the waste, the composition being fixed. The models used for recycling are referred to Ecoinvent database (Hischier et al., 2010). The indicators chosen, referred to the CML methodology (CML, 2001), are: Global Warming Potential at 100 years (GWP100), Acidification Potential (AP), Eutrophication Potential (EP); Photochemical, Ozone Creation Potential (POCP); Ozone Layer Depletion Potential, (OLDP), Abiotic Depletion Potential (ADP), Human Toxicity Potential, (HTP) and Terrestrial Ecotoxicity Potential (TEP).

Table 1. Main features of the mechanical treatment processes  
(a=iron, b=aluminium, c= 60% renewable).

	<i>Losses</i>	<i>Metals</i>	<i>SRF</i>	<i>Disposal in landfill</i>	<i>Energy consumption</i>
<b>TMB</b>	25	3 <sup>a</sup> -0.3 <sup>b</sup>	-	71.0	33
<b>TMB and SRF</b>	25	3 <sup>a</sup> -0.3 <sup>b</sup>	40.7 <sup>c</sup>	31.0	45
<b>MBS</b>	30	3 <sup>a</sup> -0.3 <sup>b</sup>	57.0 <sup>c</sup>	9.40	45

### 3. Results and discussion

The assessment of impacts (Fig. 2) highlights that energy recovery of RMSW is very beneficial. Indeed scenarios 4 and 5 have negative values with regards to the GWP, HTP, POP, AP and ADP. The last indicator, in particular, is related to the consumption of resources and therefore the substitution for coal in the cement gives a benefit that grows if the SRF produced is higher. Also in the other indicators, the benefit derives from the avoided emissions by substituting SRF for coal. Scenario 5 has a negative impact with regard to EP and OLDP, while this does not happen for the scenario 4.

This happens because in the scenario 5, compared to the scenario 4, a greater production of SRF takes place and the quantity of waste which is sent to the landfill is reduced. The landfilling of RMSW in fact, as shown in scenario 1, involves in all indicators, except HTP, a load on the environment. Regarding the indicator TEP, both scenarios 4 and 5 show a load of the environment, which is due to the emissions resulted in iron recycling process. However, the impact is reduced by increasing the production of SRF, while it remains still high in scenario 3 where the benefit due to the substitution of energy is limited to the combustion of LFG.

Instead in the other indicators the primary materials substitution contributes to a significant environmental benefit. Scenario 3 for indicators GWP, ADP, POP, HTP, AP and EP turns out to be better than the direct landfilling. The benefit, however, is mainly due to the avoided emissions due to recycling of metals separated by mechanical selection. In this scenario all other processes involve only loads, except for the energy recovery from the landfill, but this is a benefit much lower than the one related to recycling. Scenario 2 instead shows a benefit on the environment relative to the indicators ADP, OLDP, POP, AP, and this is due to the substitution of energy from fossil fuels.

The indicators GWP, HTP, TEP, EP instead present a burden on the environment and largely depend on the emissions generated by the process itself. The impacts related to collection activities appear to be marginal compared to those of the treatments or subsequent processes.

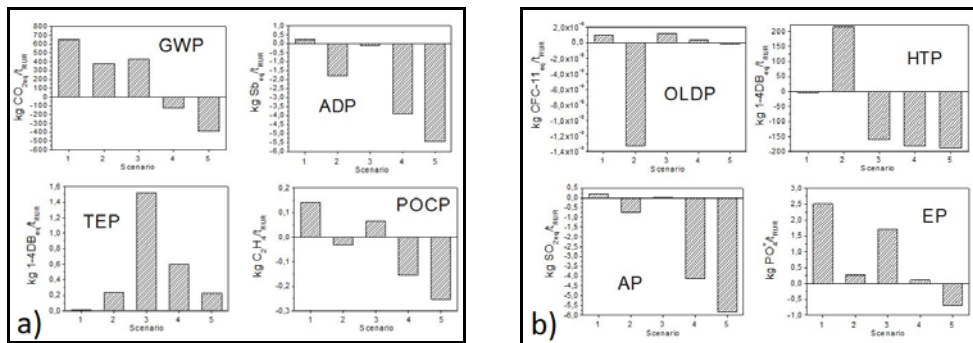


Fig. 2. Impact assessment for the scenarios 1 - 5

#### 4. Concluding remarks

An LCA analysis was performed on different Residual Waste Management scenarios referring to an urban area in central Italy. The scenarios with the energetic exploitation of the waste, through the production of Solid Recovered Fuel or incineration, turn out to be the best environmental solutions. The Mechanical-Biological Treatment of RMSW before landfilling implies limited environmental benefits.

The benefit from recycling of materials, commingled with the RMSW, extracted by mechanical selection, is high. An important role is played by the substitution of energy, and impacts are highly dependent on the energy mix of the area to which the analysis is referred.

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## **OIL CONCENTRATION MEASUREMENT IN METALWORKING FLUIDS BY OPTICAL SPECTROSCOPY\***

**Marco Grossi\*\***, Bruno Riccò

*Department of Electrical, Electronic and Information Engineering (D.E.I.),  
University of Bologna, Italy*

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### **Abstract**

MetalWorking Fluids (MWFs) are commonly used in metal cutting industries mainly to decrease temperature and weaken friction. The lubrication properties of such fluids degrade over time due to contamination and microbial attack and, when exhausted, they become a waste. Most MWFs are oil-in-water emulsions and maintaining the proper oil concentration is critical in order to maximize machine performance and MWFs' lifetime, this latter effect resulting in less costs for fluids disposal and lower ambient impact. This paper presents a novel method, based on optical spectroscopy, to estimate oil concentration in MWFs with good accuracy ( $R^2 = 0.9118$ ) that can be realized as a compact, low-cost instrument suitable for use in actual working environment.

*Keywords:* embedded systems, metalworking fluids, oil concentration, sensors

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### **1. Introduction**

MetalWorking Fluids (MWFs) are commonly used in metal cutting industries during various metal finishing processing steps to decrease the temperature and weaken friction, resulting in more efficient performance (Stephenson and Agapiou, 2005).

In order to perform well and have a long lifetime, MWFs contain a number of additives such as antimicrobial compounds to control the growth of bacteria and molds (Cyprowski et al., 2007), corrosion inhibitors, emulsifiers and antifoam agents. MWFs degrade over time due to contaminants entering the lubrication system and microbial attack that change the fluids' chemical properties. When their lubrication properties are no longer

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\* Selection and peer-review under responsibility of the ECOMONDO

\*\* Corresponding author: marco.grossi8@unibo.it

adequate, these fluids become waste and legal procedures (such as ultrafiltration using polymeric or ceramic membranes) must be followed for disposal to mitigate their impact on the environment (Bakalova et al., 2007).

Most MWFs are oil-in-water emulsion with oil concentration ranging from 1% to 10%. Once the emulsion is created in the tank by mixing the proper concentration of soluble oil and water, oil concentration does not remain constant over time because of physical and chemical effects such as: bacterial attack, reaction of oil molecules with elements in water or coming from the metal under work, lubricant adhesion to the metal parts, degradation due to temperature and pressure in the cutting region. Moreover water evaporation requires the tank to be re-filled to the standard level and this may lead to significant variations in oil concentration.

Maintaining the proper oil concentration is critical in order to optimize machine performance, since low concentration results in poor lubrication (affecting both product quality and tool lifetime), potential corrosion of both products and tools and less effective antimicrobial resistance. On the other hand, high oil concentrations lead to foaming, tool malfunction (due to excessive lubrication) and safety problems for the exposed workers (as MWFs can be dispersed in the air in the form of aerosol and inhaled by workers) (Cohen and White, 2006). Moreover, high oil concentration implies higher oil costs.

In addition, proper oil concentration results in longer MWF lifetime, hence in lower costs for fluids disposal and lower ambient impact. Thus, MWFs oil concentration should be accurately controlled at regular times (Dhar et al., 2006).

The official technique to measure oil concentration in MWFs is titration with 0.5M HCl. This method is accurate and insensitive to tramp oil and water contamination. However, it is a manual, chemical procedure that must be carried out in laboratory environment and cannot be used for *in situ* measures in the working environment.

The industry standard for oil concentration measurements in MWFs is refractometry, namely the measurement of the refractive index of the fluid (Canter, 2011). In practice, light is exposed to a drop of fluid placed on one side of a glass prism and is focused by a lens on a number scale read by the user. Analog refractometers are inexpensive instrument (200 to 250 \$) but must be carefully managed for proper use and the result is sensitive to tramp oil and water contaminants. Moreover the instrument needs frequent recalibration to avoid excessive inaccuracy in the measurements.

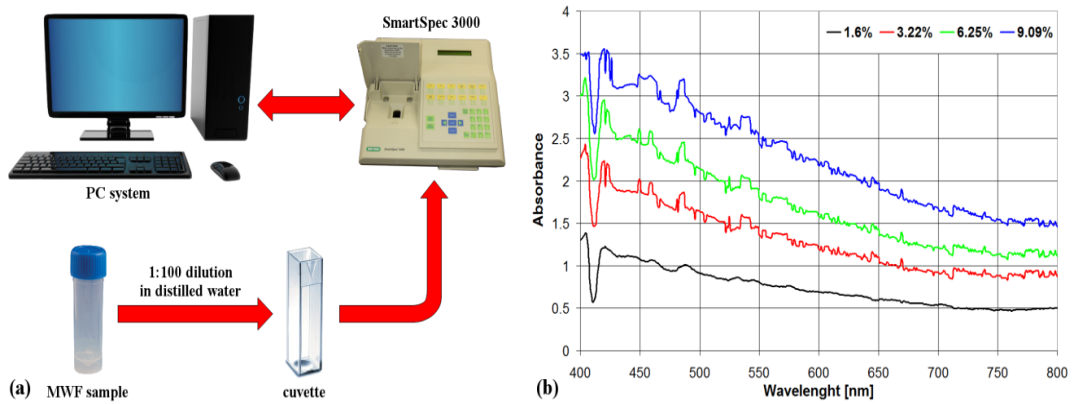
In this context, the present paper suggests an alternative method for oil concentration measurement in MWFs, based on optical spectroscopy. The proposed technique has significant advantages compared with refractometry, mainly because it can be realized in the form of a compact, low cost instrument to be used in working environment for frequent and/or continuous monitoring of MWF conditions. The proposed method makes it possible approach to maintain the oil concentration to the optimal level with significant advantages in terms of production efficiency, costs and ambient impact (longer lifetime of MWFs before disposal).

## 2. Materials and methods

All the tested MWFs are oil-in-water emulsions with oil concentration in the range 1% to 10%. Some samples have been created by mixing a soluble oil (produced by Total) with tap water in the desired concentration (fresh, non-contaminated samples) while others have been collected from metalworking plants near Bologna (Italy). In this latter case, control measurements of oil concentration have been made using an analog refractometer.

All the measurements have been carried out using the experimental setup shown in Fig. 1 (a). The MWF sample is diluted in ratio 1:100 with distilled water and the result

placed in a cuvette to be read in a SmartSpec 3000 spectrophotometer in the visible wavelength range (400 – 800 nm).



**Fig. 1.** Measurement setup used in the study (a), Absorbance spectra for samples featuring different oil concentrations in the wavelength range 400 – 800 nm (b)

The spectrophotometer is controlled via serial interface by a PC system, used also to display and file the measured data. Before the measurements the spectrophotometer is “blanked” using a sample with tap water in order to remove the contributions to absorbance due to water and cuvette.

The measured absorbance ( $A$ ) of the sample is defined as (Eq. 1):

$$A = -\text{Log}\left(\frac{I}{I_0}\right) = \text{Log}\left(\frac{I_0}{I}\right) \quad (1)$$

where:  $I$  and  $I_0$  are the light intensity transmitted through the sample under test (SUT) and under “blank” condition, respectively.

### 3. Results and discussion

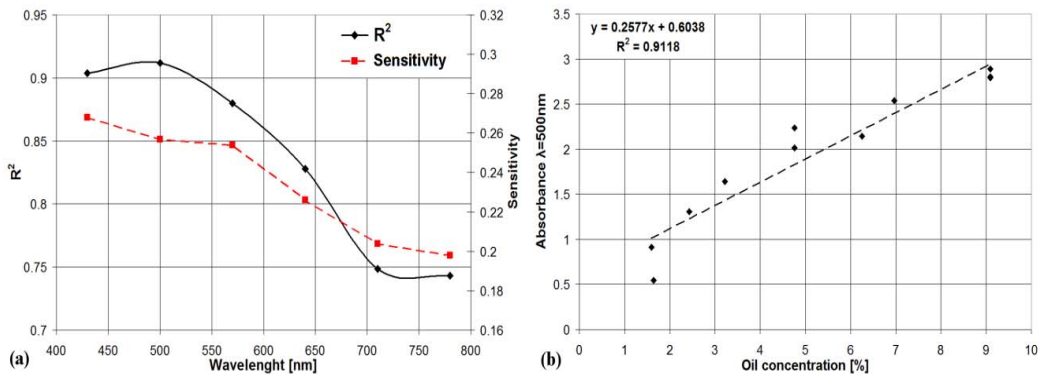
A number of samples featuring different values of oil concentration have been tested. Fig. 1 (b) shows the absorbance spectra for four samples featuring oil concentration of 1.6%, 3.22%, 6.25% and 9.09%, respectively. For all the investigated wavelengths the measured absorbance increases with oil concentration, although the sensitivity is higher for lower wavelengths. The results for six different wavelengths in the visible range are presented in Table 1 for a set of 10 MWFs samples: for each wavelength, the linear regression line defining the correlation between optical absorbance and oil concentration has been calculated and such an equation has been used to estimate the oil concentration from the absorbance data.

The residuals (difference between estimated and real oil concentration) have been used to calculate the standard deviation, essentially defining the measurement accuracy. As can be seen, the lowest standard deviation (i.e. highest accuracy in oil concentration measurement) is found at 500 nm, with a value that is almost half that achieved at high wavelengths.

**Table 1.** Linear regression line equations and standard deviations for different wavelengths in the range 400 – 800 nm

Wavelength (nm)	Linear regression line equation	Standard deviation
430	$y = 0.2688 \cdot x + 0.7509$	0.9632
500	$y = 0.2577 \cdot x + 0.6038$	0.9174
570	$y = 0.2549 \cdot x + 0.4942$	1.0902
640	$y = 0.2267 \cdot x + 0.3990$	1.3457
710	$y = 0.2042 \cdot x + 0.3330$	1.7087
780	$y = 0.1986 \cdot x + 0.3484$	1.7340

This is also shown in Fig. 2 (a), where the coefficient of determination  $R^2$  (showing the percent of variation in absorbance that can be explained by variation in oil concentration) and the sensitivity (absorbance variation in response to unity variations of oil concentration) are plotted vs. the wavelength of the incident light. As can be seen,  $R^2$  increases slightly in the wavelength range 400 – 500 nm, and then it decreases for higher wavelengths and reaches a plateau after 700 nm. Since, sensitivity is decreasing for increasing wavelength, for accurate measurements a wavelength in the range 400 – 500 nm represents the best solution.



**Fig. 2.** Determination coefficient and sensitivity plotted vs. wavelength of the incident light (a). Scatter plot for the absorbance measured at wavelength 500 nm vs. oil concentration (b)

Fig. 2 (b) shows the scatter plot of optical absorbance vs. oil concentration in the case of a wavelength of 500 nm. The calculated linear regression line (also presented in Table 1) is  $y = 0.2577 \cdot x + 0.6038$  and  $R^2 = 0.9118$ , indicating that over 90% of the variations in the measured absorbance can be explained by the variations in oil concentration. The oil concentration can thus be estimated with high accuracy from measurements at a single wavelength (500 nm).

#### 4. Concluding remarks

This work has presented a novel optical technique to determine the oil concentration in MWFs. The experimental data show that measurements at a single wavelength (in particular the best results have been obtained at 500 nm) can be used to estimate the oil concentration with good accuracy ( $R^2 = 0.9118$ ).

The presented technique is suitable to be realized in the form of either a low-cost, easy-to-use instrument to be used for instantaneous measurements in real working environment, or an automatic addition to MWF tanks for continuous monitoring of fluid condition. In both cases, important benefits would be obtained in terms of machine

performance, product quality, costs and MWFs' lifetime. This latter effect, in turn, would significantly decrease ambient impact due to fluids disposal.

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## **INDUSTRIAL SYMBIOSIS IN ITALY AS A TOOL FOR SUSTAINABILITY: CASE STUDY ANALYSIS AND REPLICABILITY\***

**Antonella Iacondini<sup>1</sup>, Ugo Mencherini<sup>3,4\*\*</sup>, Luciano Morselli<sup>2</sup>,  
Fabrizio Passarini<sup>1,2</sup>, Ivano Vassura<sup>1,2</sup>**

<sup>1</sup>*University of Bologna, Interdepartmental Centre for Industrial Research  
"Energy and Environment", Italy*

<sup>2</sup>*University of Bologna, Department of Industrial Chemistry "Toso Montanari", Italy*

<sup>3</sup>*Aster S. Cons. P. A., Italy*

<sup>4</sup>*University of Bologna, Department of Industrial Engineering, Italy*

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### **Abstract**

The aim of this paper is to evaluate the opportunities existing on the Italian territory and the useful experiences realized in this area for purposes of development of a joint system (businesses – institutional bodies) intended to apply Industrial Symbiosis and to disseminate the methodology. Pilot projects, undertaken or in progress in the region, targeted to study the potential for application of circular economy by closing production cycles are described and analyzed with a SWOT analysis.

*Keywords:* circular economy, industrial symbiosis, SWOT analysis, waste valorization

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### **1. Introduction**

Industrial Symbiosis, as instrument to optimize the use of resources, requires attention by local and regional economies and institutions. The key to develop Industrial Symbiosis is collaboration, but this requires a thorough study of the area in order to maximize the effectiveness of application of the instrument.

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\*Selection and peer-review under responsibility of the ECOMONDO

\*\*Corresponding author: [ugo.mencherini@aster.it](mailto:ugo.mencherini@aster.it)

One of the proposed tools in all documents regarding the EU Cohesion Policy, the European strategies and, recently, also in the Italian Regional Policies, is Industrial Symbiosis. This instrument is also suggested within the waste plan of Emilia Romagna Region as “useful to the reduction of special wastes quantity”.

Many examples of symbiosis processes studied by industrial research could be applied in Italian productive system, so as to reduce waste amount, increase the efficiency and re-use of resources and make related environmental improvement an attractive process for industrial stakeholders (Laybourn and Lombardi, 2012).

## **2. Materials and work context**

### *2.1. The Italian Effort for economic and industrial growth to achieve the Europe2020 Strategy objectives: SSS Smart Specialization Strategies*

The new “Cohesion Policy 2014-2020 Programming Cycle” represents the new rules and legislation governing the next round of EU Cohesion Policy investment for 2014-2020.

Financial instruments are an efficient way of deploying cohesion policy resources in pursuit of the Europe 2020 Strategy objectives.

This programme expects that national and regional authorities develop research and innovation strategies aimed at the "smart specialization". The goal is to allow a more efficient use of structural funds and to increase synergies between EU, national and regional authorities.

Smart Specialization is a strategic approach to economic development through targeted support to Research and Innovation (R&I). It will be the basis for European Structural and Investment Fund interventions in R&I as part of the future Regional and Cohesion Policy's contribution to the Europe 2020 jobs and growth agenda.

In Italy this program was implemented by the Ministry of Economic Development (MISE) in agreement with the Italian Ministry of Education, University and Research (MIUR).

The goal is:

- To support regional governments in designing and implementing their own SSS through the possibility of sharing, at national level, experiences underway in different regions.
- The arrangement of the various initiatives of SSS, with the extent of avoiding overlaps between different levels of governance.

In this perspective of targeted support, every region has worked in order to bring out the excellence of the territory with the prospects of success on the global market, and to identify more effective instruments for economic and territorial growth.

Two Italian regions, Emilia Romagna (INVITALIA, 2014) and Lazio (Regione Lazio S3, 2014), have inserted Industrial Symbiosis in their strategic plans, as tools / specialization in order to reduce waste quantity and to increase regional sustainability, materials reuse and raw materials saving.

### *2.2. The Emilia Romagna case study: Industrial Symbiosis as a strategic instrument for the Territorial development?*

Developing operationally the SSS strategies, in Emilia Romagna five technological specializations were decided to be strategic and considered most relevant for a growth strategy of the territory.

- Agrifood Building Mechatronics and motor design and manufacture Healthiness industries.

- Creative and cultural industries.

In the first three specializations, Industrial Symbiosis and resources management are included as important tools to increase efficiency and sustainability in industrial processes.

Industrial Symbiosis has been included in the Waste Management Plan of Emilia Romagna Region, as “instrument for the amount and hazard reduction of special wastes and for the re-use of materials from production processes”. Emilia Romagna Region “is considering whether to activate work tables to study the conditions facilitating the use of by-products and identify possible agreement conditions between involved actors” (Emilia Romagna – PRG, 2014).

In Emilia Romagna an Industrial Symbiosis pilot action was conducted: the “Green Project”, developed by Unioncamere Emilia Romagna and Aster (with the scientific support of ENEA UTTAMB), has been aimed at the dissemination of an Industrial Symbiosis culture in Emilia Romagna, involving traditionally separate industries in a collective approach (ASTER, 2014; Cutaia et al, 2014).

The pilot action results (13 companies, 4 laboratories and 2 institutional bodies involved, 90 symbiosis paths identified) show that Emilia Romagna is a good substrate to start a network of companies involved in Industrial Symbiosis processes: the proactive participation and the feedback received by participants and other representatives of the Emilia Romagna business network is indicative of a widespread interest on the matter. This is undoubtedly a strength with the perspective of replicability and diffusion of the model.

The feedback analysis also allowed to highlight some “resistance”, due to:

- Complex authorization processes (different institutional bodies are involved in the process).
- Reluctance to the sharing of internal data (due to an industrial culture not very accustomed to cooperation): weakness.

In this paper has been analyzed the case study of Emilia Romagna Region in facing Industrial Symbiosis as a tool to reach the National objectives.

### **3. Methods: SWOT analysis**

Looking at Italy as an industrial system, in this paper the working methodology has provided for the application of a SWOT analysis, in order to understand the best strategies to plan a successful implementation of Industrial Symbiosis in our country.

SWOT Analysis is one of many possible strategic planning tools used to evaluate the Strengths, Weakness, Opportunities and Threats involved in a project, or any other situation requiring a decision or a possible implementation.

Consequently, the objective of this paper was to apply this method of planning to Industrial Symbiosis, on the basis of the data obtained from the experiences and studies realized in Italy, with the intent that concepts described here can be used to strengthen and guide this emerging discipline.

Among the methodological prescriptions adopted in implementation phase of SWOT analysis:

- Realism about the strengths and weaknesses of the territory: we have tried to distinguish between current condition and potential for future development.
- Specificity by avoiding grey areas.
- Brevity and simplicity, avoiding complexity and over-analysis, since in SWOT method much of the information is subjective.

In theory, SWOTs parameters (Strengths, Weakness, Opportunities and Threats) are used as inputs to the creative generation of possible strategies, by asking and answering the following four questions numerous times:

- 1) How can we Use each Strength?
- 2) How can we Stop each Weakness?
- 3) How can we Exploit each Opportunity?
- 4) How can we Defend against each Threat?

In practice, once our objective has been established (estimate the replicability of Industrial Symbiosis methodology in Italy), a multidisciplinary team (representing a broad range of perspectives) has developed SWOT analysis, presented in the form of a matrix.

In our analysis, SWOTs are defined based on the following criteria, helpful to the implementation of Industrial Symbiosis:

- Strengths and Weaknesses are internal attributes of the Italian territory (business system and institutional bodies).
- Opportunities and Threats are external conditions (European context, socio-political context, cultural context).

To reap the full benefits of SWOT analysis it is important to use this tool correctly.

Firstly, the aim of this work and analysis should provide information that helps institutional bodies, decision makers and opinion groups (professional associations) in operating for the diffusion of Industrial Symbiosis methodology on Italian territory. Consequently we avoided laundry-lists of strengths, weaknesses, etc., that are not in themselves very useful: it is only when the potential implications of this information on the territory/instrument are assessed that meaningful analysis emerges.

Secondly, it is most beneficial to look at the strengths and weaknesses originating within the instrument or territory; we have worked in order to identify some focus points: what do Italian industrial system does better than anyone else, what/where could be improved, what are others likely to see as weakness?

Conversely, the analysis has externally focused opportunities and threats: what trends could Italian territory take advantage of, how can it turn its strengths into opportunities, what trends could do harm?

## **4. Results and discussion: Industrial Symbiosis SWOT analysis and replicability in Italy**

### *4.1. Strengths (internal)*

- Big production districts: areas in which the same kind of production is performed are more able to influence policies and regional regulation.
- Many companies are located in the same area: even if it is not strictly requested, the “geographic proximity” is a key success factor in order to implement Industrial Symbiosis (Jensen et al, 2011).
- High technological skills.
- Trade associations: their capacity to aggregate companies could be a success factor in order to create the exchange network and to influence policies (great decision weight).
- Good response from enterprises in the pilot experiences realized in Italy: proactive participation, widespread interest in the instrument.
- Regional and National policies (e.g. S3 - Smart Specialization Strategies): Industrial Symbiosis recognized as a strategic tool for the territorial growth

### *4.2. Weaknesses (internal)*

- Authoritative problems: different institutional bodies involved in the process.
- Lack or wrong communication towards enterprises.

- Distrust by the companies because of bureaucratic difficulties.
- Weak collaboration between different enterprises: “cultural” problem.
- Lack of links between different production chains.
- Resistance to spread sensitive data about waste fluxes.
- Weak collaboration between industry and research: lack of mutual trust (different timescales and approach).

*4.3. Opportunities (external)*

- Business opportunities for enterprises: reduction in disposal costs, revenue from the sale of scrap materials.
- EU funding: EU Cohesion Policy (Climate KIC, Horizon 2020, Cosme, LEIT, PPP)
- Positive exiting experiences abroad: NISP programme, KIKOX – South Korea, Kalundborg EIP.
- Social, environmental and economic good perspectives.

*4.4. Threats (external)*

- Complexity of the regulatory framework.
- Difficulties in the interpretation of waste legislation.
- Possible niche market could be not economically convenient for SMEs.
- Possible conflict of interest with big waste treatment companies.
- Lack of a strong coordination plan from a leader institution.

In Table 1 the SWOT analysis, by crossing internal and external peculiarities of Industrial Symbiosis feasibility process.

**Table 1.** SWOT analysis of Industrial Symbiosis feasibility process

SWOT Analysis		Internal analysis	
		Strengths	Weaknesses
E x t e r n a l	Opportunities	<p>S-O Strategies: Improve communication and collaborations between enterprises using districts and trade associations as a link Develop the knowledge of tools such as EU funding and policies both in the productive and the research areas, in order to develop the open data culture and increase the link between industry and research.</p>	<p>W-O strategies: Training of experts in economic and legal aspects of industrial innovation processes (e.g. LCA, waste and environmental regulation)</p>
	Threats	<p>S-T strategies: Districts and trade associations has to understand the importance of industrial symbiosis as powerful stakeholders able to influence the improvement of the complex regulatory framework. Big production districts and trade associations can plan strategies on the feasibility of niche processes</p>	<p>W-T strategies: Technical stakeholders have to focus on the economic convenience of industrial symbiosis to develop it as an accelerator for companies to get out from the economic crisis. The aim is to emphasize the need of a strong public coordinator on the subject of waste valorization and renewable resources which could influence the normative simplification process</p>

**5. Conclusions**

As a conclusion, Industrial Symbiosis proved to be a quite effective tool in a perspective of increasing sustainability: in this perspective SWOT analysis demonstrated to

be an useful instrument to deepen the actions needed to develop a circular economy culture in the Italian industrial network.

The experiences carried out on the territory underline the general interest by the production system: Italian territory has good potential, but also needs for a strong commitment by a leader institution that coordinates the application of the instrument.

### **Acknowledgements**

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Procedia Environmental Science, Engineering and Management 1 (2014) (1) 25-29

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## **LANTHANUM UPTAKE BY CLAYS AND ORGANO-CLAYS: EFFECT OF THE POLYMER\***

**Elena Maria Iannicelli-Zubiani<sup>1\*\*</sup>, Cinzia Cristiani<sup>1</sup>, Giovanni Dotelli<sup>1</sup>,  
Paola Gallo Stampino<sup>1</sup>, Irene Bengo<sup>2</sup>**

<sup>1</sup>*Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering,  
Piazza Leonardo da Vinci 32 Milano, Italy*

<sup>2</sup>*Politecnico di Milano, Department of Management, Economics and Industrial Engineering,  
Via Lambruschini 4/b Milano, Italy*

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### **Abstract**

Two natural smectite clays (STx-1b and SWy-2) were studied as solid sorbents for uptake and release of lanthanum. Since the obtained global efficiencies of lanthanum recovery were about 30-35%, the same considered natural clays were modified by intercalating a PEGylated ethylene diamine having chelating properties, in order to evaluate a possible improvement effect of the polymer. The pristine and the organo-clays were characterized by XRD analyses while the amounts of intercalated polymer and captured lanthanum were estimated respectively by COD and ICP-OES analyses. The results showed that pristine clays and modified clay had similar lanthanum uptake efficiencies while modified clays presented a better behaviour towards release processes, ensuring a recovery global efficiency of 43%.

*Keywords:* clays, organo-clays, rare earths, recovery, solid phase extraction

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### **1. Introduction**

Nowadays there is an increasing need of REs due to their usage in numerous high-technology applications (Iannicelli-Zubiani et al., 2013a). Increasing demand for the different products containing REs has resulted in a restriction of supply from producing Countries, particularly China. Since currently each EU citizen produces about 17 kg of

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\*Selection and peer-review under responsibility of the ECOMONDO

\*\*Corresponding author: [elenamaria.iannicelli@polimi.it](mailto:elenamaria.iannicelli@polimi.it)



WEEE per year and since these wastes are rich in precious and strategic metals, 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).

Different methods have been proposed for REs recovery and recently the use of Solid-Phase Extraction (SPE) is obtaining more and more attention because of its advantages of high recovery, short extraction time, high enrichment factor, low cost and low consumption of organic solvents. 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. Furthermore, clay minerals show a natural adsorption behaviour towards REs (Coppin et al., 2002).

Since the compositions of leached electronic scraps are very complex, a model solution with one RE ion was studied: lanthanum was chosen as representing elements of REs family.

## 2. Objectives

In this context, the main objective of the present study was to recover REs, in particular lanthanum, by solid-liquid extraction. The solid sorbents used are of different kind: two pristine clays (STx-1b and SWy-2) and two ad hoc synthesized organo-clays.

Another objective of this work was to obtain the release of the captured lanthanum varying the operating conditions such as the pH, since the final aim is not only the uptake but also the recovery of valuable metals from WEEE. Further, the results obtained with the clays and the organo-clays were compared, both in the adsorption and in the release phases. Finally an analysis of the global process efficiencies was carried out.

## 3. Outline of the work

This work is divided in three main parts:

- The first part is about the synthesis of the organo-clays, compared during the study with the pristine clays for what concerns the adsorption and release capability of lanthanum.
- The second part covers the lanthanum adsorption tests by using the different solids.
- The third part covers the release experiments obtained varying the pH conditions.

## 4. Materials and methods

STx-1b and SWy-2 are two natural standard smectite mineral clays, respectively a Ca-montmorillonite and a Na-rich montmorillonite (supplied by the Clay Mineral Society). The polymer used as intercalating agent is a PEGylated ethylene diamine (POL in the following), whose formula is reported in Fig. 1. It was supplied by Bozzetto Group. Lanthanum (III) nitrate pentahydrate and nitric acid ACS reagent, both of them from Sigma-Aldrich, were the other reactants used in this study.

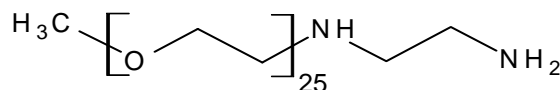


Fig. 1. Chemical formula of POL

Hybrid materials were obtained following a standard procedure developed elsewhere (Zampori et al. 2010). In brief, 2.5 g of clay (STx or SWy) were mixed, in a closed reactor under vigorous stirring, with 50 mL of aqueous polymer solution for a fixed time of 90 min.

The initial polymer concentration ( $CP_0$ ) was of 35mM. All the intercalation experiments were carried out at 30°C while the pH of the solutions was measured before and after dispersing the clays using a Mettler Toledo FE20/EL20 digital pH meter and it was constant throughout the preparation at about pH 11. After the intercalation reaction, the solid phase was separated by the liquid one using a centrifuge (HETTICH 32 RotoFix). The solid, upon drying (one day at room temperature) was ground in a mortar.

A determined amount of the different solids (clays and organo-clays) was contacted with an aqueous solution of  $La(NO_3)_3$  at known concentration ( $C_0 = 19$  mM), vigorously stirred at room temperature and separated from liquid using a centrifuge. In a previous paper it was demonstrated that the lanthanum uptake was not quantitatively affected by contact time, thus very fast (Iannicelli-Zubiani et al., 2013a). Accordingly, in this study, the adsorption contact time was fixed at 1.30 h, long-lasting enough to be sure of the equilibration between solid and solution and fast enough to avoid lanthanum release at this step. The contact experiments were carried out using a solid/liquid ratio of 0.04 g/mL and the amount of lanthanum captured by the solid phase ( $C_s$ ) was determined by ICP-OES of the liquid solution before and after the contacting experiments and calculated by difference.

Release tests were performed on the different samples in order to verify the solid capability not only to capture, but also to release metal ions (Fig. 2). The release was obtained contacting the enriched lanthanum solids with solutions of  $HNO_3$  1M since previous studies (Iannicelli Zubiani et al., 2013b) proved that effective release was obtained at very acidic pHs. The operating conditions were: 1.30 h of contact time, solid/liquid ratio of 0.026 g/mL, room temperature and stirring at 500 rpm. Also in this case, the lanthanum content in the liquid phase after release ( $C_w$ ) was achieved by ICP-OES.



Fig. 2. General process scheme

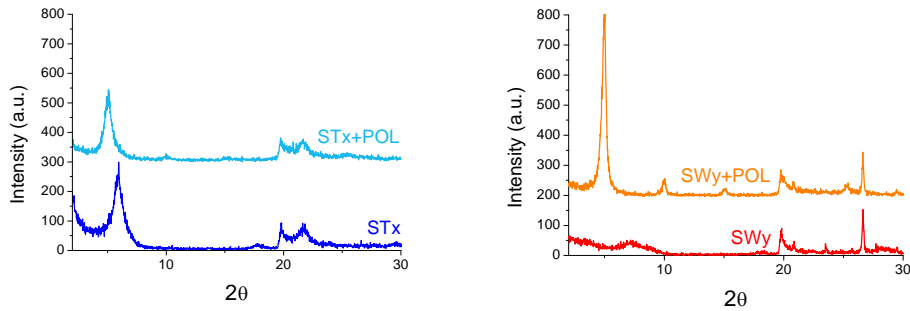
The metal-ion concentrations were measured by an Optima 2000DV inductively plasma optical emission spectrometer (Perkin Elmer).

X-ray diffraction (XRD) measurements were carried out on powder samples with a Bruker D8 Advance diffractometer using graphite monochromated  $Cu-K\alpha$  radiation; the scan step was  $0.02^\circ 2\theta$  and the measurement time 1 s per step.

The Chemical Oxygen Demand (COD) analyses were carried out using a Spectrodirect Lovibond instrument. In a standard instrumental procedure the unknown sample was oxidised by heating for 120 min at 150 °C.

## 5. Results and discussion

The XRD measurements provided that the polymer intercalation occurred since the basal reflection related to pristine clays showed for both organo-clays the typical shift towards lower  $2\theta$  angles (from 5.7 to 5 for  $STx$  samples and from 7.4 to 5 for  $SWy$  samples), resulting from the interlayer enlargement due to the polymer intercalation (Fig. 3).



**Fig. 3.** XRD analyses and relative basal spacings of *STx* and *SWy* pristine and organo-clays

The amount of intercalated polymer ( $CP_S$ ) was calculated by difference between the initial and the residual amount using the COD (Chemical Oxygen Demand) analysis (Zampori et al., 2010) on the liquid solutions and the results are reported in Table 1.

**Table 1.** Polymer initial ( $CP_0$ ) and after intercalation concentrations ( $CP_S$  = amount of polymer in the solid phase)

Sample	$CP_0$ [g/g <sub>clay</sub> ]	$CP_S$ [g/g <sub>clay</sub> ]
<i>STx+POL</i>	0.8	0.2
<i>SWy+POL</i>	0.8	0.3

The lanthanum adsorption experiments (Table 2) showed that both pristine and organo-clays were effective in lanthanum uptake and that the uptake efficiencies obtained with organo-clays ( $C_S/C_0$  [(mg/g<sub>clay</sub>)/(mg/g<sub>clay</sub>)] = 41/80 for *STx+POL*) were not higher but just comparable than the ones obtained using pristine clays ( $C_S/C_0$  [(mg/g<sub>clay</sub>)/(mg/g<sub>clay</sub>)] = 35/67 for *STx*), thus the presence of the polymer was in this step, apparently, not significant.

**Table 2.** Lanthanum uptake, release and global process efficiencies of pristine and organo-clays

Sample	Uptake [%]	Release [%]	Global efficiency [%]
<i>STx</i>	52	62	32
<i>STx+POL</i>	51	83	43
<i>SWy</i>	47	74	35
<i>SWy+POL</i>	43	83	36

Lanthanum release was obtained in any case but it is evident (Table 2) how pristine clays were less effective to release the captured lanthanum ions ( $C_W/C_S$  [(mg/g<sub>clay</sub>)/(mg/g<sub>clay</sub>)] = 22/35 for *STx* compared to  $C_W/C_S$  [(mg/g<sub>clay</sub>)/(mg/g<sub>clay</sub>)] = 34/41 for *STx+POL*).

## 6. Concluding remarks

From the comparison between pristine and organo-clays the following conclusions can be drawn: the experimental procedure was appropriate to intercalate the polymer in both clays; similar uptake efficiencies were obtained with both natural and modified clays (around 50% for *STx* and *STx+POL* and around 45 for *SWy* and *SWy+POL*); the release efficiency was higher using organo-clays (83%) than using pristine clays (62-74%), thus the polymer seems to play an important role in the release step; from the global efficiencies data: the

modified clay *STx+POL* ensured the best global process efficiency. Accordingly, the proposed clay-polymer system seems promising for the proposed application.

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Procedia Environmental Science, Engineering and Management **1** (2014) (1) 31-34

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## **RECYCLING SCENARIOS FOR WASTE CATHODE RAY TUBES\***

**Laura Rocchetti<sup>1\*\*</sup>, Francesco Vegliò<sup>2</sup>, Francesca Beolchini<sup>1</sup>**

<sup>1</sup>*Università Politecnica delle Marche, Department of Life and Environmental Sciences,  
via Brecce Bianche, 60131, Ancona, Italy*

<sup>2</sup>*Università dell'Aquila, Department of Industrial Engineering, of Information and Economy,  
Via Campo di Pile, 67100, L'Aquila, Italy*

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### **Abstract**

With the diffusion of the technological progress we have lost the habit of repair, re-use and recycle many goods. To contrast the production of waste and favor sustainable management actions, the European Parliament has promulgated the WEEE (waste electrical and electronic equipment) directive. In this context, the present study deals with management options for waste cathode ray tubes (CRTs). Different recycling scenarios were evaluated for the recovery of valuable secondary raw materials, such as the fluorescent powders containing yttrium, glass cullet and lead. Our results suggest that the recovery of secondary raw materials from CRTs creates benefits for the environment.

*Keywords:* life cycle assessment, recycling, waste CRT, yttrium

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### **1. Introduction**

Today the habit of repair, re-use and recycling of goods is not common as in the past, especially for electric and electronic equipment (EEE). This phenomenon is enhanced by the rapid evolution of new technologies, that favors the purchase new EEE and throw away the old one. In Europe the WEEE directive (EC Directive, 2012), aims at the prevention of WEEE, the re-use, recycling and recovery to reduce the disposal of waste and retrieval of secondary raw materials. For cathode ray tubes (CRTs), the WEEE directive establishes that

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\*Selection and peer-review under responsibility of the ECOMONDO

\*\* Corresponding author: l.rocchetti@univpm.it

from WEEE separately collected, at minimum CRTs and the fluorescent powders must be removed. Indeed, in the fluorescent powders are present metals of concern, such as yttrium that can be recycled as a secondary raw material for the production of the red phosphors of monitors (Beolchini et al., 2012).

At present the CRT technology for monitors has been gradually replaced by the flat display technology. In order to fulfill the WEEE directive for the end-of-life of these WEEE, glass-to-glass recycling is an option based on the use of parts (funnel and panel glass) of waste CRT for the production of new goods (Kang and Schoenung, 2005). This scenario represents the conventional recycling option that was applied when CRT monitors were produced at a large scale. Glass-to-lead recycling is an alternative strategy, where the major concern is represented by lead, which is separated from glass. Currently the fluorescent powders of CRT monitors are not treated by recycler companies, but disposed of in landfill (Lee and Hsi, 2002; Nnorom et al., 2011). In this regard our research group has developed a recycling process aimed at the recovery of rare earth elements, within the European research projects called HydroWEEE 231962 (Innovative Hydrometallurgical Process to recover Metals from WEEE including lamps and batteries), and its follow-up, HydroWEEE Demo 308549 (Rocchetti et al., 2013; Toro et al., 2010).

## 2. Objectives

In this context, the main objective of the present study was to evaluate the potential impact on the environment of different options for waste CRTs by means of simplified life cycle assessment (LCA). Three scenarios were considered for the management of waste CRTs: (i) conventional recycling addressed to the production of new CRT monitors; (ii) recycling of the CRT components for other purposes; (iii) disposal in landfill for hazardous waste.

## 3. Materials and methods

In the present study we compared the environmental impacts of conventional recycling of steel, funnel and panel glass (when CRTs were produced at large scale, “CRT technology”; scenario 1) and up-to-date recycling of one CRT monitor (when CRT, are replaced by the flat screen technology, “flat display technology”). In the “flat display technology”, steel and the panel glass are recycled in a case (scenario 2), and in the other also lead from the funnel glass (scenario 3).

These scenarios were also compared to the disposal in landfill (scenario 0). Moreover, special attention has been directed to the recycling of yttrium from fluorescent powders of a CRT applying a hydrometallurgical process developed by Rocchetti et al. (2013), and compared with disposal in landfill. Other details about the methods applied in the present study can be found elsewhere (Rocchetti and Beolchini, 2014).

## 4. Results and discussion

The potential CO<sub>2</sub> emissions in the considered scenarios within the two frameworks with a different technology of monitor production (CRT or flat screen displays) are reported in Fig. 1. In scenario 1 of “CRT technology” a net credit (1.0 kg CO<sub>2</sub>-eq.) for the environment was observed for the management of a CRT. Most of the emissions of CO<sub>2</sub> were associated to the use of energy necessary for the separation of panel and funnel glass. Conversely, if a waste CRT was disposed of in landfill the impact was evaluated as 0.8 kg CO<sub>2</sub>-eq. (scenario 0). In the framework “flat display technology”, scenario 2 determined a credit equal to 0.7 kg CO<sub>2</sub>-eq. towards the environment.

Thanks to the recycling of the steel and panel glass it was possible to compensate the CO<sub>2</sub> emissions due to the treatment. In the same framework, also in scenario 3 a credit (0.9 kg CO<sub>2</sub>-eq.) for the environment was achieved, less waste was conferred in landfill and more secondary raw materials were recovered.

The recovery of yttrium from the fluorescent powders of one waste CRT resulted in a credit for the environment (0.76 Kg CO<sub>2</sub>), while the disposal in landfill determined an impact of 0.01 kg CO<sub>2</sub>-eq. (Fig. 2). These results are promising as an high impact is associated to the primary production of yttrium.

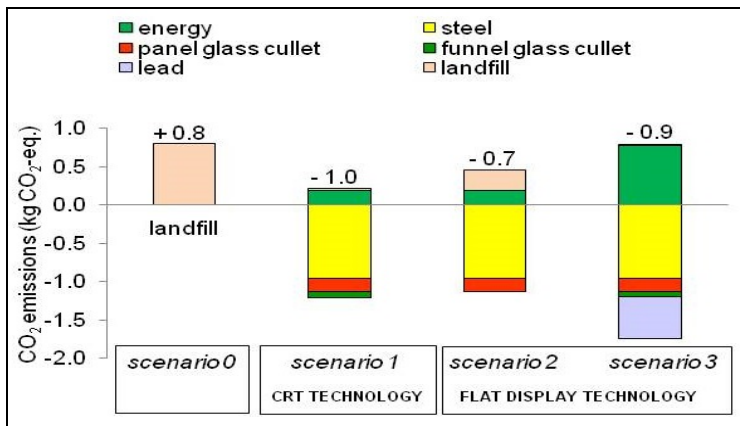


Fig. 1. Emissions of CO<sub>2</sub> for the management options of one waste CRT (Rocchetti and Beolchini, 2014).

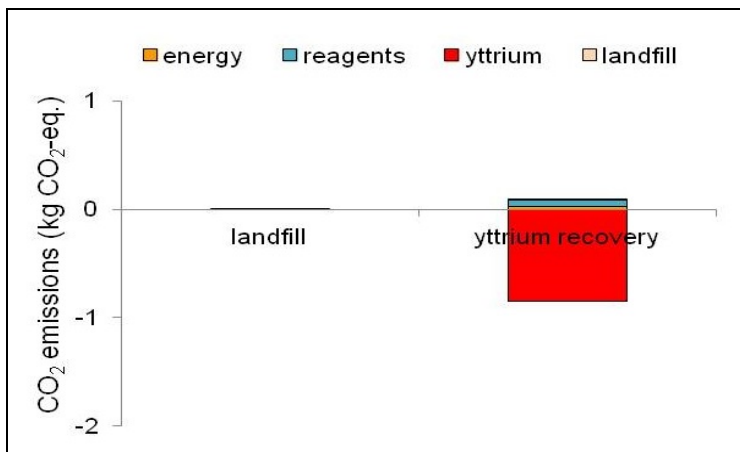


Fig. 2. Emissions of CO<sub>2</sub> for disposal in a landfill and treatment for yttrium recovery from one waste CRT (Rocchetti and Beolchini, 2014).

## 5. Conclusions

The present study has considered several options for the management of waste CRT, and through life cycle assessment has quantified the impacts and the credits for the environment. According to our results the way directed to the recycling of CRT and recovering secondary raw materials, as well as reducing the amount of CRTs conferred in landfill is the right one to cover.



## Acknowledgements

The European Union is acknowledged for funding the project HydroWEEE 231962 (Innovative Hydrometallurgical Process to recover Metals from WEEE including lamps and batteries) and its follow-up, HydroWEEE Demo 308549.

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Procedia Environmental Science, Engineering and Management **1** (2014) (1) 35-39

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**WASTE2 - Technical Seminar: Waste, byproduct or end of waste?**

**THE DEFINITION OF “BIOMASS” IN EUROPEAN  
AND ITALIAN LEGISLATION: WHEN IT IS WASTE,  
BY-PRODUCT OR END-OF-WASTE\***

**Valeria Briigliadori**

*Renewable Energy Consultancy, Via Patrignani, 61, Santarcangelo di Romagna, 47822, Rimini, Italy  
e-mail: [valeriabrigliadori@bit-services.it](mailto:valeriabrigliadori@bit-services.it)*

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**Abstract**

To understand the definition of biomass in the Italian legal system it is necessary to analyze first the Community European legislation on biomass, by-product and waste.

In the Italian system, the first definition of biomass is given in the Article 2 of Law 387/2003, which was later extended by Law 28/2011 for the implementation of Directive 2009/98/EC, which repealed Directives 2001/77/CE and 2003/30/EC. The biomass can be considered a by-product as long as it follows the requirements imposed by article 184 bis of Law 152/2006 and when it isn't considered waste according to the waste legislation.

*Keywords:* biomass, by-product, End-of-Waste criteria, strategy 20-20-20

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**1. Introduction**

During the Nineties, a new awareness appeared in Europe, that renewable energy and energy efficiency are the future produces a change of strategies and legal instruments. The White Book of 1997 (EC Communication, 1997) sets the first global objective: to have a 12% contribution of renewable energy sources in the inland energy consumption by 2010.

Gradually, the European Union introduces the Directive 2001/77/EC (later repealed by Directive 2009/98/EC) for the promotion of electricity production from renewable energy sources which is a priority for several reasons, such as the security and diversification of energy supply, environmental protection and social and economic cohesion (EC Directive,

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2001). Every country must contribute with their share and give feedback through reports every five years and the European Commission has to publish a biannual report based on the national reports. This Directive contains the first legal definition of biomass (art. 2, b).

Since the energy-saving potential of cogeneration was under-utilized in the European Union, in 2004 the EC Directive (2004) promotes cogeneration based on a useful heat demand in the internal energy market by facilitating the installation and operation of electrical cogeneration plants.

A year later, the European Commission issues the “Biomass Action Plan” (EC Communication, 2005) and biomass becomes one of the key to the new energy policy, the three main objective of which are competitiveness, sustainable development and security of supply.

The European Union starts planning a new community policy: in 2006 the Green Paper for an European strategy for sustainable, competitive and secure energy (EC Communication, 2007); in 2007 the Communication from the Commission to the European Council and the European Parliament “An energy policy for Europe” (EC Communication, 2007); in 2009 the Climate and Energy Package is promulgated.

Among its key objectives for 2020 are:

- 20% reduction in EU greenhouse gas emissions from 1990 levels;
- raising the share of EU energy consumption produced from renewable resources to 20%;
- 20% improvement in the EU’s energy efficiency.

In 2014, a communication from the European Commission to the European Parliament, the Council, the European Economic and Social Committee and Committee of the Regions, introduces a new policy framework for climate and energy in the period from 2020 to 2030 (EC Communication, 2014).

## **2. Objectives**

The objective of this paper is to describe the regulatory context of biomass, highlighting problematic aspects and potential normative solutions. In the Italian legal system there isn’t a single and exhaustive definition of biomass, therefore it is important to correctly understand the legislation to be able to enforce it.

## **3. Outline of the work**

This work is divided in two parts:

- The first part analyzes the regulatory contest of energy strategy in Europe;
- The second part analyzes the definition of biomass in the Italian legislation. In particular, the definition of biomass for energy production, as biofuels, as bioliquids and the connection between biomass, by-products and waste normative.

## **4. Materials and methods**

The definition of biomass has a different meaning depending on the scope of application or the relevant normative. Contextualizing the legal definition of waste, by-product and End-of-Waste Criteria allows us to better understand the definition of biomass in the Italian legal system.

In the Italian legislation, the definition of waste is regulated by the Article 183, Law 152 (2006) (Consolidated Law on Environmental – TUA), which is the same one of the Directive on waste, Article 3 (EC Directive, 2008):

“waste means any substance or object which the holder discards or intends or is required or discard”.

This article should be read together with Article 7, point 1 of the same (EC Directive, 2008):

“The inclusion of a substance or object in the list shall not mean that it is waste in all circumstances. A substance or object shall be considered to be waste only where the definition in point (1) of Article 3 is met”.

The Article 185 of Law 152 (2006), which has been entirely replaced by the Article 13 of Law 205 (2010), introduced exclusions from the scope of application of Part IV of Consolidated Law on Environmental (waste legislation).

From 2000 onwards the legislative evolution is influenced by the Community jurisprudence. In fact, the European Courte of Justice with the “Palin/Granit sentence” offered a first definition of by-product (Ferrara and Sandulli, 2014).

The Directive on Waste (EC Directive, 2008) introduced the definition of by-product which has been adopted by the Italian legislation with Law 205 (2010), which introduced the new article 184-bis of Law 152 (2006). In accordance with the Article 5 Directive on Waste (EC Directive, 2008) by-product is defined as:

“A substance or object, resulting from a production process, the primary aim of which is not the production of that item, may be regarded as not being waste referred to in point (1) of Article 3 but as being a by-product only if the following conditions are met:

- (a) further use of the substance or object is certain;
- (b) the substance or object can be used directly without any further processing other than normal industrial practice;
- (c) the substance or object is produced as an integral part of a production process; and
- (d) further use is lawful, i.e. the substance or object fulfils all relevant product, environmental and health protection requirements for the specific use and will not lead to overall adverse environmental or human health impacts.

On the basis of the conditions laid down in paragraph 1, measures may be adopted to determine the criteria to be met for specific substances or objects to be regarded as a by-product and not as waste referred to in point (1) of Article 3. Those measures, designed to amend non-essential elements of this Directive by supplementing it, shall be adopted in accordance with the regulatory procedure with scrutiny referred to in Article 39”.

Under these conditions by-product never becomes waste. The definitions of waste and by-product have been the subject of doctrinal and case law discussions because of the difficulty to define concepts like “normal industrial practice” in legal terms.

The Article 6 of Directive on waste (EC Directive, 2008) regulates the End-of-Waste criteria and states as follow:

“Certain specified waste shall cease to be waste within the meaning of point (1) of Article 3 when it has undergone a recovery, including recycling, operation and complies with specific criteria to be developed in accordance with the following conditions:

- (a) the substance or object is commonly used for specific purposes;
- (b) a market or demand exists for such a substance or object;
- (c) the substance or object fulfils the technical requirements for the specific purposes and meets the existing legislation and standards applicable to products; and
- (d) the use of the substance or object will not lead to overall adverse environmental or human health impacts (omissis)”.

The Article 184 of Law 152 (2006) regulates the End-of-Waste criteria in the Italian legal system. The difference between by-product and End-of-Waste is that the former, under certain conditions, never becomes waste and the latter regulates the conditions under which waste ceases to be that.

## **5. Results and discussion**

The first definition of biomass in the Italian legal system is found in the Article 2 of Law 28 (2011) for the implementation of EC Directive (2009) as:

“The biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, the cuttings and prunings from public and private green as well as the biodegradable fraction of industrial and municipal waste”.

The same Article offers other three important definitions:

1. “bioliquids: liquid fuel for energy purposes other than for transport, including electricity and heating and cooling, produced from biomass”;
2. “biofuel: liquid or gaseous fuel for transport produced from biomass”;
3. “biomethane: gas produced from renewable sources with features and operating conditions corresponding to those of natural gas and to be suitable for injection into natural gas grid”.

In the case of biomass as bio-combustible in the authorization procedures of emissions into the atmosphere, in accordance with the Article 293 of Law 152 (2006) in Part V and in Annex X of Law 152 (2006), biomass is: biodiesel, firewood, charcoal, biomass fuels, syngas. The Annex X, Part II, section 1, 4 and 6 indicates characteristics and conditions for the use of biomass as combustible.

The article 7, point 1, of Directive on Waste (EC Directive, 2008) states that:

“The inclusion of a substance or object in the list shall not mean that it is waste in all circumstances. A substance or object shall be considered to be waste only where the definition in point (1) of Article 3 is met”.

To understand when biomass is included or not in the waste legislation in the Italian legal system we refer to the Article 185 of Law 152 (2006) (Part IV) which introduces exclusions in the scope of application. Especially relevant is the exclusion of faecal materials, agricultural and forestry materials used in agriculture or in the production of energy, by-products of animal origin.

Considering the difference between biomass as fuel or as waste product for combustion produces important legal consequences because the former falls under the legislation for the authorization of atmosphere emissions (unless exempt by law), while the latter falls under the legislation for the authorization for waste treatment plants. Furthermore, the Article 12 of Law 387 (2003) regulates the legislation for the authorization for renewable energy plants. If biomass is listed in Annex X, the authorization of Article 12 shall absorb the legislation for the authorization of atmosphere emissions; if biomass is considered waste, the waste treatment authorization shall refer to the legislation on limit values for incinerators.

When biomass is considered by-product it follows all the conditions established in Article 184 bis of Law 152 (2006). If biomass isn't included in Annex X or if it doesn't follow the conditions of the Article 184 bis, it falls under the waste legislation (Part IV).

## **6. Concluding remarks**

In conclusion, the definition of biomass as fuel, waste or by-product is not clear. It is necessary to always to inquire about the intentions of the producer of biomass, the productive process that originated it and if biomass is included in Annex X.

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## **THE “END OF WASTE” CRITERIA FOR SCRAP METAL \***

**Francesca Sarli**

*Environmental Consultant at MATTM, sarli.francesca@gmail.com*

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### **Abstract**

This paper describes the main contents of the Regulation No. 333/2011 “establishing criteria determining when certain types of scrap metal cease to be waste under Directive 2008/98/EC of the European Parliament and of the Council” referring to: Types of waste used as recycled materials; treatment techniques; qualitative characteristics of scrap resulting from the recovery operation; statement of compliance and quality management system.

*Keywords:* end-of-waste, recycling, reuse, scrap, waste management

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### **1. Introduction**

The EC Directive 2008/98/EC of 19 November 2008 “*on waste and repealing certain Directives*” (EC Directive, 2008), transposed into Italian law by Law 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”. The main requirements that the waste must have in order to cease to be such are:

- a) is commonly used for specific purposes;
- b) a market or demand exists;
- c) meets the technical requirements for the specific purposes and comply with the existing legislation and standards applicable to products;
- d) the use will not lead to negative impacts on environment or human health.

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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.

The Regulation 333 (2011), which has been the first to be issued at the European level, lays down the end-of-waste criteria for certain types of scrap metal, such as aluminum, steel and iron.

## **2. End-of-Waste Criteria**

The Regulation sets out separately for scraps of iron and steel and of aluminum, both the conditions that must be met to obtain the cessation of waste (Art. 3 and 4) and the criteria for management and control, during the recovery operation, to ensure the satisfaction of the technical requirements of the metallurgical industry (Annex I and II). More specifically the Annexes are arranged in two columns: the first contains the criteria to be applied, while the second defines the minimum requirements for the internal monitoring that the producer must follow for each criterion. Point 2 of each annex lists wastes which may be subject to recovery finalized at EoW and those who are excluded. It is pointed out both for scrap iron and steel to aluminum scrap that Hazardous waste shall not be used as an input except where proof is provided that the processes and techniques to remove all hazardous properties have been applied. The point 3 describes the techniques and processes for treatment of the scrap in order to obtain materials EoW, including the separation from non-metallic elements and non-ferrous / aluminum, mechanical treatments for direct reuse, specific treatments for certain waste containing hazardous components.

The most important point of both Annexes is the point 1, which defines the requirements and characteristics of scrap resulting from the recovery. In particular, for ferrous materials shall be indicated the correspondence to specific standards for use in foundries and the percentage of foreign material defining the type, the conditions for the presence of iron oxides, oils, of radioactivity, hazardous properties and pressurized containers.

Unlike the ferrous scrap, for those of aluminum the Regulation requires that the percentage of foreign materials shall not exceed 5%, or that the metal yield must be above 90%, listing which are the materials regarded as extraneous to the assessment. In addition, among the minimum requirements for the internal monitoring, the Regulation introduces a series of procedures to be followed for both the samples of scrap submitted periodically for analysis, and the determination of the amount of foreign material, and the extent of the metal yield.

## **3. Additional requirements for the reuse of scrap metal**

The Regulation, in accordance with the EC Directive (2008) on the end of waste, with the Articles 5 and 6 also establishes a set of obligations and requirements, which are:

- The declaration of conformity by the manufacturer, attesting that, for each sub-lot of scrap metal, verification of compliance with the quality requirements set out in Articles 3 and 4 and all the other requirements laid down by the Regulation. This certification, which also contains data identifying the user, weight of the lot, certificate of radioactivity and statement on the existence of a System of Quality Management, must be kept for one year and presented at the request of the competent authority;
- A Quality Management System that demonstrates conformity with the criteria laid down by the Regulation. This system must be subjected to scrutiny every three years by an organization recognized under EC Regulation 765 (2008) (for accreditation and supervision for the marketing of products) or under the EC Regulation 1221 (2009) (EMAS).

These additional requirements for the manufacturer imply an increasing attention to the business conduct, which must be authorized in accordance with the procedures of waste recovery, by properly educating the staff as well as suitably applying the quality management system.

**Table 1.** Criteria for iron and steel scrap and for aluminium scrap

<i>ANNEX I</i>	<i>ANNEX II</i>
<i>Criteria for iron and steel scrap</i>	<i>Criteria for aluminium scrap</i>
<i>1. Quality of scrap resulting from the recovery operation</i>	<i>1. Scrap quality</i>
1.1. The scrap shall be graded according to a customer specification, an industry specification or a standard for direct use in the production of metal substances or objects by steel works or foundries.	1.1. The scrap shall be graded in accordance with a customer specification, an industry specification or a standard for direct use in the production of metal substance or objects by refining or remelting.
1.2. The total amount of foreign materials (steriles) shall be ≤ 2 % by weight. Foreign materials are:	1.2. The total amount of foreign materials shall be ≤ 5 % by weight or the metal yield shall be ≥ 90 %. Foreign materials are:
(1) non-ferrous metals (excluding alloying elements in any ferrous metal substrate) and non-metallic materials such as earth, dust, insulation and glass;	(1) metals other than aluminium and aluminium alloys;
(2) combustible non-metallic materials such as rubber, plastic, fabric, wood and other chemical or organic substances;	(2) non-metallic materials such as earth, dust, insulation materials and glass;
(3) larger pieces (brick-size) which are non-conductors of electricity such as tyres, pipes filled with cement, wood or concrete;	(3) combustible non-metallic materials such as rubber, plastic, fabric, wood and other chemical or organic substances;
(4) residues arising from steel melting, heating, surface conditioning (including scarfing), grinding, sawing, welding and torch cutting operations, such as slag, mill scale, baghouse dust, grinder dust, sludge.	(4) larger pieces (brick-size) which are non-conductors of electricity such as tyres, pipes filled with cement, wood or concrete; or
	(5) residues arising from the melting of aluminium and aluminium alloys, heating, surface conditioning (including scarfing), grinding, sawing, welding and torch cutting operations such as slag, dross, skimmings, baghouse dust, grinder dust, sludge.
1.3. The scrap shall not contain excessive ferrous oxide in any form, except for typical amounts arising from outside storage of prepared scrap under normal atmospheric conditions.	1.3. The scrap shall not contain polyvinyl chloride (PVC) in form of coatings, paints, plastics.
1.4. Scrap shall be free of visible oil, oily emulsions, lubricants or grease except negligible amounts that will not lead to any dripping.	1.4. The Scrap shall be free of visible oil, oily emulsions, lubricants or grease except negligible amounts that will not lead to any dripping.

1.5. Radioactivity: there is no need for response action according to national or international rules on monitoring and response procedures for radioactive scrap metal.	1.5. Radioactivity: there is no need for response action according to national or international rules on monitoring and response procedures for radioactive scrap metal.
This requirement is without prejudice to the basic standards on the health protection of workers and members of the public adopted in acts falling under Chapter III of the Euratom Treaty, in particular Directive 96/29/Euratom.	This requirement is without prejudice to the basic standards on the health protection of workers and members of the public adopted in acts falling under Chapter III of the Euratom Treaty, in particular Council Directive 96/29/Euratom.
1.6. The scrap shall not display any of the hazardous properties listed in Annex III to Directive 2008/98/EC. The scrap shall comply with the concentration limits laid down in Decision 2000/532/EC and shall not exceed the concentration limits laid down in Annex IV to Regulation (EC) No 850/2004.	1.6. The scrap shall not display any of the hazardous properties listed in Annex III to Directive 2008/98/EC. The scrap shall comply with the concentration limits laid down in Commission Decision 2000/532/EC and shall not exceed the concentration limits laid down in Annex IV to Regulation (EC) No 850/2004.
Properties of individual elements included in iron and steel alloys are not relevant for this requirement.	Properties of individual elements included in aluminum alloys are not relevant for this requirement.
1.7. The scrap shall not contain any pressurized, closed or insufficiently open containers that could cause an explosion in a metalwork furnace.	1.7. The scrap shall not contain any pressurized, closed or insufficiently open containers that could cause an explosion in a metalwork furnace.

#### 4. Conclusions

The Regulation 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".

Companies can make the processes scrapping metals, such as steel, iron, aluminum and aluminum alloys, to turn them into secondary raw material and sell them through a system of quality management, which must be duly attested by the declaration of conformity. The company thus implements a quality system that ensures the monitoring and control of processes and products obtained, while protecting the environment.

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*The “end of waste” criteria for scrap metal*

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**OROBLU2 - Water resources management in the Mediterranean:  
problems and experiences**

## **WATER SAFETY OF IMPROVED SOURCE: THE CASE STUDY OF VILANCULOS (MOZAMBIQUE)\***

**Andrea Pollmann Gomez, Sabrina Sorlini\*\* , Carlo Collivignarelli**

*CeTAmb LAB – Research laboratory on appropriate technologies for environmental management in  
resource-limited Countries, University of Brescia, Department of Civil Engineering, Architecture, Land,  
Environment and of Mathematics, Via Branze 43, 25123 Brescia, Italy*

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### **Abstract**

Access to safe water is a major global challenge. WHO aims at ensuring it supporting actions for the improvement of water sources, but not always water from improved sources is really safe. Moreover water facilities are often located far from households, requiring collection and transport from the source to the point of use. All these steps are potentially source of recontamination. The study investigated water quality in Vilanculos, Mozambique, along the entire water supply chain to verify if drinking water from improved sources is safe. Then and identification of which are the causes of its deterioration took place.

*Keywords:* drinking water quality, Mozambique, water supply chain

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### **1. Introduction**

One of the major health problems globally are water-related diseases and the Joint Monitoring Program (JMP) reports that 783 million people in the world (11% of the total population) have no access to safe water. Target 7c of the Millennium Development Goals (MDGs) aims to halve the proportion of people counted in 1990 without sustainable access to safe drinking water and basic sanitation. The JMP has classified water sources into

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\*Selection and peer-review under responsibility of the ECOMONDO

\*\*Corresponding author: [sabrina.sorlini@unibs.it](mailto:sabrina.sorlini@unibs.it)

‘improved’ and ‘unimproved’ categories as an interim measure of drinking water safety (WHO&UNICEF, 2010), and this is used as a simple indicator of access to safe drinking water, assuming that water collected from ‘improved sources’ is more likely to be ‘safe drinking water’ than water collected from ‘unimproved sources’ (Sorlini et al., 2012). Consequently, one of the major strategies for tackling this problem is the installation of protected sources such as boreholes, standpipes or wells to provide water of better quality. But ‘safe drinking water’ is defined by WHO as drinking water which ‘does not represent any significant risk to health over a lifetime of consumption, including different sensitivities that may occur between life stages’ (WHO, 2011) and not always improved sources provide safe water (Godfrey et al., 2011; Wright et al., 2004).

Moreover often water facilities are located far from households, requiring collection and transport from the source to the point of use. It has frequently been observed that the microbiological quality of water in buckets in the home is lower than that at the source, suggesting that contamination is increasing during collection, transport, storage and drawing of water (Wright et al., 2004) and this re-contamination decreases the benefits of water source improvements.

## 2. Objectives

The objective of the present study is to analyse the drinking water quality in Vilanculos (Inhambane Region, Mozambique) both in the improved and in unimproved water sources. Water was analysed at the source and at the point-of-use to investigate which factors mostly affect the recontamination along the water supply chain before the final consumption.

## 3. Materials and methods

### 3.1. Study area

The study area is the municipality of Vilanculos located in the region of Inhambane (south Mozambique). Vilanculos is a small town of 50,000 inhabitants and characterized by some basic services such as public transportation system that run in the main roads and the aqueduct that supplies almost 50% of the municipal population through public fountains and private taps (placed in the lot, outside the house).

The remaining population uses other types of sources as open wells (public or private, protected from parapets of cement, tin or tires, with depths ranging from 3 m up to 30 m) and protected wells equipped with electric pump or hand pump. Finally regarding wastewater management, Vilanculos is widely provided (80%) by traditional latrines located in each home.

### 3.2. Water quality indicators

WHO guidelines for safe water state that no fecal indicators should be present in a 100 mL sample, and Mozambique, through the Ley de Agua and later regulations (2004), follows consistently these guidelines, imposing the absence of many (but not all) micro-organism indicators of fecal contamination in the water for drinking purposes. The present study investigated the microbiological contamination of drinking water sources based on the presence of *Escherichia coli* and *Faecal streptococci*.

### 3.3. Water sampling and microbiological analyses

The monitoring campaign took place between August and September 2013. In the field work some households of Vilanculos have been visited to collect drinking water samples, one at the source and one at the point of use. Water samples were then analyzed to determine microbiological contamination. The goal was the creation of a map of water sources and related quality and the identification of the factors that most influence the quality along the supply chain from the source to the point of consumption.

### 3.4. Questionnaires

The same families were interviewed by means of a questionnaire to gather information about the water supply system, the financial capacity to have an improved source access, the sanitation facility used (if any) and their hygiene habits. The aim was to characterize the water supply chain to identify the factors that impact on the recontamination of the water after the collection at the source, through transport and storage.

## 4. Results and discussion

In this study 116 water points were analyzed: 32% were open wells, 21% protected wells (equipped with hand pump or electric pump) , 7% public fountains and 40% of private taps. Table 1 shows the number of water points analyzed and the related water quality.

**Table 1.** Water quality by type of source (average and, in brackets, the minimum and maximum)

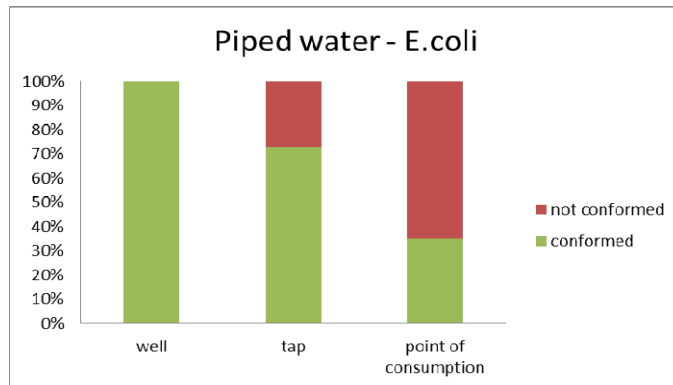
<i>WATER SOURCE</i>	<i>N</i>	<i>E. COLI</i> (UFC/100mL)		<i>ENTEROCOCCI</i> (UFC/100mL)	
Public open well	4	127	(5-600)	1513	(15-5500)
Private open well	34	372	(10-5000)	1768	(150-9300)
Protected well equipped with hand pump	13	12	(0-230)	39	(0-300)
Protected well equipped with electrical pump	11	5	(0-45)	261	(0-1000)
Public fountain	8	0	(0-2)	34	(0-100)
Private tap	46	2	(0-21)	59	(0-400)

The major difference among the contamination of unimproved (open wells) and improved water sources (piped water and protected wells) brought to analyze separately these two different categories (unimproved and improved sources). Water quality from unimproved sources did not significantly vary along the supply chain: deterioration occurs in about 50% of cases, in 30% of cases did not change and in 20% of cases an improvement was even observed. This behavior was also highlighted in the case studies analyzed by Wright et al. (2004). In this specific research, the cause was probably to be due to the sedimentation phenomena developed inside the containers for domestic storage, which contributed to the microbes decrease.

In the case of improved sources a significant deterioration in water quality appeared along the supply chain. It was possible to observe the deterioration of water quality from source to point of consumption, observing the percentage of samples conformed to the regulatory limits (0 CFU/100mL). As an example, Fig. 1 reports the percentage of compliance from the source to the point of consumption referring to *Escherichia coli*, along the water supply chain of piped water. Based on the results obtained, it has been chosen to



analyze only for improved sources (78 cases), the correlation between the levels of re-contamination along the water chain and hygiene and household water management habits.



**Fig. 1.** Percentage of conformity of piped water with the national water law along the water chain

It was therefore analyzed the magnitude of re-contamination in relation to several factors, characterizing the transport and storage of water, considered relevant to verify the effect that each of them assumes in the re-contamination process. For the transport step the impact of the type of container used and the ownership of the source was evaluated. For the domestic water storage, the incidence of hygiene practices concerning the location and protection of the container used was analyzed.

A preliminary analysis revealed that the ownership of the source is the factor that most affects the re-contamination process of drinking water. For this reason, all other factors were investigated dividing the samples in two categories: families with the ownership of the source (45 cases) and families without ownership (33 cases).

It was found that in the two categories and both in transport and storage steps, the practice that more influences the water recontamination and is the habit of keeping the containers open (with respect to the type of container and its location). Even this result confirms the ones found by Wright et al. (2004).

## 5. Concluding remarks

The study focused on the analysis of drinking water quality from the source to the consumption point in Vilanculos.

Water resulted contaminated at all water sources, even if more in unimproved sources. The causes could be attributed to the lack of sources protection and the high contamination level of the soil due to the lack of good sanitation practices.

The major factors influencing negatively the drinking water quality along the supply chain were the ownership of the water point and the habit to cover the containers used for transport and storage. This demonstrates the importance of supporting the structural improvements of water points with hygiene promotion activities.

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technical support. Andrea Pollmann Gomez did data collection and analysis and was responsible for the paper drafting; Sabrina Sorlini planned and supervised the research activities and the paper drafting.

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## **WATER SAFETY PLAN: AN APPROACH TO REDUCE DRINKING WATER CONTAMINATION IN A RURAL AREA OF SENEGAL\***

**Luca Rondi<sup>1</sup>, Sabrina Sorlini<sup>1\*\*</sup>, Maria Cristina Collivignarelli<sup>2</sup>**

<sup>1</sup>*CeTAmb LAB – Research laboratory on appropriate technologies for environmental management in resource-limited Countries, University of Brescia, Department of Civil Engineering, Architecture, Land, Environment and of Mathematics, Via Branze 43, 25123 Brescia, Italy*

<sup>2</sup>*University of Pavia, Department of Civil Engineering and Architecture,  
Via Ferrata 3, 27100 Pavia, Italy*

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### **Abstract**

In 2012, the Italian NGO G. Tovini Foundation, together with the Universities of Brescia (Italy) and Dakar (Senegal), started a cooperation project in the Rural Community of Patar (Diourbel Region, Senegal) aimed at improving living conditions of the people by implementing the Water Safety Plan (WSP) approach. After the identification of the main criticalities and source of pollution, the Water Safety Plan approach has been developed in order to minimize/prevent water contamination. The WSP team was set up involving managers of the drinking water supplies, local Authorities and representatives of the population, who elaborated an appropriate WSP.

*Keywords:* drinking water quality, Senegal, water safety plan

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### **1. Introduction**

The most important aspect in improving people's health is to provide users with safe and clean water. It is estimated that 1.1 billion people worldwide still do not have access to safe potable water, and a large percentage of these people comes from developing countries, especially in the rural areas and low-income communities (Venter, 2000; WHO, 1997;

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\*Selection and peer-review under responsibility of the ECOMONDO

\*\*Corresponding author: [sabrina.sorlini@unibs.it](mailto:sabrina.sorlini@unibs.it)

WHO, 2006; WHO, 2007). Consequently an estimated 5 million people lose their lives to water-related diseases each year (Baumgartner et al., 2007).

Lack of hygiene and sanitation is one of the main factors of diarrhoea's transmission routes. The World Health Organisation (WHO) estimated that improving water, sanitation and hygiene practices could prevent approximately the 9.1% of the global burden of disease and avoid the 6.3% of all deaths (Prüss-Üstün et al., 2008). For this reason, together with United Children's Fund (UNICEF), WHO encouraged the improvement of drinking water sources to gain, in short-terms and with little investments, the health gaps associated with unsafe drinking water consumes (Sobsey, 2002).

Drinking water is not only exposed to microbial contamination, but can even contain chemical (geogenic) compounds such as arsenic and fluoride. However, chemical contamination of drinking water provides risks to a smaller global population, even if is a serious human health hazard for those affected (Thompson et al., 2007).

In order to gain health gaps associated with unsafe drinking water consumption, the Water Safety Plan (WSP) approach seems to be the best solution. Indeed, the WSP methodology for ensuring the safety of drinking water from the point of catchment to the point of consumption is an approach based on the systematic preventive management and risk assessment (Bartram et al., 2009). The objectives of a WSP are threefold: 1) to prevent or to minimise the contamination of source waters, 2) to reduce or to remove the contamination through treatment processes and 3) to prevent the contamination during storage, distribution and handling of drinking-water (Davison et al., 2005).

## **2. Objectives**

The objective of the present study was to elaborate and implement the WSP approach in the Rural Community of Patar (Diourbel region, Senegal), where drinking water was characterised by both microbial and chemical contamination directly at the source level. In order to guarantee the sustainability of the WSP, this has been elaborated by a local team, which managers of the drinking water supplies, local Authorities and representatives of the population were involved in.

## **3. Outline of the work**

This work is divided in two main parts:

- The first part covers the identification of the entire drinking water supply chain and the determination of all the possible hazards that can cause water contamination.
- The second part covers the elaboration of the WSP by the local team.

## **4. Materials and methods**

The research was carried out in the Rural Community of Patar (RCP), and in particular in Sambé and Dabel Bara villages, considered representative of the Community.

Jointly with the identification of the drinking water sources, a sanitary survey of each water point was conducted according to the standardised forms suggested by WHO (WHO, 1997) as well as physical-chemical and microbiological analyses. Some of 45 households were then interviewed for gathering information related to drinking water (which source and which container for transport and storage were used, frequency of cleaning of these containers, type of treatment carried out, etc.), hygiene and sanitation (type of defecation, frequency of use and cleaning of latrines, hand-washing etc.) and health conditions (type of diseases contracted in previous months, frequency and level of access to the Health Centres, etc.).

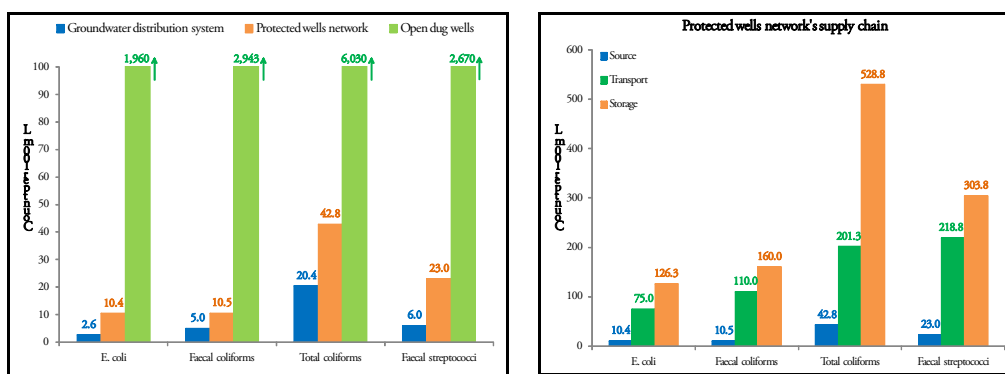
For each household, drinking water samples were collected both in the transport and storage containers and subjected to microbiological analyses (focusing on *E. coli* and *Faecal streptococci*).

A specific WSP was developed for the different drinking water sources (3 globally) used by the local people. Moreover, a WSP for the transport and storage steps was elaborated. The development of the whole WSP was carried out by a local team composed by 12 people: 2 representatives of ASUFOR (User Association of Rural Boreholes), 2 representatives of GIE (Association of local farmers and traders responsible for the management of protected wells network), 2 representatives of the Diourbel Hygiene Authority, the Responsible for the Patar Health Centre (RPHC) and 5 students of the University of Dakar, who lived in the RCP, as representatives of the Community. The WSP team, on one hand, elaborated the WSP and, on the other, was made aware on how manage and handle drinking water along the entire supply chain.

## 5. Results and discussion

The survey carried out in the RCP permitted to identify three different water sources used by the population for drinking purposes: a groundwater distribution system, a protected wells network and several open dug wells. The sanitary surveys applied to these sources highlighted a high level of contamination risk for the open dug wells (10 out of 12), a medium-high level for the protected wells network (7 out of 12) and a low risk for the groundwater distribution system (2 out of 10). These results appeared to be in accordance with the microbiological analyses conducted at different water points of the different sources (Fig. 1, graph on the left). From the chemical point of view, high concentrations of fluoride and chloride were determined in the groundwater distribution system, whilst high concentration of lead was found in the protected wells network and the open dug wells.

Since the protected wells network was the water source more used by the population (according to the results obtained by the household interviews), the microbiological analyses were focused on this specific supply chain. Results are shown in Fig. 1, graph on the right.



**Fig. 1.** Microbiological contamination of the different water sources (on the left) and along the protected wells network's supply chain (on the right)

A slightly simplified WSP approach (compared to the scheme proposed by WHO) was then elaborated. The WSP team was asked to list all the possible hazards that could pollute water, to define the related risks and control measures, to plan a monitoring programme for evaluating the efficacy and the respect of control measures adopted, to identify operational limits and corrective actions in order to guarantee the consumption of safe water and, finally, to plan a verification programme able to evaluate the efficacy of all

the WSP. Table 1 proposes some of the hazards, causes and related risk scores that the WSP team listed for the groundwater distribution system.

Finally, awareness campaigns on water, sanitation and hygiene were organised involving the population of Sambé and Dabel Bara, in particular 100 women and 100 students. Moreover, 5 Hygienists (each one coming from a different village of the RCP) were trained. The aim of these supporting programmes was to make aware local people on the correct behaviour to have during water handling and management, in order to minimise all the possible contaminations of drinking water and, hence, guaranteeing the sustainability of the WSP implemented.

**Table 1.** Some of the hazards, causes and risk scores determined for the groundwater distribution system

<i>Hazard</i>	<i>Cause</i>	<i>Risk</i>		
		<i>Likelihood</i>	<i>Severity</i>	<i>Score</i>
Microbial	Animals entry through open inspection hatches of tanks	1	5	5
	Improper hygiene practices during feed tanks' cleansing	2	4	8
	Rupture of a water supply distribution pipe	3	5	15
	Lack of pressure in the supply system	4	3	12
	Dirty taps	5	5	25
	Improper fence around the installation	1	2	2
Chemical	Corrosion of iron pipes and valves	3	5	15
	Chlorine overdose	1	3	3
Geological	High concentrations of fluorides, chlorides and sodium	5	5	25

## 6. Concluding remarks

This study aimed at elaborating an appropriate Water Safety Plan strategy in a rural area of Senegal. Local conditions did not permit to develop a WSP approach in strict conformity with the one suggested by WHO, thus a slightly revised framework was carried out. To guarantee the consumption of safe drinking water, disinfection with chlorine, the use of improved water containers (cans with valve) and the installation of household water treatment technologies (bone char-based filtration systems) were promoted amongst the population. Members of the local community were involved in the WSP elaboration to guarantee its efficacy and sustainability.

## Acknowledgements

Luca Rondi conducted this research as PhD student on “Appropriate Methods and Technologies for International Development Cooperation”, supported by Alberto Archetti Fund. Authors wish to thank NGO Fondazione G. Tovini for technical and economic support, Université Cheick Anta Diop de Dakar and Diourbel Hygiene Authority for the collaboration during the field missions, FCB Foundation (Brescia, Italy) for the economic support, and Eng. D. Palazzini and Eng. C.A.M. Clemente for the technical support. Luca Rondi did data collection and analysis and was responsible for the paper drafting; Sabrina Sorlini planned and supervised the research activities and the paper drafting; Maria Cristina Collivignarelli contributed to the research activities.

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Procedia Environmental Science, Engineering and Management **1** (2014) (1) 59-63

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**OROBLU3 - The management of water in the course of natural or incidental special events and interventions to combat and monitor the spread of contamination**

**EXTREME EVENTS MANAGEMENT: IMPORTANCE OF  
STORMWATER QUALITY MONITORING. PRESENCE OF  
EMERGING POLLUTANTS IN STORMWATER  
FROM INDUSTRIAL AREAS\***

**Sebastiano Carrer, Claudio Carrer, Cristina Nasci\*\***

*Thetis S.p.A., Castello 2737/f, 30122 Venice, Italy*

*Per conto del Ministero delle Infrastrutture e dei Trasporti Provveditorato Interregionale per le Opere Pubbliche del Veneto – Trentino Alto Adige – Friuli Venezia Giulia*

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**Abstract**

Stormwater quality is not easy to foresee owing to several reasons such as land use, meteorological conditions, soil and atmosphere conditions, presence of lamination and treatment systems. Climate change boosted growing interest in stormwater management and at the same time Directive 2013/39/CE pointed out the interest for emerging pollutants such as polibrominated diphenylethers (PBDEs). In the framework of a wide multiannual project for stormwater management and characterization Thetis S.p.A., on behalf of Ministero delle Infrastrutture e dei Trasporti – Provveditorato Interregionale alle OO.PP. del Veneto – Trentino Alto Adige – Friuli Venezia Giulia (the Italian Ministry of Infrastructures and Transport – Venice Water Authority), surveyed the presence of PBDEs in stormwater from industrial areas of Porto Marghera. This paper presents the results of such a survey and compares them with PBDEs contamination levels in industrial and WWTP discharges, dewatering plants and lagoon waters derived from other studies.

*Keywords:* emerging pollutants, PBDEs, polybrominated diphenylethers, stormwater quality

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\*Selection and peer-review under responsibility of the ECOMONDO

\*\*Corresponding author: [sebastiano.carrer@thetis.it](mailto:sebastiano.carrer@thetis.it)

## **1. Introduction, objectives and outline of the work**

The occurrence of PBDEs in biota, sediment, humans, milk, food and dust was extensively monitored during recent years whereas little information is available on their concentrations in water (Loos, 2014; Munsch et al., 2011). Main object of this paper is to report main findings about the occurrence of emerging pollutants such as PBDEs in water of different origins, underlining the importance of stormwater monitoring and management in view also of the increasing frequency of extreme events.

The first part of the paper describes methodology and results of the survey on stormwater quality in industrial areas, whereas the second part compares such results with those obtained through analogous surveys on industrial and WWTP discharges, dewatering plants and lagoon waters and outlines the conclusions of the work.

## **2. Materials and methods**

Stormwater samples were collected from roofs, roads and depot areas in the industrial area of Porto Marghera, bordering the lagoon of Venice. The sampling system was able to collect first flush (first 5 mm of precipitation) and following runoff via automatic samplers. Special tanks were located inside the sewage system and cleaned after each rain event.

Water samples were analysed for 6 PBDEs congeners (BDE-28, 47, 99, 100, 153 and 154). The samples were spiked with a series of 8 <sup>13</sup>C<sub>12</sub>-labeled PBDEs (Method EPA 1614 2007) and then extracted with methylene chloride (CH<sub>2</sub> Cl<sub>2</sub>) and cleaned up by Power Prep system.

The analyses were conducted by HRGC/HRMS using a HP 6890N plus gas chromatograph coupled to Micromass Waters Autospec Premier mass spectrometry operating in EI mode at 35 eV and with a resolution of 5000 (5% valley). The recovery always ranged between 55 % and 110 %. The capillary column used for PBDEs was a DB5-MS (15 m, 0.25 mm, 0.1 µm, J&W). Reproducibility was 10-17% for lower value. The laboratory blanks, repeated twice, were 8-10% lower than the minimum concentration found.

## **3. Results and discussion**

A number of 68 water samples (37 from two roofs, 30 from two different road and depot areas, one of meteoric water) were analyzed. 36 samples refers to first flush (5 mm of precipitation) whereas 31 samples refers to waters flowing after the first part (5 mm) of the rain event (MIT, 2012). Percentage of measures above detection limits (50 pg/L) ranged from 9% for BDE-28 to 85% for BDE-47 and 88% for BDE-99. No PBDEs were found in the meteoric water sample collected.

Concentrations of total PBDEs were generally higher in samples collected from roads and depot areas than in samples collected from roofs and gutters (Fig .1). Concentrations were one order of magnitude higher during the first flush than in the rest of the event for roofs, whereas for the other runoff typology (roads and depot areas) they were higher by a factor of 5.1 and 1.5, the lowest ratio between first and "second" flush being related to the site characterized by the largest drainage area.

Summary statistics for congeners and their sum are reported in Table 1. The most abundant congener was BDE-99, with a median value of 161 pg/L in stormwater from roofs and 657 pg/L from roads and depot areas (analogous values for the median of sum of congeners are 297 pg/L and 1374 pg/L respectively).

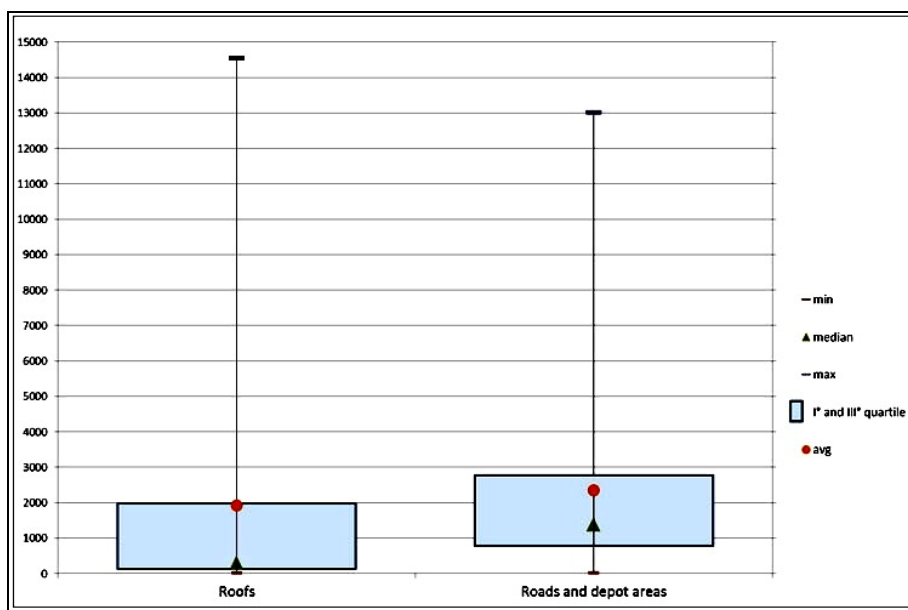
A total of 15 rain events were monitored. Very weak correlations were detected between total PBDEs concentrations and intensity of the rain event as well as number of dry days before the rain event monitored, highlighting the presence of manifold factors influencing stormwater quality.

In the outflow of the most important WWTP of the Venetian area (350.000 equivalents) only BDE-47 (62% values above Detection Limits), BDE-99 (31%) and BDE 100 (31%) may be found frequently above DL. The outflow of the WWTP shows concentrations ranging from < 50 pg/L up to a maximum of 429 pg/L for BDE-47, 338 pg/L for BDE-99 and 251 pg/L for BDE-100. The average sum of such congeners equals to 251 pg/L with a median value of 137 pg/L. As regard other industrial point sources in the area of Porto Marghera, they very rarely show relevant concentration of PBDEs.

In the framework of a specific project funded and executed by Ministero delle Infrastrutture e dei Trasporti – Provveditorato Interregionale alle OO.PP. del Veneto – Trentino Alto Adige – Friuli Venezia Giulia and the Veneto Region (2013), 22 dewatering plants discharging into the lagoon of Venice were surveyed. Only the two plants serving urban areas showed relevant PBDEs’ concentrations.

The most “urban” dewatering plant shows concentrations ranging from < 50 pg/L to 800 pg/L for BDE-47, 1027 pg/L for BDE-99 and 177pg/L for BDE-100. BDE-153 and BDE-154 were also detected with maximum concentrations of 127 pg/L and 76 pg/L respectively; BDE-28 was never detected above DLs. The average sum of such congeners equals to 1341 pg/L with a median value of 1623 pg/L, such values are very close to those of stormwater from industrial areas (roads and depot) both in term of absolute values and in term of congeners’ profile (BDE-99 is the most abundant) with the exception of the absence of peaks (up to 15000 pg/L) recorded in industrial areas (Fig. 2). Congeners profile is similar to the one recorded in a recent study on a retention basin stormwater runoff from an industrial catchment in France (Sébastien et al., 2014).

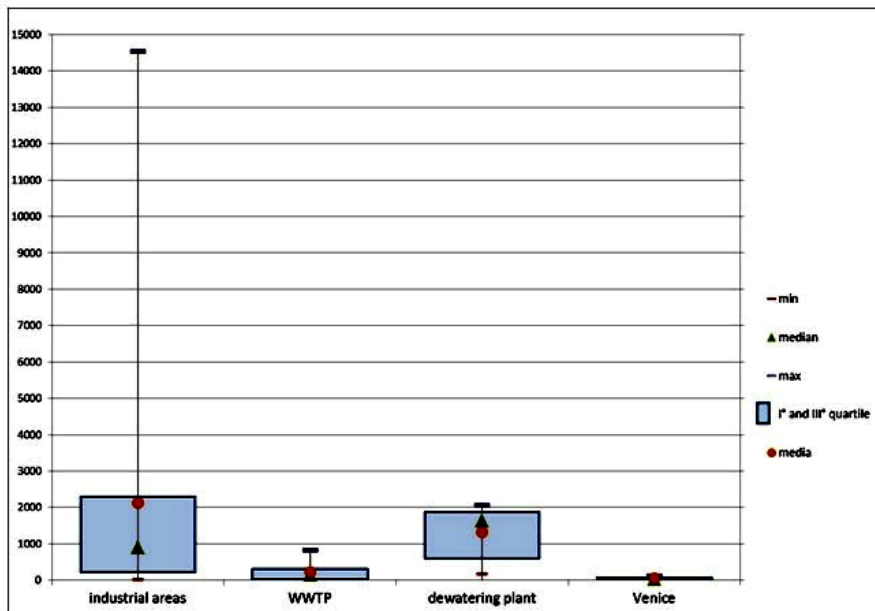
Monitoring activities executed according to WFD 2000/60/EC in 20 sites of the lagoon of Venice, during the period 2011-2013 showed only 10 concentrations out of 400 samples (3%) above the DL, with a maximum of 142 pg/L, whereas a specific survey in the canals of the city of Venice (MIT, 2012a, b; MIT, 2013) revealed the presence of only congener BDE-47 (43% data above DL, average and maximum concentration equal to 51 pg/L and 125 pg/L respectively). Fig. 2 summarizes the result of comparison between PBDEs’ concentrations in water from different origins.



**Fig. 1.** Sum PBDEs in stormwater from industrial areas (pg/L )

**Table 1.** Summary statistics for PBDEs from roofs, roads and depot industrial areas

<i>Conc. (pg/L)</i>		<i>#28</i>	<i>#47</i>	<i>#99</i>	<i>#100</i>	<i>#153</i>	<i>#154</i>	$\Sigma$ <i>PBDE</i>
Roofs and gutters	25 perc	25	54	77	25	25	25	133
	min	25	25	25	25	25	25	25
	median	25	123	161	25	25	25	297
	max	116	4074	7501	4872	893	647	14544
	75 perc	25	474	776	194	80	61	1984
Roads and depot areas	25 perc	25	255	349	69	56	25	783
	min	25	25	25	25	25	25	25
	median	25	504	657	123	84	68	1374
	max	114	3965	6706	1231	768	581	13025
	75 perc	25	768	1114	244	162	152	2786



**Fig. 2.** Sum of PBDEs' concentrations (pg/L) in stormwater, WWTP effluents, dewatering plants and Venice canals.

#### 4. Concluding remarks

The present report confirms the importance of monitoring and management of stormwater runoff from urban areas also for emerging pollutants (PBDEs) that now may be detected in water. Contamination of stormwater by PBDEs is of primary concern when compared with contamination levels of other sources such as WWTP, industrial discharges and dewatering plants serving rural areas.

#### Acknowledgements

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Procedia Environmental Science, Engineering and Management 1 (2014) (1) 65-69

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## **RISK MANAGEMENT AND EMERGENCY PROCEDURES FOR WATER INFRASTRUCTURES UNDER EXTREME EVENTS: SOME EXPERIENCES\***

**Alessandro Pagano<sup>1\*\*</sup>, Raffaele Giordano<sup>1</sup>, Ivan Portoghese<sup>1</sup>,  
Michele Vurro<sup>1</sup>, Francesco Campopiano<sup>2</sup>, Andrea Duro<sup>2</sup>,  
Davide De Battisti<sup>3</sup>, Stefano Pacitti<sup>4</sup>, Girolamo Vitucci<sup>5</sup>**

<sup>1</sup>*IRSA CNR, Viale de Blasio 5, 70132, Bari, Italy*

<sup>2</sup>*Dipartimento della Protezione Civile, via Vitorchiano 2, 00189, Roma, Italy*

<sup>3</sup>*AIMAG S.p.A., via Maestri del Lavoro 38, 41037, Mirandola (MO), Italy*

<sup>4</sup>*GSA S.p.A., via Ettore Moschino 23/B, 67100, L'Aquila, Italy*

<sup>5</sup>*AQP S.p.A., via S. Cognetti 36, 70121, Bari, Italy*

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### **Abstract**

Resilience is the ability of complex systems to anticipate, absorb, adapt to and / or rapidly recover from a disruptive event. The concept of resilience is becoming increasingly important for societies, particularly as far as critical infrastructures are concerned. Fostering resilience significantly helps in reducing the impacts of natural and anthropogenic disasters on assets and services that deserve a strategic importance on the wellness and safety of citizens, such as drinking water infrastructures.

The common objective of institutions, governments, utilities and final users is therefore to identify, select and promote the most suitable actions and responses for effectively managing risks, pursuing the development of resilient systems. Recent extreme occurrences in Italy (e.g. earthquakes), which significantly impacted communities, underlined once more the need for a conceptual and operative approach to resilience issues for infrastructural systems. Within this framework, the present research activity aims at proposing criteria for describing resilience of complex infrastructural systems through an innovative approach, mainly focusing on the issue of organizational resilience.

**Keywords:** Bayesian networks, drinking water, resilience, risk management, infrastructures, vulnerability

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\*Selection and peer-review under responsibility of the ECOMONDO

\*\*Corresponding author: [alessandro.pagano@ba.irsacnr.it](mailto:alessandro.pagano@ba.irsacnr.it)



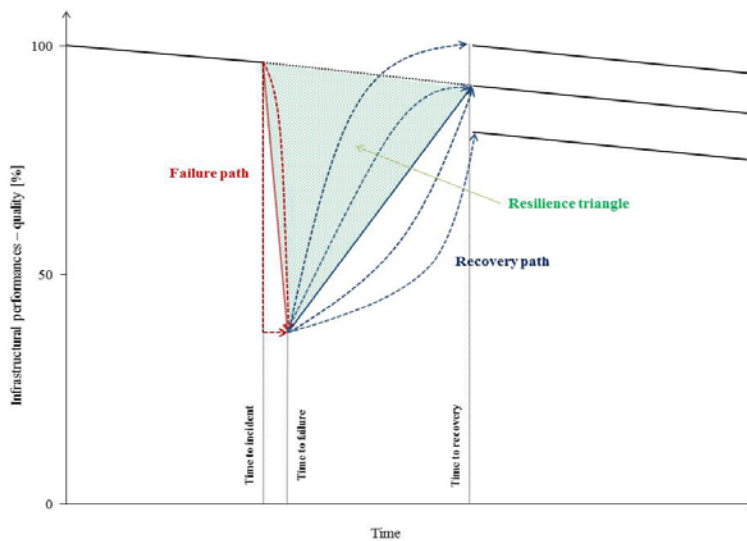
## 1. Background: resilience for complex infrastructural systems

Resilience expresses ‘the human ability to recover quickly from disruptive change, or misfortune without being overwhelmed or acting in dysfunctional or harmful ways’ (e.g. Mujumdar, 2014). Referring specifically to natural hazards, it is defined by the USA National Academy of Engineering as ‘the ability to prepare and plan for, absorb, recover from, and more successfully adapt to adverse events’). Enhancing system resilience at different levels (structural, network, community, etc.) could lead to substantial advantages, such as economic benefits and functionality optimization.

The development of resilient systems allows meeting sustainability requirements, considering the three interconnected pillars of sustainability: environment, society and economics (Ayyub, 2013).

Both vulnerability and resilience describe the capability of systems to withstand threats. Vulnerability represents those states of the system that can be adversely affected by specific threats, whereas resilience expresses the ability of the system to recover within an acceptable time and composite costs and risks.

Preparedness (the phase of risk management which is implemented before the occurrence of an hazardous event) aims at both reducing the vulnerability of a system and at improving its resilience (Haymes, 2009). A graphical representation of resilience was proposed for example by Tierney and Bruneau (2007), who discussed the “resilience triangle” (Fig. 1) representing the loss of functionality from damage and disruption, as well as the pattern of restoration and recovery over time.



**Fig. 1.** Graphical representation of resilience and of the main concepts associated

As underlined by the same authors, resilience-enhancing measures aim at reducing the size of the resilience triangle through strategies that improve infrastructural functionality and performances, and that decrease the time to recovery.

The complexity in acting upon resilience is due to the multiple dimensions associated to that framework. Resilience is indeed expressed as the combined effect of multiple dimensions, namely:

- Robustness: the ability to withstand external actions without significant degradation or loss of performance;
- Redundancy: the extent to which systems and elements are substitutable;
- Resourcefulness: the ability to diagnose and prioritize problems and to initiate solutions by identifying and mobilizing resources;
- Rapidity: the capacity to restore functionality in a timely way.

## **2. Overview of the research activity**

The activity described in the present communication is being carried out within a research agreement between the Italian Department of Civil Protection and the Water Research Institute of the National Research Council (Pagano et al., 2014). The main objective is the definition of an innovative approach to resilience for drinking water infrastructures, particularly focused on the role of water utilities and their organizational aspects. Several Italian water utilities (AQP S.p.A, GSA S.p.A., AIMAG S.p.A.), based on their experiences in the management of extreme events, supported a knowledge elicitation process based on semi-structured interviews. Actually such process allowed us to characterize the dimensions of resilience for water utilities, and to identify potential actions to foster resilience, as described in the following section.

## **3. Discussion**

Technicians of water utilities were asked to identify and describe all the aspects connected to organizational capacity, planning, training, leadership, experience, learning and information management that improved disaster-related organizational performances and problem solving (Tierney and Bruneau, 2007). Particularly, technicians of GSA S.p.A. and AIMAG S.p.A. reconstructed the events occurred during L'Aquila earthquake (2009) and Emilia Romagna earthquake (2012) respectively. The sequence of events, decisions and strategies were determined and discussed, as well as the main problems and issues raised during the emergency. Technicians of AQP S.p.A. helped instead in defining optimal tools and strategies for risk management mainly for preparedness.

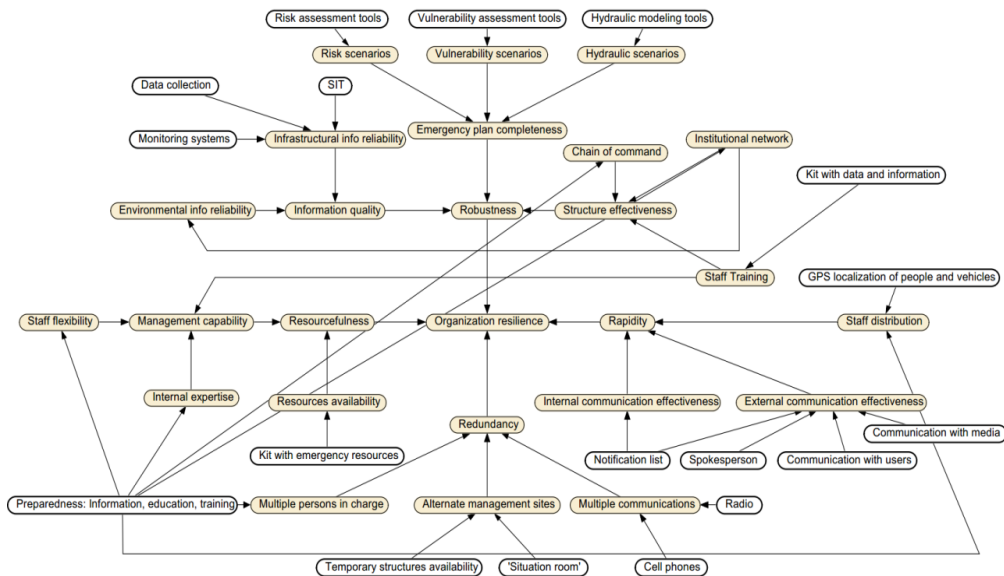
Coherently with the theoretical approach proposed in the previous sections, the main aspects of organizational resilience were classified considering their different 'dimensions'. In the following Table 1, the most influential factors, according to the judgment of the experts involved, are elaborated and structured.

The evidences deriving from the preliminary analysis represented a basis for a more structured approach, aiming at defining a methodology for characterizing the organizational resilience in a simple and effective way. A first conceptual model was built, and is proposed in Fig. 2. The organizational resilience of a water utility was modeled identifying the most influential factors and defining the causal connections between them. Variables, factors and actions capable of affecting organizational resilience are related to the dimension(s) they can exert an influence on, and the strength of these causal relationships is determined through numerical weights defined by the experts.

Variables in white boxes represent actions or strategies that can be implemented by the water utility to improve each dimension of resilience, mainly during preparedness phase, so that the role of measures fostering resilience can be also considered. Since the concept of resilience is directly connected with time (as underlined in Fig. 1), modeling resilience requires the implementation of dynamic tools such as for example the Dynamic Bayesian Networks (DBN) or the System Dynamics Modeling (SDM), which will be the focus of future activities.

**Table 1.** Factors contributing to organizational resilience of water utilities

<i>Dimension</i>	<i>Factors</i>
<b>Robustness</b>	<ul style="list-style-type: none"> <li>- Emergency plan definition and completeness</li> <li>- Models and tools for supporting risk management (e.g. scenario simulations, models, monitoring systems).</li> <li>- Availability and reliability of environmental and infrastructural information</li> <li>- Development of an institutional network for risk management</li> <li>- Effectiveness of the institutional structure</li> <li>- Staff training and expertise</li> </ul>
<b>Redundancy</b>	<ul style="list-style-type: none"> <li>- Management flexibility of the system (persons in charge and sites)</li> <li>- Capability to modify the functioning scheme</li> <li>- Capability to cope with management ‘black-outs’ (e.g. introduction of several communication channels)</li> </ul>
<b>Resourcefulness</b>	<ul style="list-style-type: none"> <li>- Integrations with resources from other utilities</li> <li>- Internal resources and know-how.</li> <li>- Availability of economic resources.</li> <li>- Flexibility of technicians.</li> </ul>
<b>Rapidity</b>	<ul style="list-style-type: none"> <li>- Efficiency of communication within the organization, and with other institutions and people</li> <li>- Number and distribution of technicians.</li> <li>- Action promptness.</li> </ul>



**Fig. 2.** Conceptual model for estimating the organizational resilience of water utilities

#### 4. Concluding remarks

This communication presents a summary of some promising preliminary results of a research activity which is being carried out in order to develop a methodology to assess organizational resilience of water utilities involved in risk management activities. The four dimensions of resilience were characterized through the support of technicians working in Italian water utilities, and the elicitation of their judgment was used to build a conceptual

model for estimating organizational resilience as well as the effect of measures and actions implemented mainly during risk preparedness phase.

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## **INNOVATIVE TEXTILE BOOM FILLED UP WITH HIGHLY EXPANDED GRAPHITE FOR DIESEL REMOVAL FROM WATER SURFACE\***

**Annalisa Pola<sup>1\*\*</sup>, Giulio Cesareo<sup>1</sup>, Emanuele Galletta<sup>2</sup>,  
Daniela De Angelis<sup>2</sup>**

<sup>1</sup>*Directa Plus SpA, via Cavour 2, 22074, Lomazzo (CO) Italy*

<sup>2</sup>*Testori SpA, Largo A. Testori 5, 20026, Novate Milanese (MI) Italy*

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### **Abstract**

We study the use of super-expanded graphite (G+) as adsorbent material for diesel fuel removal from water surface. We compare the adsorption capacity of G+ with a traditional polypropylene meltblown pulp (PPmp). G+ and PPmp were both tested as loose materials or inside a suitable textile containing system (boom), which was developed and designed for G+ in order to completely constrain it, still allowing the oil to permeate through the media and optimizing the sorption capacity. Our results shows G+'s higher sorption capacity than polypropylene or other traditional oil sorbents, both used as loose material or inside booms.

*Keywords:* expanded graphite, fabric boom, oil spills, oils adsorbents, textile boom, water treatment

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### **1. Introduction**

Sorbent materials are an efficient physical means used for the containment and removal of oils slicks that cannot be easily recovered using other mechanical techniques such as skimmers (Asadpour et al., 2013). Usually, sorbent materials are used inside specific containing systems in order to avoid their dispersion and favor their collection. The most popular type of synthetic sorbent used inside continuous booms is polypropylene (PP) thanks to its low cost and availability.

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\*Selection and peer-review under responsibility of the ECOMONDO

\*\*Corresponding author: [annalisa.pola@directa-plus.com](mailto:annalisa.pola@directa-plus.com)

However, the low adsorption capacity, the non-biodegradability, the difficulty in sorbed oil recovery – due to water retention – and the expensive landfill of this material after clean-up activities are the major disadvantages in using it (<http://www.itopf.com/knowledge-resources/documents-guides/document/tip-8-use-of-sorbent-materials-in-oil-spill-response/>).

Expanded graphite (EG) has attracted great attention for its high oil adsorption capacity, the fast sorption kinetics, the absence of toxicity, the absence of flammability, its buoyancy and the possibility of recovery of the adsorbed oil (Inagaki et al., 2001; Toyoda et al., 2003; Zheng et al., 2004). Different studies (Zheng et al., 2004) demonstrated that the adsorption capacity of EG increased with increases in the exfoliation volume. For this reason, in this study, super-expanded graphite (Graphene Plus® – G+) with an expansion volume of 2.34 g/L was used as adsorbent material for diesel fuel removal from water surface. If compared with traditional sorbent materials, the main problem in using EG for oil spills clean-up activities are its low density that prevent its application in windy areas (Qui et al., 2011).

In this context, the main objective of the present study was to develop a suitable containment mean (boom) that: 1) completely constrains G+ structures; 2) allows the selective permeation of diesel fuel through all the sorbent material; 3) optimizes the adsorption capacity of G+.

## **2. Material and methods**

G+ was synthesized in Directa Plus' laboratory through a patented plasma technology of thermal expansion of expandable graphite's flakes intercalated with sulfuric acid. G+ morphology and expansion volume are investigated by scanning electron microscope (SEM). Bulk density was measured filling up a plastic graduated cylinder with a representative sample of G+, by compacting it with a soft mixing.

After adding G+ to the brim of the cylinder, the exceeding G+ flakes were removed with a spatula. The test sample weigh ( $m$ ) was determined and the apparent volume ( $V$ ) was checked. The bulk density (g/L) was determined dividing  $m$  for  $V$ . The procedure was repeated five times in order to have a representative mean value of 2.34 g/L ( $\pm 0.15$  g/L).

PPmp used for oil sorption efficiency comparison was purchased from an European company that produced oil sorbent devices. PPmp has a declared maximum sorption capacity of 10 g/g for low viscosity oil. Two different types of confining elements, respectively a fabric and a needlefelt, have been tested to determine the impact of the media structure to the efficiency of the boom, both in terms of sorbent material confinement and diesel affinity.

a. The fabric selection has been performed through a series of comparative laboratory tests engaged between polypropylene (PP) and polyamide (PA) textiles (products coming from Testori SpA) because of their hydrophobicity, strength, availability and relative low cost. Their permeability were optimized for diesel sorption; the selected product is a monofilament fabric (PPmt) (200 g/m<sup>2</sup>; twill weave; pore size: 106  $\mu$ m; pore area: 0.09 mm<sup>2</sup>, permeability: 3000 l/dm<sup>2</sup>/min).

b. The needlefelt (PPnf) has been selected from the polypropylene light weight range of products (coming from Testori SpA); (210 g/m<sup>2</sup>; permeability of 400 l/dm<sup>2</sup>/min; pore size 30  $\mu$ m) (Figs. 1, 2).

## **3. Experimental**

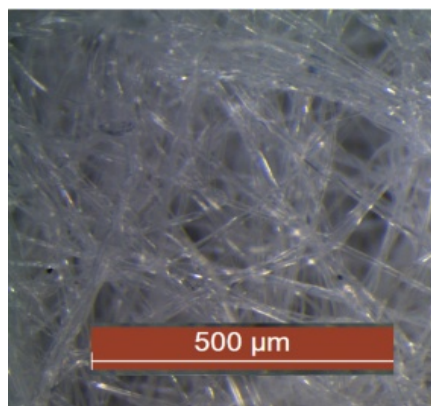
### *3.1. Maximum adsorption capacity of PPmp and G+ for diesel fuel*

Maximum adsorption capacity of PPmp and G+ for diesel fuel was determined in static condition at 20°C. 1 g of PPmp and 1 g of G+ were respectively put inside a becker

containing 100 g of diesel fuel. After 5 min the two sorbent materials were removed by a spoon, filtrated through a metallic sieve for 5 min to eliminate exciding oil, and then weighted in order to evaluate the quantity of sorbed oil. The procedure was repeated 3 times in order to have a representative mean value.



**Fig. 1.** 200 g/m<sup>2</sup> polypropylene fabric



**Fig. 2.** 210 g/m<sup>2</sup> polypropylene needlefelt

### *3.2. Maximum adsorption capacity of PPmp and G+ for diesel fuel spilled in fresh water*

1 g of PPmp and 1 g of G+ were respectively distributed on a diesel slick (94 cm<sup>2</sup>) obtained by a spillage of about 60 g of oil in 1.5 L of fresh water inside a circular vessel. After 5 min the two sorbent materials were filtrated through a metallic sieve for 5 min to eliminate exciding oil. PPmp and G+ were weighted in order to evaluate the quantity of sorbed oil. The procedure was repeated 3 times in order to have a representative mean value.

### *3.3. Maximum adsorption capacity of G+ inside PPmt and PPNf for diesel fuel spilled in fresh water*

Maximum adsorption capacity of G+ inside PPmt and PPNf for diesel fuel spilled in fresh water was determined in dynamic condition at 20°C. 20 g of G+ were put inside a cylindrical boom of PPmt or PPNf (diameter=10 cm; length=40 cm; volume=3,14 dm<sup>3</sup>). 12 L of fresh water inside a plastic vessel (50x80x15cm) were contaminated with 1200 g of diesel fuel. The boom was positioned in parallel with the short side of the vessel above the oil slick. With a manual rotational movement along the longitudinal axis of the boom, the sorbent device was trailed above the water surface for few second.

The boom was removed from the water surface and horizontally positioned inside a containing basin for 5 min. The boom was then weighted and the sorbed oil defined considering the tare. The procedure was repeated 3 times for PPmt and for PPNf in order to have a representative mean value.

### *3.4. Maximum adsorption capacity of a commercial available PP boom for diesel fuel spilled in fresh water*

1 boom prototype of 20 g of PPmp inside a PP spunbond felt (diameter=6 cm; length=12 cm; volume= 339.12 cm<sup>3</sup>) were carried out by fixing the textile sides by a sewing thread. The adsorption test was performed at 20°C in dynamic conditions as reported in point d) of this section.



#### 4. Results and discussion

Tests have showed that adsorption kinetic has been immediate for the both sorbent materials, but loose G+ has a maximum sorption capacity at least 5 times better than PPmp (Table 1). G+ inside the two selected containment booms has a sorption capacity almost halved. The better performances were obtained with PPnf, with a maximum adsorption capacity of 5 g/g higher than PPmt.

In fact, PPnf has an intrinsic sorption capacity because of its inner structure with tortuous micro paths in which the oil can move through capillary action. The sorption capacity of the two boom-prototypes is in any case about 4 times better than the PP boom commercially available. In laboratory context was not possible to define the better containment material between PPmt and PPnf for real life situation with higher volume. We can suppose that PPnf should have better efficiency in light oil removal from water, because it prevents sorbed oil to drop out from the boom because of the presence of smaller pores than PPmt.

**Table 1.** Maximum adsorption capacity ( $a_{max}$ ) of PPmp and G+ for diesel fuel in experimental condition described in point a) of *Experimental* section; maximum adsorption capacity ( $b_{max}$ ) of PPmp and G+ for diesel fuel in experimental condition described in point b) of *Experimental* section; maximum adsorption capacity ( $c_{max}$ ) of G+ inside PPmt or PPnf for diesel fuel in experimental condition described in point c); maximum adsorption capacity ( $d_{max}$ ) of PP boom for diesel fuel in experimental condition described in point d). Each sample reports Standard Deviation (Std. Dev.) and Variation Coefficient (CV)

<i>Sample name</i>	<i>Replica 1 (g)</i>	<i>Replica 2 (g)</i>	<i>Replica 3(g)</i>	$a_{max}$ (g/g)	<i>Std. Dev.</i>	<i>CV%</i>
<b>PPmp (1g)</b>	12.6	12.2	11.2	<b>12.0</b>	0.72	6.01
<b>G+ (1g)</b>	60.3	57.1	63.8	<b>60.4</b>	3.35	5.55
				$b_{max}$ (g/g)	<i>Dev. Std.</i>	<i>CV%</i>
<b>PPmp (1g)</b>	9.67	11.3	10.4	<b>10.5</b>	0.82	7.81
<b>G+ (1g)</b>	59.2	58.4	57.2	<b>58.3</b>	1.01	1.73
				$c_{max}$ (g/g)	<i>Dev. Std.</i>	<i>CV%</i>
<b>G+ inside PPmt (20 g)</b>	664	674	682	<b>33.7</b>	9.0	1.37
<b>G+ inside PPnf (20 g)</b>	746	753	760	<b>37.7</b>	7.0	0.91
				$d_{max}$ (g/g)	<i>Dev. Std.</i>	<i>CV%</i>
<b>PP boom (20 g)</b>	170	165	163	<b>8.3</b>	3.61	2.17

#### 5. Conclusions

In this study, we demonstrated that the synergy between a suitable textile with a super-expanded graphite is able to create an effective device for diesel fuel spilled on water surface, with high sorption capacity in terms of grams of sorbed oil per grams of sorbent.

#### Acknowledgements

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## **SORPTION OF ORGANIC POLLUTANTS ONTO ZEOLITIC TUFF: ISOSTERIC AND STANDARD ENTHALPY\***

**Paola Vanore\*\***, Elio Coppola, Vincenzo Leone, Pasquale Iovino,  
Stefano Salvestrini, Sante Capasso

*Department of Environmental, Biological and Pharmaceutical Sciences and Technologies, Second  
University of Naples, Via Vivaldi 43, 81100 Caserta, Italy*

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### **Abstract**

Isotherms for sorption of toluene and phenol onto zeolitic tuff from water solutions have been determined by batch experiments at 4, 14, 24 and 34 °C. For both compounds the sorbitivity was very low, particularly so for phenol. The parameters of the Freundlich equation and isosteric and standard sorption enthalpies are analyzed in the context of previous studies of sorption onto immobilized humic acid and zeolite-humic acid adducts.

*Keywords:* adduct, humic acid, sorption isotherm, toluene, zeolite

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### **1. Introduction**

This work is a part of a research project for the application of zeolitic tuffs to water purification from organic pollutants. The sorption of neutral organic molecules onto zeolite depends mainly on the Si/Al ratio of this mineral, with higher ratios increasing surface hydrophobicity and enhancing sorbitivity for hydrophobic compounds. Recent work has revealed that the zeolite sorbitivity for hydrophobic compounds is also increased by association with humic acid (HA) (Leone et al., 2013).

The thermodynamics of sorption from water solutions onto zeolite-humic acid adduct showed interesting features: it was found to be endothermic ( $\Delta H < 0$ ) for hydrocarbon compounds and exothermic ( $\Delta H > 0$ ) for hydroxyl compounds (Leone et al., 2014).

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\* Selection and peer-review under responsibility of the ECOMONDO

\*\* Corresponding author: e-mail: [paolavanore@alice.it](mailto:paolavanore@alice.it)

Consequently, as the temperature increases, the sorption efficiency for hydroxyl compounds increases, whereas it decreases for hydrocarbon compounds. In perspective, this behavior permits temperature-mediated control of sorption/desorption equilibrium, with obvious beneficial effects on the efficiency of the process. Interestingly, immobilized humic acid alone was found to be a good sorbent for a range of organic compounds, but its sorbitivity decreased with temperature ( $\Delta H < 0$ ) independently of physico-chemical properties of the sorbate (Iovino et al., 2014). Thus, clearly the association with zeolite modifies the sorption properties of humic acid.

With the aim of gaining insight into the interaction of the two materials and, specifically, the role played by zeolite in the adduct, we investigated the thermodynamics of sorption of a hydrocarbon (toluene) and a hydroxyl compound (phenol) onto zeolitic tuff with low Si/Al ratio.

## 2. Material and methods

### 2.1. Materials

The zeolitic tuff used in this and related studies (Leone et al., 2014; Leone et al., 2013), particle size range from 0.5 at 1.0 mm, Si/Al ratio = 2.4 was obtained from a quarry near Naples (Italy) and was rich in philipsite and chabazite, hence it is reported here with the acronym PCT. Further details of its chemical and mineralogical composition are in Capasso et al. (2007).

### 2.2. Sorption experiments in batch

Analytical-grade toluene and phenol were purchased from Fluka (Germany). Each compound was dissolved in water ( $10\text{-}150\text{ mg L}^{-1}$ ) containing  $1.0 \cdot 10^{-3}\text{ mol dm}^{-3}$  TrisHCl/Tris buffer, pH 6.0. A volume of 20 mL aliquots of solution were mixed with 150 mg of grounded PCT (particle size 0.5-1.0 mm) in glass containers, kept in a thermostat at 4 °C, 14 °C, 24 °C or 34 °C and periodically shaken. After seven days, 1.0  $\mu\text{L}$  aliquots of solution were taken and analyzed by gas-chromatography.

## 3. Results and discussion

The sorption isotherms of toluene and phenol onto PCT have been determined at 4, 14, 24 and 34 °C. As an example, Fig. 1a shows the sorption isotherms for toluene. The experimental data were satisfactorily described by the Freundlich equation (Eq. 1.)

$$q_e = K_F C_e^N \quad (1)$$

where:  $q_e$  and  $C_e$  are, respectively, the amount sorbed per unit mass of sorbent and the sorbate concentration in solution at the equilibrium.

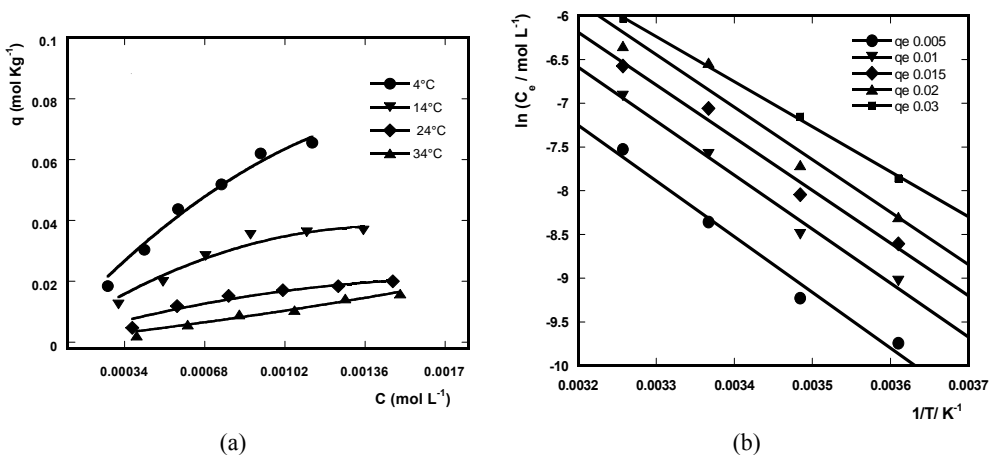
The values of the parameters  $K_F$  and  $N$ , obtained by least-square fits, are reported in Table 1. For comparison, in the same table are also reported the Freundlich parameters obtained in former work (Iovino et al., 2014; Leone et al., 2014) for the sorption of the same compounds onto immobilized humic acid (ImHA) and zeolite tuff-humic acid adduct (HA-PCT).

The Freundlich parameter  $K_F$  was higher for toluene, possibly reflecting the greater affinity of this hydroxyl compound for the aqueous phase. The higher  $K_F$  values for sorption onto ImHA may be due to intrinsic chemical properties of this material and/or to its much smaller granulometry relative to the other two sorbents tested.

It is interesting to note that the  $K_F$  values obtained for HA-PCT are markedly higher than the sum of the contributions of the two separate components. It is also worth noting that  $K_F$  indicates the amount sorbed in equilibrium with a unitary concentration of sorbate in solution.

**Table 1.** Freundlich parameters for the sorption of toluene and phenol onto philipsite-chabazite-rich tuff (PCT), immobilized humic acid (ImHA) and a PCT-humic acid adduct (HA-PCT).  $K_F$  dimensions are  $mmol^{n-1} L kg^{-n}$ . <sup>a</sup>from Iovino et al., 2014; <sup>b</sup>from Leone et al., 2014.

Sorbate	Temp. (°C)	PCT		ImHA <sup>a</sup>		HA-PCT <sup>b</sup> (organic carbon content=0.57)	
		$K_F$	$N$	$K_F$	$N$	$K_F$	$N$
toluene	4	63±3	0.6±0.1	924±49	0.6±0.1	113±6	0.71±0.08
	14	33±2	0.8±0.1	805±40	0.6±0.1	61 ± 3	0.62 ± 0.10
	24	16±1	0.7±0.1	702±27	0.9±0.1	36 ± 1	0.67 ± 0.05
	34	10±1	1.2±0.2	352±17	1.2±0.2	22 ± 1	0.78 ± 0.06
phenol	4	7.0±0.3	0.9±0.1	275±3	0.6±0.1	29 ± 1	0.71 ± 0.08
	14	8.4±0.5	0.7±0.1	219±4	0.4±0.1	34 ± 1	0.99 ± 0.01
	24	7.6±0.2	0.9±0.1	189±4	0.5±0.1	41 ± 1	0.63 ± 0.06
	34	7.3±0.3	1.0±0.1	133±3	0.7±0.1	58 ± 1	0.56 ± 0.03



**Fig. 1.** a) Sorption isotherms for toluene onto the zeolitic tuff at the temperatures indicated; b) plots of logarithms of equilibrium concentrations ( $C_e$ ) of toluene in solution against the reciprocal of temperature

As regards the sorption enthalpy, it is well known that the isosteric enthalpy of sorption ( $\Delta_{ist}H$ ), i.e. the enthalpy change at constant amount of solute sorbed, is given by Eq. (2):

$$\Delta_{ist}H = -RT^2 \frac{d \ln C_e}{dT} \quad (2)$$

where:  $C_e$  is the equilibrium concentration in solution divided by the unitary concentration (Salvestrini et al., 2014). Integration of this equation, assuming that  $\Delta_{ist}H$  is constant over the temperature range analyzed, gives Eq. (3):

$$\ln C_e = \frac{\Delta_{ist}H}{R} \frac{1}{T} + C_{on} \quad (3)$$

$C_{on}$  is an integration constant.

Plots of the logarithm of the equilibrium concentrations in solution against  $1/T$  at constant amount of solute sorbed give the isosteric enthalpies of sorption (Salvestrini et al., 2014). The  $\ln C_e-1/T$  plots for toluene onto PCT are shown in Fig. 1b. Extrapolation of  $\Delta_{ist}H$  at zero amount of solute sorbed gives the Standard Enthalpy of sorption ( $\Delta_{sorp}H^\circ$ ).

Table 2 reports  $\Delta_{ist}H$  and  $\Delta_{sorp}H^\circ$  for toluene onto PCT. Previously published values of  $\Delta_{sorp}H^\circ$  for sorption onto ImHA and HA-PCT are also reported for comparison. For phenol, in agreement with the relatively low value of the  $K_F$  parameter (Table 1), the values of  $\Delta_{ist}H$  (not reported) were characterised by so large errors as to be meaningless.

**Table 2:** Isosteric enthalpy ( $\Delta_{ist}H$ ) and Standard enthalpy change ( $\Delta_{sorp}H^\circ$ ) for sorption of toluene onto PCT, and  $\Delta_{sorp}H^\circ$  for sorption of toluene onto ImHA and HA-PCT. <sup>a</sup> from Iovino et al., 2014; <sup>b</sup> calculated from data in Leone et al., 2014

Sorption degree for toluene (mol kg <sup>-1</sup> )	PCT		ImHA <sup>a</sup>	HA-PCT <sup>b</sup>
	$\Delta_{ist}H$ (kJ mol <sup>-1</sup> )	$\Delta_{sorp}H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta_{sorp}H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta_{sorp}H^\circ$ (kJ mol <sup>-1</sup> )
0.0035	-39±6	-36±6	- 88±3	- 58±1
0.007	-39±5			
0.0105	-38±4			
0.014	-42±3			
0.01	-32±11			
0.0125	-26±8			
0.015	-26±7			
0.0175	-26±6			

The  $K_F$  parameters as reported in Table 1 and the values of  $\Delta_{sorp}H^\circ$  reported in Table 2 clearly show that the thermodynamic properties of sorption onto the humic acid-zeolitic tuff adduct cannot be explained as a simple sum of its components.

#### 4. Conclusions

The results confirm that zeolites with low Si/Al ratio are poor sorbents for organic compounds. Comparison of the thermodynamic data reported here with formerly published data points to the zeolite-humic acid adduct as a highly promising novel sorbent for environmental applications.

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Procedia Environmental Science, Engineering and Management **1** (2014) (1) 83-86

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**AIR1 - Technological innovations and new approaches for the management  
and control of odor emissions**

## **MONITORING ODOUR EMISSIONS FROM WASTEWATER TREATMENT PLANTS BY MEANS OF METHODOLOGIES BASED ON HYDROGEN SULFIDE DISTRIBUTION\***

**Giancarlo Cecchini\*\*, Paolo Cirello, Biagio Eramo**

*LaboratoRI S.p.A. gruppo ACEA S.p.A., Via Vitorchiano, 165 Roma, Italy*

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### **Abstract**

Odour impact assessment essentially uses two different methodological approaches: intensity measurements through olfactometry or detection of specific odorous compounds.

The selection of the monitoring methodology depends on the nature of emission sources and on the possibility of assessing the odour plume with specific tracers, detectable at concentrations close to the perception or annoyance threshold.

Hydrogen sulfide represents a proper indicator of odour emissions from municipal wastewater treatment plants. The paper describes development and application of a monitoring methodology, which combines discrete field monitoring and passive sampling, to evaluate odour emissions in wastewater treatment plants and their impact on neighbouring areas.

*Keywords:* hydrogen sulfide, odour emissions, passive sampling, wastewater treatment plants

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### **1. Introduction**

Odour emissions from wastewater treatment plants typically show high spatial and temporal variability. Given that, the definition of an appropriate methodological approach aimed at assessing the evolution and distribution of odour plume requires, as a priority, the ability to detect/foresee emissions (including occasional releases) which may cause

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\*Selection and peer-review under responsibility of the ECOMONDO

\*\*Corresponding author: Giancarlo.Cecchini@aceaspa.it

annoyance to sensitive receivers. The ultimate goal is to identify control measures in order to minimize, if not remove, olfactory impacts on the exposed population, even in case of sporadic odour problems.

The above objectives have to be met by means of structured monitoring programmes, enabling the detection of odorous compounds at concentration levels close enough to perception thresholds or the quantification of odour concentrations in a space/time frame. Continuous monitoring by means of specific sensor networks and electronic nose systems appropriately addresses the above requisites; though, this instrumentation needs significant investment and operation costs, which limits the spread of this technology.

Similarly, dynamic olfactometry and modeling is highly performing for predictive assessment, but its use could be less efficient for evaluating occasional odour emissions in WWTPs. With respect to wastewater treatment plants (WWTPs), efficient and successful applications can be implemented by use of monitoring methodologies based on the detection of hydrogen sulfide ( $H_2S$ ), as indicator of anaerobic biodegradation of organic matter (Laing et al., 1994).  $H_2S$  can be easily detected by specific field instrumentation even at low levels.

## **2. Outline of the work**

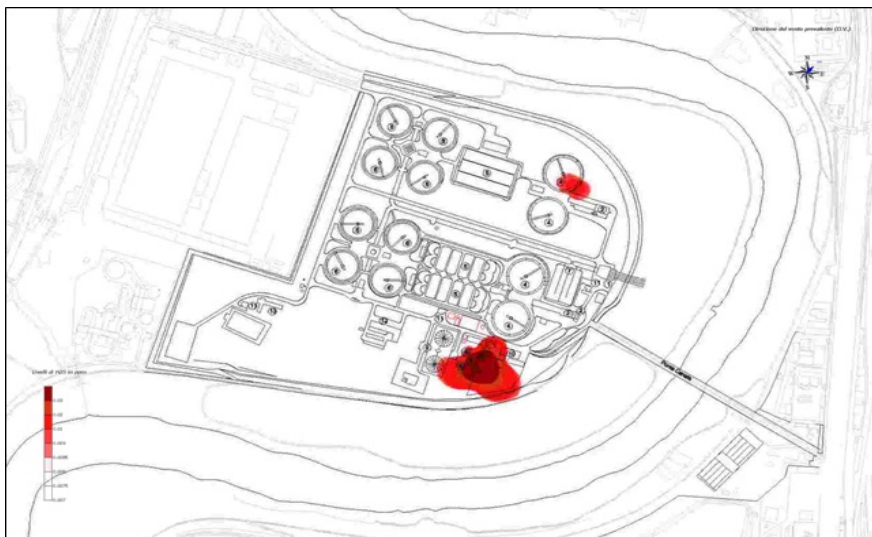
Italian legislation has not set regulatory limits for odour emissions and monitoring guidelines specifically concerning WWTPs have not been issued yet. Nevertheless, since 2003 LaboratoRI has applied a monitoring methodology, based on  $H_2S$  measurements and meteorological data, and the elaboration of isoconcentration maps by means of dedicated software. More recently, it was felt essential to improve the adopted methodology in order to assess odour levels over longer time periods. For this reason, discrete measurements, performed during daytime working hours, have been complemented with passive sampling. This technique allows an integrated evaluation of contaminant levels over different time scales, ranging from hours to weeks, and the simultaneous coverage of many different sites. As a result, depending on exposure times, obtained data may reflect various meteorological and operational conditions.

## **3. Material and methods**

Discrete field data of  $H_2S$  were taken with portable analyzer Jerome 631-XE (Arizona Instrument). The instrument is able to detect very low concentrations of hydrogen sulfide, close to human perception threshold, and operates in a 0.003 - 50 ppm range. Sampling has been performed on a monthly basis.

Results are processed with Surfer® software, and  $H_2S$  spatial distribution displayed on isoconcentration maps, where possible odour emission sources and connected impact areas are shown. Fig. 1 offers an example of graphic elaboration, where emission sources and impacted areas are shown, including the ones outside of WWTP boundaries.

The methodology also includes meteorological monitoring: wind speed and direction, temperature and relative humidity. At each sampling station, perceived olfactive sensation was also registered, according to a four class system. Passive sampling has been performed with a Radiello® sampler with  $H_2S$  specific cartridge made of microporous polyethylene. Sampling, recovery and detection of  $H_2S$  are described elsewhere (Supelco, 2006). The limit of detection is 30 ppb for 1 hour exposure or 1 ppb for 24h exposure, with higher sensitivity than the field measurements. The uncertainty at  $2\sigma$  is 8.7% over the whole allowed exposure range.



**Fig. 1.** H<sub>2</sub>S isoconcentration map

Two different sampling times have been used: short (24h) and medium (1 week). Samples have been collected on different days of the week, in order to make sampling more representative.

#### **4. Application of the methodology**

The methodological approach involves the identification of sampling points for discrete monitoring by application of a homogeneous-specific criterion with a 100m square grid. Passive sampling spots have been selected by identifying the most critical points inside and outside of the plant area, close to sensitive receivers, or based on discrete monitoring historical data. As an example, the following Fig. 2 summarizes an application of the above described methodology to a large size WWTP. For each sampling point, average results of passive sampling (1 week and 24h exposure times) and historical data from discrete monitoring are compared.

Given that odour emissions in WWTPs are not constant over time, average data shows:

- major impact sources, internal to WWTP (sludge treatment units: K and L);
- concentration levels at receivers, in neighbouring areas (A, B and C);
- results from discrete and passive (both 24h and 1 week exposure time) basically comparable;
- Detailed analysis of the results from each single monitoring campaign, makes possible to define:
- spatial distribution of H<sub>2</sub>S and its temporal variability at the single sampling points, by means of discrete field measurements;
- possible occasional emissions, which may not detected by discrete monitoring, through integrated H<sub>2</sub>S measures, as a result of passive sampling.

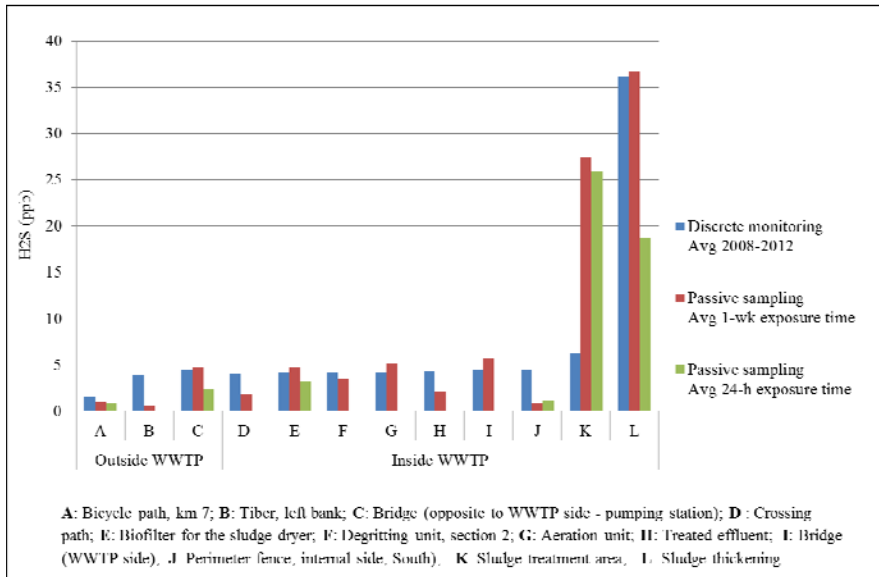


Fig. 2. Average results of discrete and passive monitoring

## 5. Conclusions

The proposed methodological approach, in light of the significance of H<sub>2</sub>S as a tracer for odour emissions in WWTPs, combines operational simplicity and contained costs. These factors make it suitable for routine controls, aimed at both identifying emission sources and critical areas, and detecting occasional emissions from operational malfunctioning.

The above approach is essentially based on simple analytical techniques, which combined together in routine monitoring programmes, allow the identification of critical situations and provide useful information aimed at directing mitigation measures in order to minimize olfactory impacts on neighbouring areas.

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18th International Trade Fair of Material & Energy Recovery and Sustainable Development,  
ECOMONDO, 5<sup>th</sup>-8<sup>th</sup> November, 2014, Rimini, Italy

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**AIR2 - The indoor air quality in Italy: the situation, prospects and controls**

**THE MONITORING OF INDOOR AIR QUALITY  
AND COMFORT: THE EXPERIENCE  
OF THE PROJECT CETIEB\***

**Gian Marco Revel<sup>1</sup>, Marco Arnesano<sup>1\*\*</sup>, Filippo Pietroni<sup>1</sup>, Jürgen Frick<sup>2</sup>,  
Manuela Reichert<sup>2</sup>, Markus Krüger<sup>3</sup>, Katrin Schmitt<sup>4</sup>, Jochen Huber<sup>4</sup>,  
Martin Ebermann<sup>5</sup>, Luc Pockelé<sup>6</sup>**

<sup>1</sup>*Università Politecnica delle Marche, Department of Industrial Engineering  
and Mathematical Science, Ancona, Italy*

<sup>2</sup>*University of Stuttgart, Materials Testing Institute Stuttgart, Germany*

<sup>3</sup>*TTI GmbH – TGU Smartmote, Stuttgart, Germany*

<sup>4</sup>*Fraunhofer Institute for Physical Measurement Techniques, Freiburg, Germany*

<sup>5</sup>*InfraTec GmbH, Germany*

<sup>6</sup>*R.E.D. srl, Italy*

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**Abstract**

Refurbishing old buildings to make them energy efficient often leaves them so tightly sealed that indoor air quality suffers, with possible damaging consequences for human health and productivity. The EU-funded Cetieb research project is working to solve this problem by developing innovative ways of both monitoring and controlling the indoor environment in the most cost-effective ways possible. The development includes a set of tools based on innovative sensors. The concept of those tools was presented in a previous work.

This paper presents the results obtained from the field-testing in laboratory environment and real case studies.

*Keywords:* gas sensor, indoor environment, light sensor, measurement, thermal comfort

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\* Selection and peer-review under responsibility of the ECOMONDO

\*\* Corresponding author: [m.arnesano@univpm.it](mailto:m.arnesano@univpm.it)

## 1. Introduction

The refurbishing of old buildings to an energy efficient standard leads to tight buildings and affects the indoor climate. This is a relevant problem given that people in Europe spend more than 90% of their time indoors.

Improving the health and comfort of occupants consequently brings to a certain number of advantages as increased productivity, reduced sick leave and medical costs, but also by the prevention of potential liabilities. However, the actual monitoring and control solutions are not able to take into account all the aspects related to the indoor air quality, or, if able, they are too expensive. The FP7 European project called Cetieb is moving towards this lack with a set of cost-effective tools specific for the measurement and control of the indoor air quality.

## 2. Objectives

The main scope of the Cetieb project is to develop a set of tools to monitor and control the indoor air quality covering all the needed aspects. Cleaning the air with the maximum efficiency requires first the measurement of several pollutant categories typical of the indoor living spaces. This scope is addressed with a dedicated set of sensors developed within the project.

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), CO<sub>2</sub> luminance and thermal comfort using an innovative sensor for retrieving the PMV index (Predicted Mean Vote). Concerning the control tools developed, the air quality is guaranteed with active systems for actuating the mechanical ventilation, with or without bio-filters, starting from the 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.

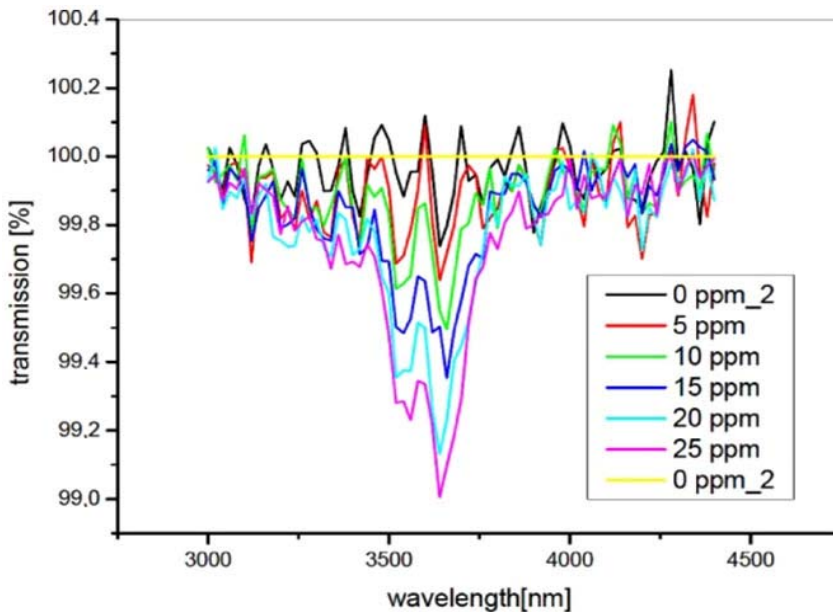
The aim of the paper is to present the results from the laboratory and real cases concerning the monitoring technologies developed within the project and already presented together with the other technologies in a previous work (Revel at al., 2013).

## 3. Materials and methods

### 3.1. Detection of VOC

The partners Fraunhofer IPM and InfraTec developed innovative sensor technologies to monitor indoor air quality. The focus is on volatile organic compounds (VOCs) as indicator for health influence situation in a room. The objectives of our VOC sensor development are the qualitative and quantitative assessment of VOCs, while providing affordable and small-sized systems for integration in smart sensor networks. Two different concepts for VOC monitoring are considered: a spectroscopic VOC sensor to selectively monitor typical indoor contaminants absorbing in the mid-IR range and a gas sensor array consisting of four metal-oxide sensors.

Methane and acetaldehyde were used as test gases for indoor air quality assessment with the spectroscopic system. Acetaldehyde (peak absorption at 3.65  $\mu\text{m}$ ) was measured from 0-100 ppm in N<sub>2</sub> in 10 ppm steps. The maximum allowable concentration (MAC) for acetaldehyde is 50 ppm, so that this concentration needs to be reliably detected (Fig. 1). The limit of detection (LOD) for acetaldehyde was determined to be lower than 10 ppm.



**Fig. 1.** IR spectra of acetaldehyde in N<sub>2</sub> from 0 – 25 ppm in 5 ppm steps measured with the spectroscopic VOC sensor

## 4. Results and discussions

### 4.1. CO<sub>2</sub> sensor performances

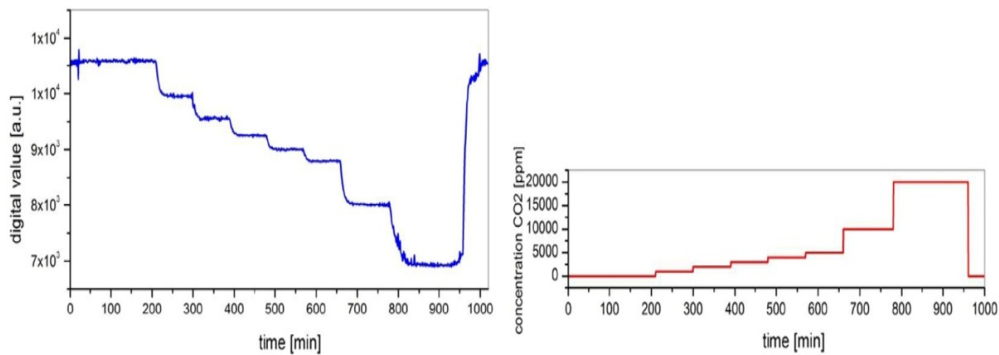
For the assessment of indoor air quality, CO<sub>2</sub> is a crucial parameter since it directly correlates with the number of people present. The atmospheric concentration is today around 390 ppm. For indoors, concentrations above 1000 ppm are known to cause fatigue, headache and dizziness in people. The requirements for a suitable CO<sub>2</sub> sensor include high long-term stability, small size, and low production and maintenance costs. Therefore, our sensor principle is based on the concept of filterphotometry, that makes use of the specific absorption of infrared (IR) radiation of molecules. With the defined filter and absorption path, we reach a measurement range from 0-20.000 ppm (0-2%).

The system was characterized in the laboratory with defined CO<sub>2</sub> concentrations in N<sub>2</sub>. Fig. 2 shows a measurement with CO<sub>2</sub> concentrations from 0-20.000 ppm (blue). The red curve shows the gas concentration vs time. The system was placed into a larger chamber of about 1 dm<sup>3</sup> volume to simulate its situation in an indoor environment. The test showed a limit of detection of 20 ppm with an accuracy of about 50 ppm.

### 4.2. Illumination

The project includes the development of a low cost light sensor measuring the colour temperature of light and the light intensity. The design and realization of this instrument consists out of the identification of the sensor and the design of the casing respecting the standards for reading of photonic data, the design of an interface transforming the raw sensor data in significant values to be used later to drive an illumination system. As sensor, the TCS 3414 from TAOS has been selected. This sensor belongs to the class of RGB sensors, called colorimeters, in contrast with the spectrophotometric sensors that are much more costly.

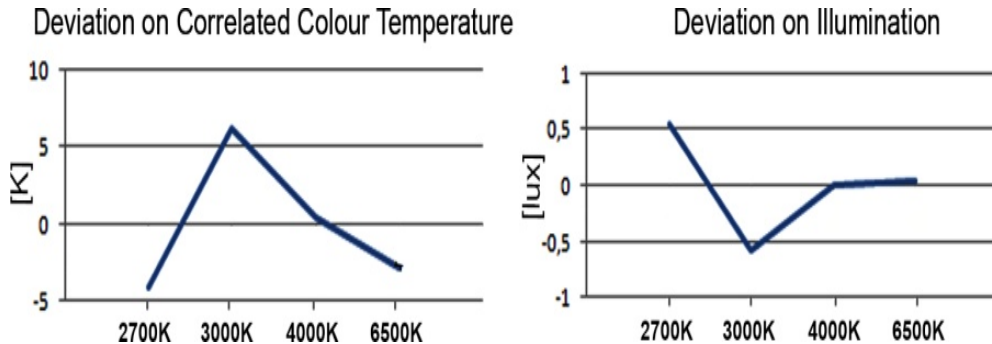




**Fig. 2.** Sensor response (blue) vs time for CO<sub>2</sub> concentrations from 0-20.000 ppm  
The red curve gives the CO<sub>2</sub> concentration in N<sub>2</sub> in ppm

The calibration was done by associating the sensor to be calibrated with a reference instrument (Minolta CL-500) on an optical bench in front of a given light source.

The values of the sensor are then being compared with the values of the reference instrument for a sufficient number of light sources in order to cover the requested measuring range. The result of the calibration can be seen in Fig. 3 from the confrontation of the Correlated Colour Temperature (CCT) and the Lux of the light sources obtained respectively from the sensor and from the reference instrument CL-500. The curves almost overlap and the differences as shown below are inside the band  $\pm 5$  K for the CCT and  $\pm 0.5$  lux for the illumination.

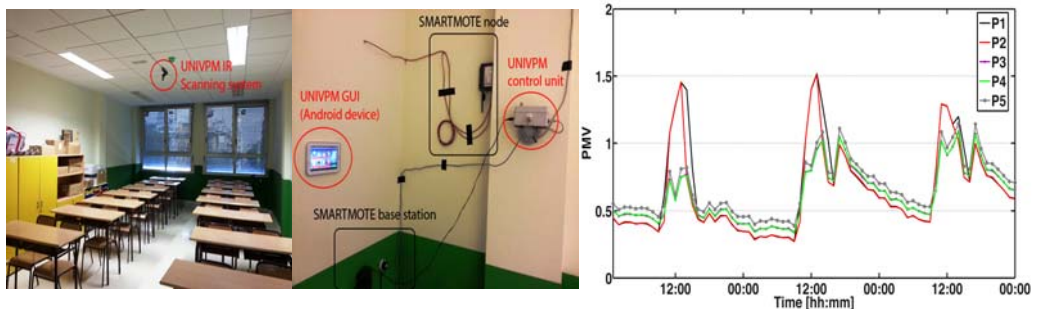


**Fig. 3.** Plot of the deviations between CL-500 and RGB sensor for 4 different light sources

### 4.3. Thermal comfort measurement

Università Politecnica delle Marche focused in the development of a low-cost infrared system for real-time monitoring of human thermal comfort. The system measures the indoor surfaces and environment to derive the PMV for several positions in the space. The device working principle and its measuring performance are described in (Revel et al., 2012 and 2014). The thermal comfort system was tested in a school in Madrid (Colegio El Porvenir). The thermal comfort monitoring system was placed in the reference room (9.4x5.0x2.8m) and integrated with the overall monitoring framework from Stuttgart TTI (SmartMote). Fig. 4 shows the installation setup in the classroom.

Five different positions were measured to see how students perceive the same environment according to their relative position. The positions P1 and P2 correspond to students nearby the glazed facades and thus subject to direct solar radiation.



**Fig. 4.** Colegio El Porvenir demo: installation of the IR scanning system and the other sensor nodes (left). PMV profiles within the classroom according to the different positions (right)

Fig. 4 shows that all the positions follow a similar profile, with a positive comfort deviation of 0.2 from P5 (farthest from windows) to P1 and P2 (near the windows). The deviation increases when the solar radiation enters the room, with a peak of 0.7 (and a resulting increase of 6°C in the mean radiant temperature).

### 3. Concluding remarks

This paper presents a set of tools developed for an improved building retrofitting, which aims at optimal living environments with the lower energy consumption. The paper presents the measurement characteristics of four sensors integrated with the sensor network developed in the project.

The VOC and CO<sub>2</sub> sensors are able to reproduce the performance of typical solutions currently used, but with reduced cost and high integration capability. The thermal comfort can be monitored for all the occupants with the IR-based sensor. The results from the school in Madrid showed how the system is able to take into account the thermal requirements of different occupants in the space. Finally, the RGB sensor is able to provide the measurement of the light spectrum with a level of accuracy comparable to the expensive sensors present in the market.

The complete monitoring solution is thus able to perform the accurate measurement of the indoor air and environment quality with cheap tools embedded in a modular sensor network. Further tests in other environments to test the monitoring technologies with the active and passive control systems will show more results.

### Acknowledgements

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ECOMONDO, 5<sup>th</sup>-8<sup>th</sup> November, 2014, Rimini, Italy

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**AIR3 - Carcinogenicity of air pollution: new approaches to the assessment of air quality  
after delivery of the IARC**

**ASSESSMENT OF REDUCTION STRATEGIES  
FOR THE MITIGATION OF THE ENVIRONMENTAL  
IMPACT OF THE PRIMARY PACKAGING  
WITHIN THE LARGE SCALE RETAIL TRADE\***

**Giacomo Magnone, Pierantonio De Luca\*\*, Antonio Salituro,  
Maria Gemma Cosenza**

*Dipartimento di Ingegneria per l'ambiente ed il territorio e Ingegneria Chimica,  
Università della Calabria, Arcavacata di Rende CS*

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**Abstract**

The current work concerns the assessment and the reduction of the environmental impact of a series of factors (carbon content, total energy consumed, air acidification and water eutrophication), involved by packaging within large scale retail trade through minimization strategies. By using the lifecycle assessment, resulting data were processed with the aid of the software SolidWorks Sustainability.

The material, the manufacturing area, the production technique, the transport mean, the site of use and the final disposal were evaluated for each packaging. Strategies adopted were: the replacement of the glass container with a can as regards beer, the reduction of the distance from the collecting point of the mineral water and the increase of the packaging volume of detergents.

*Keywords:* Life Cycle Assessment, packaging,

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\*Selection and peer-review under responsibility of the ECOMONDO

\*\*Corresponding author: pierantonio.deluca @unical.it

## 1. Introduction

Nowadays, the increasing production and consumption within the society inevitably involves a rise in the waste production. The latter gives an indication about the degree of interaction between human activities and the surrounding environment, actually representing a loss of primary resources and energy.

According to European Environment Agency, the yearly waste production in Europe is of about 2 billion tons. In order to tackle this growth, it is crucial to establish some appropriate management techniques based onto the waste prevention as recommended by the European community.

The Framework Directive 2008/98/CE emphasizes particular attention to the prevention policy which is properly defined. It is interpreted as “measures taken before a substance, material or product has become waste, that reduce: the quantity of waste, including through the re-use of products or the extension of the life span of products; the adverse impacts of the generated waste on the environment and human health; the content of harmful substances in materials and products” (EC Directive, 2008). Therefore it requires that the entire waste management system has to be involved: from the resources withdrawal and disposal to the recovery of matter and energy.

This implies a change of the process for the materials production and the distribution service. In order to find useful solutions to extend the products life cycle, ad use less resources and employ cleaner production processes, it is necessary to act upstream, avoiding the production of the waste. This can be done by diverting the consumers demand towards products which generate a significantly lower quantity of waste (Region Lombardia, 2009).

## 2. Material and methods

The methodology adopted aimed to model different scenarios related to the waste minimization and the subsequent benefits in terms of ecological sustainability. This method was applied onto the packaging associated with the products implying the largest amount of waste (IIP, 2011) and it allowed to evaluate the relevant environmental impact.

The following products with relevant packaging were taken into consideration: cans and glass bottles of beer, glass and PET bottles of mineral water and different types of packaging related to liquid detergents (both household and for personal care). The aforementioned products were chosen since recycling their packaging is extremely problematic (CONAI, 2010).

## 3. Experimental

3D model, weight and the type of packaging for each of the products were given as input to the software SolidWorks Sustainability®. This software was provided with the following databases: Ecoinvent v2, U.S. Life Cycle Inventory Database (USLCI, 2009), and GaBi LCA Database. For each packaging, by using the sustainability module, the analysis of the materials, the manufacturing area, the production technique, the transport mean and the site of use were considered. Also the disposal of the residue at the end of the lifecycle, divided in recycle, incineration and landfill, was studied (Planchard and Planchard, 2012). Environmental impacts were evaluated through the Life Cycle Assessment (LCA) according to four categories: greenhouse effect, consumption of primary energy, acidification and eutrophication (Horne et al., 2009).

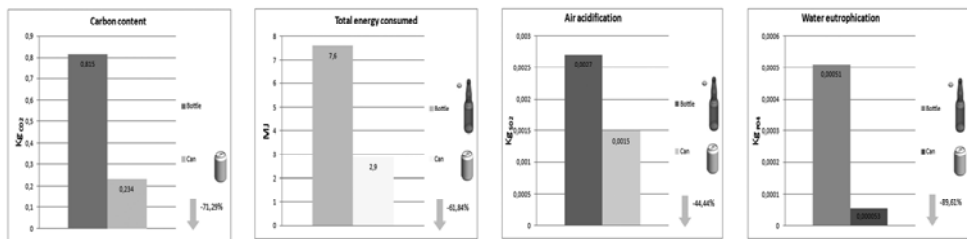
These impacts were calculated by applying the CML methodology (de Bruijn et al., 2002) provided by the Centre of Environmental Studies of the University of Leiden in Netherland. This method takes into account four indicators: *carbon content* ( $kg_{CO_2}$ ), *total energy consumed* ( $MJ$ ), *air acidification* ( $kgSO_2$ ), *water eutrophication* ( $kgPO_4$ ).

For each product, the overall impact was calculated as the sum of the impacts related to every single packaging involved by the product itself. Energy demand and environmental impact associated with the primary packaging of each product, the materials used and the emission released were evaluated. Later on, different scenarios concerning strategies for the minimization of the environmental impacts were studied: *replacement of glass bottle with can for the beer*; *reduction of the distance from the mineral water source*; *sale in container having larger volumes of liquid detergents (both household and for personal care)*.

In particular, the latter strategy (volume increase container) enabled to estimate the potential reduction of waste packaging which can be obtained. The software SWs, coupled with MS Excel worksheet, was used to calculate the final values of the impacts involved by each packaging.

#### 4. Results and discussion

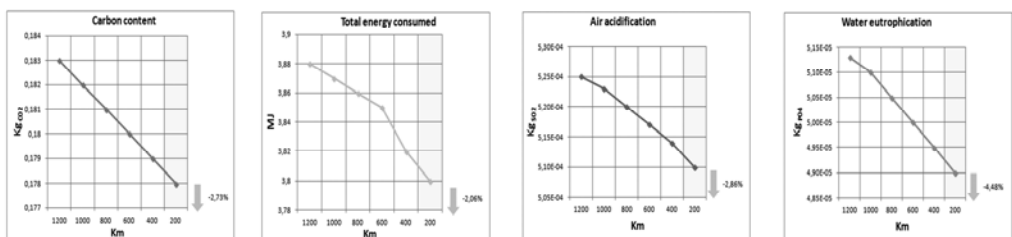
As regards the first strategy, it was crucial to perform a comparison of the environmental impacts involved by the two different types of packaging (glass container vs can). As reported by Fig.1, the use of the glass bottle implied a much higher impact than that associated with the can. Using a can rather than a glass bottle caused a reduction of 71,29%, 61.84%, 44.44% and 89.61% for carbon content, total energy consumed, air acidification and water eutrophication respectively.



**Fig. 1.** Variation of the environmental impact indicators after replacing the glass bottle(0.33l) with the can (0.33l) of beer

Conversely, the second strategy, *reduction of the distance from the mineral water source*, led to a trivial reduction of the indicators, which ranges from 2 to 4% (Fig. 2).

This negligible reduction enlightens that the parameter “transport” does not significantly affect the environmental impact of the packaging. On the contrary, other parameters like type of material, manufacturing, use and life cycle have a noticeable influence. This suggests that further strategies need to be introduced in an attempt to achieve a greater reduction.

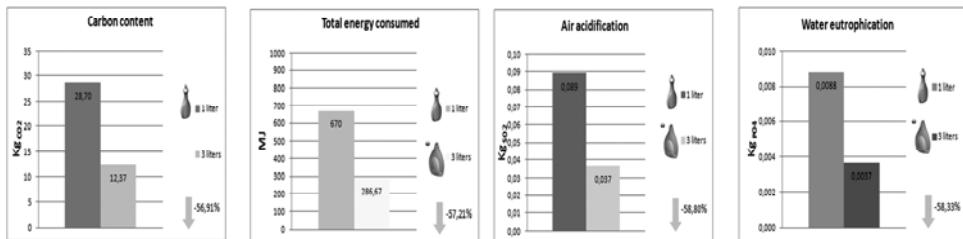


**Fig. 2.** Variation of the environmental impact indicators depending upon the distance related to the mineral water packaging (1.5 L, PET)

In the following strategies, *sale of liquid detergent in container having larger volumes*, it was supposed to sell 100 liters of product in containers of different volumes. It may be seen that the sale of a same amount of product in larger containers, involves a considerable reduction of the environmental impact indicators. The increase of the volume of the packaging in PE for the liquid detergents (both household and for personal care), in particular from 1L to 3 L container, calculated over the whole amount of products sold (100L), involved a considerable decrease of the indicators, i.e. 56.91%, 57.21%, 58.80% and 58.33% for carbon content, total energy consumed, air acidification and water eutrophication respectively (Fig. 3).

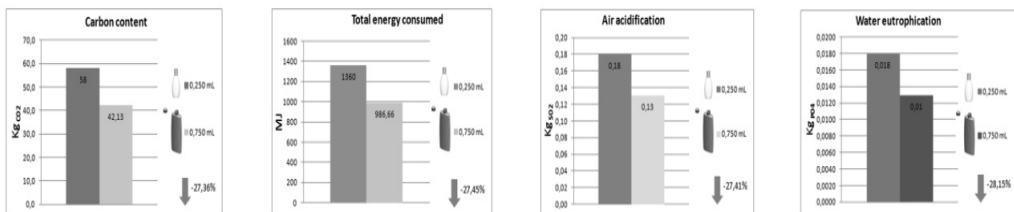
In addition to the change of the indicators, this last strategy also enabled to calculate the reduction of the amount of waste packaging (containers for household detergents) which could be obtained if this option would be adopted. Considering the same quantity of product sold, the total weight of the packaging associated with original and final increased size was determined.

The decrease correspond to a waste reduction of 56.96%. With respect to detergents for personal care, the same procedure was applied, implying to use larger containers (0.750 L rather than 0.250 L). Similarly to household detergents, for each type of container size the potential reduction was evaluated over the same amount of product sold (100 L).



**Fig. 3.** Variation of the environmental impact indicators with increasing container (PE) volume from 1L to 3 L, calculated over the whole amount of products sold (100L) of liquid detergents (both household and for personal care)

In particular, the following reduction figures were calculated: 27.36%, 27.45%, 27.41% and 28.15% for carbon content, total energy consumed, air acidification and water eutrophication respectively (Fig. 4).



**Fig. 4.** Variation of the environmental impact indicators with increasing container volume from 0.250 mL to 0.750 mL, calculated over the whole amount of products sold (100L) of household detergents

## 5. Conclusions

Four different strategies for the minimization of the environmental impact were studied. From the results obtained it is possible to conclude that:

- Regarding beer, the replacement of the glass container with the can successfully led to impact decays of 71.29% for the carbon content, 61.84% for the total energy consumed, 44.44% for air acidification and 89.61% for water eutrophication.

- On the contrary, results related to the second strategy (i.e. decrease of the distance from the source of mineral water) did not fulfill the initial expectations. It comes that the parameter “transport” does not considerably influence the total environmental impact of packaging. On the other hand, other factors like type of material, manufacturing, usage and lifecycle are more important.

- The increase of the container volume (from 1 to 3L) for household detergents, caused a noticeable decline of all the indicators: 56.91% for the carbon content, 57.21% for the total energy consumed, 58.80% for air acidification and 58.33% for water eutrophication. The same procedure (container size increased from 0.250 L to 0.750 L) implied an impact reduction for the detergents for personal care. Particularly, a decrease of 27.36% for the carbon content, 27.45% for the total energy consumed, 27.41% for air acidification and 28.15% for water eutrophication were achieved.

To sum up, this work proved that the strategies adopted (except the one considering the parameter “transport”) can promote the environmental sustainability, since they can actually contribute at reducing the waste production.

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## Instructions for authors

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### Books:

Faber K., (2000), *Biotransformations in Organic Chemistry - A Textbook*, vol.VIII, 4th Edition, Springer, Berlin-Heidelberg-New York.

Handbook, (1951), *Handbook of Chemical Engineer*, vol. II, (in Romanian), Technical Press, Bucharest, Romania.

**Symposia volumes:** Names and initials of authors; year; article title; full title; symposium abbreviated; volume number; place; date; page number:

Masutti D.C., Borgognoni A., Scardovi F., Vaccari C., Setti L., (2014), *Production of Lignocellulosic Enzymes from Different Agro-Food Wastes by Solid State Fermentation*, Proc. of 5<sup>th</sup> International Conference on Engineering for Waste and Biomass Valorisation - Rio de Janeiro, September 6th-8th, Brazil.

**Journal papers:** Names and initials of authors; year (between brackets); full title of the paper; full name of the journal (italic); volume number (bold); first and last page numbers:

Setti L., Giuliani S., Spinozzi G., Pifferi P.G., (1999), Laccase-catalyzed oxidative coupling of 3-methyl 2-benzothiazolinone hydrazone and methoxyphenols, *Enzyme Microbial Technology*, **25**, 285-289.

**Patents:** Names and initials of authors; year; patent title; country; patent number:  
Grant P., (1989), Device for Elementary Analyses. USA Patent, No. 123456.

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Guikema J.W., (2004), *scanning hall probe microscopy of magnetic vortices in very underdoped yttrium-barium-copper-oxide*, PhD Thesis, Stanford University, Stanford, USA.

Star K., (2008), *Environmental risk assessment generated by natural hazards*, MSc Thesis, Institute of Hazard Research, Town, Country.

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JRC European Commission, (2011), *Supporting Environmentally Sound Decisions for Construction and Demolition (C&D) Waste Management*, A practical guide to Life Cycle Thinking (LCT) and Life Cycle Assessment (LCA), On line at: <http://lct.jrc.ec.europa.eu/pdf-directory/ReqNo-JRC65850-LB-NA-24916-EN-N.pdf>.

EC Directive, (2010), Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (Integrated Pollution Prevention and Control), *Official Journal of the European Union*, **L334**, 17-119.

EC, (2014), Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions Towards a Circular Economy: A zero waste programme for Europe, European Commission, On line at: <http://ec.europa.eu/environment/circular-economy/>

Law 152 (2006), Legislative Decree No. 152 of the 03 April 2006, Environmental Regulations, *Official Journal*, No. 88 of the 14 April 2006 – Ordinary Supplement No. 96.

GD, (2004), Governmental Decision no. 1076/2004 surnamed SEA Governmental Decision, regarding the procedure for strategic environmental impact assessment for plans or programs, published in Romanian Official Monitor, part I, no. 707 from 5th of August, 2004.

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Lorint C., (2012), *Natural Protected Areas and Biodiversity Preservation* (in Romanian), Universitas Press, Petroșani, Romania.

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