



UNIVERSITA' DEGLI STUDI DI NAPOLI FEDERICO II
CIRAM - CENTRO INTERDIPARTIMENTALE DI RICERCA AMBIENTE

Via Mezzocannone, 16 – 80134 Napoli – ITALY
Tel: (+39) 081.2534646 - fax: (+39) 081.2534645, e-mail: ciram@unina.it.



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SVILUPPO DI PROTOCOLLI ECO-COMPATIBILI PER LA BONIFICA DEI SUOLI INQUINATI NELL'EX SIN LITORALE DOMIZIO- AGRO AVERSANO

IMPLEMENTATION OF ECO-COMPATIBLE PROTOCOLS FOR AGRICULTURAL SOIL REMEDIATION IN LITORALE DOMIZIO- AGRO AVERSANO NIPS



TECHNICAL REPORT

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INTRODUCTION

The scientific and technical staff of LIFE ECOREMED working group is composed of 62 units with expertise in various subjects, mainly Agricultural Sciences and Engineering, but also Geological Sciences, as well as Urban Planning and Occupational Medicine.

As a result, during the five-year project (2012-2017) many scientific and technical communication activities have been carried out. They are represented not only by the publications in the scientific journals, but also by all the oral or written presentations delivered during the national and international meetings.

This report gathers the works related to LIFE ECOREMED project that were published or presented during the period 2012-2014: they are part of a set of more than 60 works drawn up in the whole period of activity of the LIFE project.

The present report, that collects the first page of the abstracts and the conclusions of the works, is meant to give an idea to the reader of the subjects that were analyzed by the scientific and technical staff (a more in-depth analysis of the works would be possible by reading the full texts or by asking for more information directly to the authors).

Azione	Coordinator	Sector
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B1a. Contribution of air pollutants deposition to soil contamination	A. Senatore	industrial engineering
B1b. Geochemical characterization of agricultural soils.	B. De Vivo, S. Albanese	environmental geochemistry
B1c. Hydrological and hydrogeological characterization	D. Ducci, N. Romano	hydraulic engineering; hydrogeology
B1d. Human exposure and health assessment	M. Manno	occupational medicine
B1e. GIS inventory of environmental conditions	L. Boccia	territorial Engineering
B2) STRENGTHENING BIO- PHYTO-REMEDICATION OF CONTAMINATED SOILS	N. Fiorentino	agronomy environmental
B2a. Isolation and selection of biodegrading bacteria from microbial community of contaminated soil, preparation and application of formulates in situ.	O. Pepe, V. Ventorino	agricultural microbiology
B2b. Bioremediation improvement by white-rot fungi inoculums in open field conditions.	V. Faraco	biotechnology
B2c. Assisted phytoremediation with compost amendment and Trichoderma inoculation of energy crops.	M. Mori	Agronomy and field crops
B3) USE OF CONTAMINATED BIOMASSES FOR ENERGY PRODUCTION	S. Pindoizzi	agricultural engineering
B3a. Syngas Production from Gasification of Biomasses	A. Cavaliere, S. Faugno	chemical plants
B3b. Contaminated biomasses for II-generation biodiesel synthesis	D. Pirozzi	chemical engineering
B4. SOIL WASHING OF CONTAMINATED SOILS	R. Andreozzi	Industrial chemistry
B4a. Chemical, bio-chemical washing of contaminated soils	M. Fabbicino	health-environmental engineering
B4b. Oxidative photocatalytic treatment of aqueous stream produced during soil washing	R. Andreozzi	industrial chemistry
C1 ANALYSIS OF MOBILITY AND BIOAVAILABILITY OF POLLUTANTS IN PILOT FIELDS.	S. Di Rosa P. Adamo	agrochemical
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C2a. Bio-monitoring of air pollution by moss transplants and characterization of airborne particles	S. Giordano	environmental botany
C2b. Evaluation of the microbial community structure.	O. Pepe, V. Ventorino	agricultural microbiology
C2c. Bio-monitoring of oxidative damage and characterization of reproductive health status of selected species	G. Guerriero	biology
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C6. MONITORING WATER TRANSFER PROCESSES IN THE SOIL-VEGETATIONATMOSPHERE SYSTEM	N. Romano	hydraulic engineering
C7. MONITORING SOCIAL AND ECONOMICAL IMPACT OF SOIL REMEDIATION	G. Cicia, T. Del Giudice	agrarian economy

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“Gheorghe Asachi” Technical University of Iasi, Romania



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SYNTHESIS OF BIODIESEL FROM HYDROLYSATES OF ARUNDO DONAX

Domenico Pirozzi, Abu Yousuf, Gaetano Zuccaro, Rosaria Aruta, Filomena Sannino

Dipartimento di Ingegneria Chimica, Facoltà di Ingegneria, Università di Napoli Federico II, P.le Tecchio, 80, 80125 Napoli, Italy; Dipartimento di Scienze del Suolo, della Pianta, dell'Ambiente e delle Produzioni Animali, Facoltà di Scienze Biotecnologiche, Università di Napoli Federico II, Via Università 100, 80055 Portici (Napoli), Italy

Abstract

The market penetration of the 1st generation biodiesel is limited by the relatively high cost of the feedstock (i.e. vegetable oils and animal fats), the insufficient availability of fertile land, as well as the social and environmental problems caused in different developing countries.

New promising perspectives are offered by the hydrolysis of lignocellulosic materials to obtain fermentable sugars, as a large range of waste materials can be recycled, such as non-food parts of crops, forest products, and industry wastes. Though so far the hydrolysates of lignocellulose have been mainly used for the production of bioethanol, they can be alternatively employed for culturing oleaginous microorganisms, producing more than 20% of their weight in the form of lipids. These lipids are mainly triglycerides, potentially exploitable as feedstock for the synthesis of biodiesel. In this study, we demonstrate that the oleaginous yeast *Lipomyces starkeyi* can be grown in the presence of lignocellulose hydrolysates obtained from different samples of *Arundo donax*.

L. starkeyi were cultured in the presence of the raw hydrolysate of *A. donax* (ADH) with no external organic supplement. A preliminary dilution was required to obtain a satisfactory cell growth, due to the presence of some products of the lignocellulose hydrolysis that inhibit the cellular growth (furfural, phenolic compounds, etc.). The yeast growth was accompanied by the complete consumption of the reducing sugars and a significant reduction of TOC.

In order to remove the inhibitors, the ADH was treated following three different protocols: (a) overliming treatment with concentrated $\text{Ca}(\text{OH})_2$, (b) neutralization with NaOH and adsorption on active carbons, (c) overliming followed by neutralization and adsorption. These treatments made possible the growth of *L. Starkeyi* in the presence of undiluted raw ADH. The experimental data demonstrate that the best results are obtained by the method (b).

Conclusions

This study demonstrated that it is possible to produce triglycerides from *Arundo donax* cultivated in marginal lands, to reduce the competition with food crops for fertile lands, and to offer a sustainable way to produce renewable energy (biodiesel) or building blocks for biopolymers. The conditions of the agronomical treatments affected the composition of the lignocellulosic biomass, and eventually the lipid and biomass yields obtained by yeast grown in the hydrolysates. Preliminary dilution or pre-treatment of hydrolysates, as well as yeasts pre-adaptation by progressive increases of the hydrolysate concentration, were effective in reducing the effect of the microbial growth inhibitors. The composition of the microbial triglycerides was suitable to obtain a biodiesel with reduced tendency to oxidation and good cold performance.

*Domenico Pirozzi, Abu Yousuf, Gaetano Zuccaro, Rosaria Aruta, Filomena Sannino (2012)
SYNTHESIS OF BIODIESEL FROM HYDROLYSATES OF Arundo donax
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Prediction of spatially variable unsaturated hydraulic conductivity using scaled particle-size distribution functions

Paolo Nasta,^{1,4} Nunzio Romano,² Shmuel Assouline,³ Jasper A. Vrugt,⁴ and Jan W. Hopmans⁵

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[1] Simultaneous scaling of soil water retention and hydraulic conductivity functions provides an effective means to characterize the heterogeneity and spatial variability of soil hydraulic properties in a given study area. The statistical significance of this approach largely depends on the number of soil samples collected. Unfortunately, direct measurement of the soil hydraulic functions is tedious, expensive and time consuming. Here we present a simple and cost-effective hybrid scaling approach that combines the use of ancillary information (e.g., particle-size distribution and soil bulk density) with direct measurements of saturated soil water content and saturated hydraulic conductivity. Our results demonstrate that the presented approach requires far fewer laboratory measurements than conventional scaling methods to adequately capture the spatial variability of soil hydraulic properties.

Citation: Nasta, P., N. Romano, S. Assouline, J. A. Vrugt, and J. W. Hopmans (2013), Prediction of spatially variable unsaturated hydraulic conductivity using scaled particle-size distribution functions, *Water Resour. Res.*, 49, 4219–4229, doi:10.1002/wrcr.20255.

1. Introduction

[2] The predictive ability and utility of large-scale distributed hydrologic models heavily relies on a detailed description of the spatial variability of the soil hydraulic properties, namely the water retention function (WRF) and the unsaturated hydraulic conductivity function (HCF). The WRF relates the volumetric water content θ ($L^3 L^{-3}$) to the corresponding soil water matric head h (L). The HCF relates the unsaturated hydraulic conductivity K ($L T^{-1}$) to the soil matric head or water content. The spatial distribution of WRF and HCF can be characterized with effective soil hydraulic parameters [Zhu and Mohanty, 2002; Zhu and Mohanty, 2003; Vrugt et al., 2004; Mohanty and Zhu, 2007]. Although this approach provides a reasonable description of the lumped behavior of the soil system, it does not accurately characterize the inherent spatially distributed soil water fluxes.

[3] In the past decades, the scaling approach has been developed as an effective method to describe the spatial variability of the soil hydraulic properties in a given study

area [Warrick and Nielsen, 1980; Tillotson and Nielsen, 1984; Clausnitzer et al., 1992]. This approach was introduced in soil physics by the seminal paper of Miller and Miller [1956] and is based on the assumption that geometrically similar porous media differ only by a characteristic length of their respective pore-size distributions, which in turn provide a good proxy for the soil hydraulic properties. Spatial variability is defined through the statistical distribution of scaling factors that relate the soil hydraulic functions sampled in different locations to the corresponding average hydraulic properties of a reference porous medium (representative for the study area). This geometric scaling approach has been successfully applied for Kosugi's soil hydraulic functions [Kosugi, 1996], assuming that scaling factors are lognormally distributed in the sampled soil domain. This includes individual scaling of soil WRFs only [Kosugi and Hopmans, 1998; Hayashi et al., 2009] or simultaneous scaling of soil water retention and unsaturated HCFs [Hendrayanto et al., 2000; Tuli et al., 2001].

[4] Notwithstanding this progress made, the inherent spatial variability of soils necessitates a very large number of samples to accurately characterize the hydraulic properties of the considered spatial domain [Hopmans et al., 2002a; Minasny and McBratney, 2007; Vereecken et al., 2007]. Unfortunately, direct measurement of the soil hydraulic properties (hereafter referred to as primary data or PD) is time consuming and tedious [Hopmans et al., 2002b]. Alternatively, pedotransfer functions (PTFs) can be used to indirectly estimate the soil hydraulic functions from soil physical and chemical data (hereafter defined as secondary data or SD) that are more readily available because of their ease in collection and simplicity in measurement [Haverkamp et al., 2002]. Most PTFs estimate the soil hydraulic functions through mathematical and statistical relations by using oven-dry bulk density, organic carbon content, and soil texture [Pachepsky and Rawls, 2004]. We emphasize that PTFs necessitate empirical

¹Department of Earth and Atmospheric Sciences, University of Nebraska, Lincoln, Nebraska, USA.

²Department of Agriculture, Division of Agricultural, Forest and Biosystems Engineering, University of Napoli Federico II, Portici, Naples, Italy.

³Department of Environmental Physics and Irrigation, A.R.O, Volcani Center, Bet Dagan, Israel.

⁴Department of Civil and Environmental Engineering, University of California, Irvine, California, USA.

⁵Department of Land, Air and Water Resources, University of California, Davis, California, USA.

Corresponding author: P. Nasta, Department of Earth and Atmospheric Sciences, University of Nebraska, Lincoln, NE 68588, USA. (paolo.nasta@unl.edu)

Conclusions

The scaling approach of Miller and Miller [1956] is still widely employed to characterize the spatial variability of soil hydraulic properties. This technique seems particularly appealing as it provides the opportunity to stochastically generate new soil hydraulic parameters in unknown locations of a study area through the lognormal pdf of the scaling factors and the corresponding reference soil hydraulic properties [Nasta et al., 2013]. Successful applications of this procedure to real cases require a relatively large number of soil samples for large-scale hydrological applications. This task is rather expensive, time consuming, and labor intensive. To characterize the spatial variation of soil hydraulic properties, in this paper, we have developed an alternative hybrid scaling approach that uses more easily to be determined secondary soil data coupled with easily obtainable PD (such as saturated soil water content and saturated hydraulic conductivity).

This study is a followup of the work presented by Nasta et al. [2009], providing the prediction of both water retention and unsaturated HCFs. The proposed method is a compromise between effectiveness in describing the soil spatial variation over relatively larger scales and the sustainability of experimental efforts. However, we caution on the potential issues affecting this method since soil texture measurements are generally insufficient to explain all observed spatial variations in soil hydraulic functions, especially the hydraulic conductivity characteristic.

A possible way to overcome this limitation in our hybrid scaling method is to consider bimodal hydraulic relationships in lieu of the conventional unimodal forms of Kosugi's WRF and HCF. Such functions would better describe the effect of soil structure near saturation [Romano et al., 2011].

Nasta, P., N. Romano, S. Assouline, J.A. Vrugt, and J.W. Hopmans (2013)

Prediction of spatially-variable unsaturated hydraulic conductivity using scaled particle-size distribution functions. Water Resour. Res., 49(5):2918–2925, doi:10.1002/wrcr.20269, ISSN: 0043-1397.



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Procedia

Environmental Sciences

Four Decades of Progress in Monitoring and Modeling of Processes in the Soil-Plant-
Atmosphere System: Applications and Challenges

Prediction of unsaturated relative hydraulic conductivity from Kosugi's water retention function

Paolo Nasta^{a*}, Shmuel Assouline^b, John B. Gates^a, Jan W. Hopmans^c, Nunzio Romano^d

^aEarth and Atmospheric Sciences, University of Nebraska-Lincoln, Lincoln, NE, USA

^bDepartment of Environmental Physics and Irrigation, A.R.O - Volcani Center, Bet Dagan, Israel.

^cDepartment of Land, Air and Water Resources - University of California, Davis, CA, USA.

^dDepartment of Agriculture, Division of Agricultural, Forest and Biosystems Engineering - University of Napoli Federico II, Portici (NA), Italy.

Abstract

Reliable large-scale characterization of soil water retention (WRF) and hydraulic conductivity (HCF) functions requires a large amount of direct measurements for hydrological modeling applications. Although direct measurements of WRF are time consuming, they tend to be far less time and labor-intensive than direct measurements of HCF. Therefore, WRF experimental data are often exploited to predict the HCF through available existing models. Current popular approaches include the well known physically-based Mualem's model. We hereby propose a novel, simple and physically sound model to predict the relative HCF from Kosugi's WRF expression [14]. The proposed model is based on the introduction of a new conductivity parameter, η , that is related to the coefficient of variation of the WRF. The model is calibrated on 20 soil samples and subsequently tested on an independent data set of 57 samples. The predictions show relatively high accuracy and reliability when compared to those derived from Mualem's model.

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Keywords: soil water retention; tortuosity; connectivity; pore-size distribution; relative unsaturated soil hydraulic conductivity.

* Corresponding author. Tel.: +39-081-2539421

E-mail address: paolo.nasta@unina.it

Conclusions

A new parametric relation is proposed to predict unsaturated hydraulic conductivity when describing the soil water retention function through the model of [14]. Our approach offers increased flexibility relative to Mualem model [18] by relating Assouline's parameter to the CV of the WRF. The proposed analytical expression has been calibrated and tested using a relatively large data set and the results demonstrate reliability and compare favorably to the widely-used model of Mualem [18].the soil water retention function through the model of [14]. Our approach offers increased flexibility relative to Mualem model [18] by relating Assouline's parameter to the CV of the WRF. The proposed analytical expression has been calibrated and tested using a relatively large data set and the results demonstrate reliability and compare favorably to the widely-used model of Mualem [18].

*Nasta, P., S. Assouline, J.B. Gates, J.W. Hopmans, and N. Romano (2013)
Prediction of unsaturated relative hydraulic conductivity from Kosugi's water retention function.
Procedia Environmental Sciences 19:609-617, doi: 10.1016/j.proenv.2013.06.069, ISSN: 1878-0296.*

Chestnut Biomass Biodegradation for Sustainable Agriculture

Valeria Ventorino, Rita Parillo, Antonino Testa, Alberto Aliberti, and Olimpia Pepe*

Biodegradation of lignocellulosic waste from chestnut residues is an important biological process of added value for this sector according to the Chestnut National Plan for agriculture. Dynamic parameters during biodegradation under natural conditions of chestnut burr, leaf, and plant biomass litter are reported in this study. Microbiological and physical-chemical characterisation of chestnut wastes was carried out to monitor this specific biodegradation, to understand the progress and limits of the process and to analyse the compost-like organic substance obtained. Physical-chemical parameters, such as temperature, pH, and water activity, were influenced by the composition of the raw materials and by seasonal climatic conditions. Moreover, microbiological monitoring was assessed by culture-dependent and independent methods. Cellulolytic, hemicellulolytic, and ligninolytic populations were counted to determine different microbial activity during biodegradation process. The functional microbial groups analysed showed different trends, but all were found at high concentrations (7 to 9 log CFU/g). In addition, PCR-DGGE was performed for bacterial and fungal populations to evaluate the microbial diversity. The similarity level during the process was generally very high, both for bacterial and fungal populations. These data are the first on suitable natural degradation for chestnut forests.

Keywords: Chestnut composting; Microbiological monitoring; PCR-DGGE; Sustainable fertilisation

*Contact information: Department of Agriculture, University of Naples Federico II, Via Università, 100, 80055, Portici, Naples, Italy; *Corresponding author: olipepe@unina.it*

INTRODUCTION

The Italian Chestnut National Plan in Italy supports the need to guide the chestnut population toward more sustainable forms of production, characterised by a higher ability to meet the needs and interests of consumers and producers by offering new economic opportunities in agriculture. These measures are justified by the need to sequester carbon, reducing greenhouse gas emissions into the atmosphere, recovering biomass for agronomic purposes, and increasing the sustainability of agricultural productions (Marmo 2007).

The use of biomass is interesting at both the EU and national level, especially after the agreements of the Kyoto Protocol (reduction of CO₂ emissions into the atmosphere). Recently, on-farm composting processes have been developed to transform biomass waste of agricultural origin (Tuomela *et al.* 2000). The use of lignocellulosic materials in composting has several important roles, such as structural, absorptive, and biochemical changes (Hubbe *et al.* 2010). An interesting example is the composting of lignocellulosic winery wastes (Paradelo *et al.* 2013). The evaluation of compost made from chestnut residues obtained from cleaning and pruning can be a source of added value for the sector. Although composting procedures are well known, very few reports

Conclusions

1. The temperature values in the internal part of the pile were strongly affected by the seasonal climatic conditions.
2. Cellulolytics increased during biodegradation of chestnut biomass, while ligninolytics decreased as an effect of microbial competition and environmental conditions.
3. DGGE analysis showed similar profiles during the natural degradation process for both bacterial and fungal populations except at the beginning of the process.
4. Because lignocellulosic biomass is also an attractive waste material for production of a wide range of high value-added products, cellulolytic, hemicellulolytic, and ligninolytic microorganisms should be isolated and selected for their biotechnological applications and used to improve the process.
5. To the authors' knowledge, there have been no previous investigations of the microbiological characterisation of chestnut biomass submitted to biodegradation under natural conditions. The first preliminary results are encouraging, but further tests must be carried out to improve the understanding of natural degradation of chestnut and the final product.

*Ventorino V., Parillo R., Testa A., Aliberti A., Pepe O. (2013)
Chestnut biomass biodegradation for sustainable agriculture
The Scientific World Journal, Article ID 931793 p. 1-11; DOI: 10.1155/2014/93179*

EUROPEAN HYDROPEDOLOGICAL DATA INVENTORY (EU-HYDI) JRC TECHNICAL REPORT (2013)

14 Soil data from Italy (Campania)

N. Romano, M. Palladino, B. Sica, P. Di Fiore

Department of Agriculture, Division of Agricultural, Forest and Biosystems Engineering - University of Naples Federico II, Via Università n. 100, 80055 Portici, Italy (nunzio.romano@unina.it; mario.palladino@unina.it; benedetto.sica@unina.it; pdifiore@unina.it).

14.1 Introduction

The Soil Hydrology Laboratory at University of Naples Federico II has been operating for more than 50 years. During these decades, consolidating certain techniques and developing new measurement methods have always been a target for us and represented an excellence in the field of soil hydrology. Many field campaigns have been undertaken during these years with the major aim of supporting the various research activities of the different groups of our Division. All of the data contained in the database that we provided have been measured in our laboratory.

14.2 Number of samples, geographical distribution and pedological variability

In addition to the data we already provided for the HYPRES soil database, our new set of soil data comprises 451 soil profiles, for which we have determined the physico-chemical and hydraulic characteristics of 623 soil horizons. This new database cover three Nations (Italy, Spain, and Germany; see Figure 14.1). The data collected in Italy pertain to a relatively wide variety of pedological and climatological conditions. However, because of the location of our university, it is worth noting that many soil samples show “andic” features since the investigated sites are affected by the presence of volcanos, like the Vesuvio or Vulture. A detailed list of sampling location is given in Table 14.1 .

Table 14.1. Sampling locations for the HYDI database.

Location	Nation	Project	horizons
Barrax	Spain	ESA-SEN2Flex	14
Demmin	Germany	ESA-AGRISAR	14
Upper Alento River catchment	Italy	MiUR/PON-AQUATEC	143
Gromola-Paestum	Italy	Local project	98
Torre Lama – Battipaglia	Italy	Local project	68
Corleto Perticara	Italy	EU-MEDALUS ; MiUR/PRIN	6
Catania	Italy	Local project	78
Monteforte Irpino	Italy	MiUR/PON- <i>PetitOSA</i>	9
Acerra	Italy	Local project	183
Giugliano	Italy	Local project	4
Succivo	Italy	Local project	3
Lusciano	Italy	Local project	3


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Soil moisture at local scale: Measurements and simulations



Nunzio Romano*

Department of Agriculture, Division of Agricultural, Forest and Biosystems Engineering, University of Napoli Federico II, Portici (Napoli), Italy

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SUMMARY

Soil moisture refers to the water present in the uppermost part of a field soil and is a state variable controlling a wide array of ecological, hydrological, geotechnical, and meteorological processes. The literature on soil moisture is very extensive and is developing so rapidly that it might be considered ambitious to seek to present the state of the art concerning research into this key variable. Even when covering investigations about only one aspect of the problem, there is a risk of some inevitable omission. A specific feature of the present essay, which may make this overview if not comprehensive at least of particular interest, is that the reader is guided through the various traditional and more up-to-date methods by the central thread of techniques developed to measure soil moisture interwoven with applications of modeling tools that exploit the observed datasets.

This paper restricts its analysis to the evolution of soil moisture at the local (spatial) scale. Though a somewhat loosely defined term, it is linked here to a characteristic length of the soil volume investigated by the soil moisture sensing probe. After presenting the most common concepts and definitions about the amount of water stored in a certain volume of soil close to the land surface, this paper proceeds to review ground-based methods for monitoring soil moisture and evaluates modeling tools for the analysis of the gathered information in various applications. Concluding remarks address questions of monitoring and modeling of soil moisture at scales larger than the local scale with the related issue of data aggregation. An extensive, but not exhaustive, list of references is provided, enabling the reader to gain further insights into this subject.

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1. Introduction

In general, soil moisture refers to the water present in the uppermost part of a field soil and is a state variable controlling a wide array of ecological, hydrological, geotechnical, and meteorological processes. Soil moisture also regulates the partitioning of the incoming solar energy at the land surface into the outgoing sensible, latent, and surface heat fluxes, mainly through the processes of soil evaporation and plant transpiration.

However, soil moisture does not have a single shared meaning among researchers belonging to different disciplines (Seneviratne et al., 2010). For example, agronomists and climatologists may prefer to look at soil moisture as the water-holding capacity of a land area, eco-hydrologists speculate more on the amount of water present in the rooting zone of a vegetated soil profile, whereas vadose zone modelers are mostly interested in water movement and solute transport issues, and often prefer to view soil moisture in

terms of total potential energy gradients. In an attempt to clarify and reconcile some different positions and perceptions that can be found in the literature on this topic, water held in the soil should be conveniently characterized in a unified way in terms of water energy status. Specifically, this status should be identified by the magnitude of the energy of water (the volumetric soil water content, θ) present in the soil volume at a certain energy level (the soil water potential, ψ). When addressing the issues of soil moisture dynamics, in principle one might refer to either θ or ψ , since a relationship exists between these two variables. For the definition and measuring methods of soil water potential the reader is directed to the many treatises and textbooks available in the literature (e.g., Young, 2002; Durner and Or, 2005). Instead, this review paper will address in greater depth the monitoring and modeling of soil water content as it is customarily accepted that soil moisture is the volume of water contained in a certain volume of soil in the field.

A more focused definition of soil moisture and its measuring techniques at a certain scale is imperative to avoid being swamped by documents of various types, with the risk of not being able to extract the information useful for the specific problem in hand.

* Address: Department of Agriculture, Division of Agricultural, Forest and Biosystems Engineering, University of Napoli Federico II, Via Università 100, 80055 Portici (Napoli), Italy. Tel.: +39 081 2539421; fax: +39 081 2539412.

E-mail address: nunzio.romano@unina.it

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Indirect field technology for detecting areas object of illegal spills harmful to human health: application of drones, photogrammetry and hydrological models

Alessandra Capolupo¹, Stefania Pindozi¹, Collins Okello², Lorenzo Boccia¹

¹University of Naples Federico II, Department of Agricultural Sciences, Portici, Italy; ²Gulu University, Department of Biosystems Engineering, Gulu, Uganda

Abstract. The accumulation of heavy metals in agricultural soils is a serious environmental problem. The Campania region in southern Italy has higher levels of cancer risk, presumably due to the accumulation of geogenic and anthropogenic soil pollutants, some of which have been incorporated into organic matter. The aim of this study was to introduce and test an innovative, field-applicable methodology to detect heavy metal accumulation using drone-based photogrammetry and micro-rill network modelling, specifically to generate wetlands prediction indices normally applied at large catchment scales, such as a large geographic basin. The processing of aerial photos taken using a hexacopter equipped with fifth-generation software for photogrammetry allowed the generation of a digital elevation model (DEM) with a resolution as high as 30 mm. Not only this provided a high potential for the study of micro-rill processes, but it was also useful for testing and comparing the capability of the topographic index (*TI*) and the clima-topographic index (*CTI*) to predict heavy metal sedimentation points at scales from 0.1 to 10 ha. Our results indicate that the *TI* and *CTI* indices can be used to predict points of heavy metal accumulation for small field catchments.

Keywords: photogrammetry, drones, topographic index, heavy metals soil pollution, health, Italy.

Introduction

The accumulation of heavy metals in agricultural soils is one of the currently most critical environmental problems, as these soil contaminations are absorbed by crops and ultimately affect food quality. It is important to know the concentrations of heavy metals in soil, since excessive accumulation causes serious health problems (Oliver, 1997; Muchuweti et al., 2006) of various kinds, particularly neurotoxicity, carcinogenicity and mutagenicity (European Union, 2002). For example, arsenic (As), mercury (Hg), zinc (Zn), copper (Cu) and aluminium (Al) affect the gastrointestinal system, generally resulting in diarrhoea and vomiting; at higher levels, these compounds cause systemic effects, such as depression tremor, ataxia, convulsions, paralysis, or pneumonia (McCluggage, 1991); Cadmium (Cd) is a potential carcinogen, commonly associated with symptoms from the cardiovascular, urinary and nervous systems (Jarup, 2003); lead

(Pb) and Cd may decrease human life expectancy up to 10 years (Lăcătușu et al., 1996).

The Italian situation with regard to soil contamination is extremely heterogeneous and complex. As many as 55 environmental sites of national interest (SIN) have been identified; six of them situated in the Campania region in southern Italy (Vito et al., 2009). These Campania areas are also among the 44 places listed by the National Institute of Health due to high levels of cancer risk correlated with high soil concentrations of heavy metals resulting from a combination of geogenic and anthropogenic pollution (Cicchella et al., 2005). Geogenic pollution is mainly linked to natural phenomena, such as volcanic activities and related hot springs and fumaroles (De Vivo, 1995), while anthropogenic pollution essentially has to do with industrial activity. The voluntary or accidental pollution of the latter has produced high concentrations of Cd, chromium (Cr), Cu, Hg, Pb, nickel (Ni) and Zn (Filippelli et al., 2012). High concentrations of most of these metals, as well as selenium (Se), can also be found along the road system, where they constitute pollution from motorized traffic (Albanese et al., 2012), while the use of inorganic pesticides and chemical fertilizers produce high concentrations of Cu, Hg, Mn, Pb and Zn in the fields used for agriculture (Swaine et al., 1962). Soil pollution includes also point sources like gasoline pumps and places where house-

Corresponding author:
Lorenzo Boccia
University of Naples Federico II
Department of Agriculture
Via Università 100, 80055 Portici, Naples, Italy
Tel. +39 081 253-9151
E-mail: lorenzo.boccia@unina.it

Conclusions

In this study, we introduced an innovative methodology for predicting the accumulation zones of substances that can disperse through aquifers. This approach looks promising because it reduces the cost of soil sampling by making it sufficient to take samples only from the points of maximum CTI (or TI) to determinate the sedimentation points of heavy metals.

Indeed, these reasons motivated us to apply this model in the Campania region in Italy, since it is characterized by a complex and difficult environmental situation.

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Hydrogeochemical characterization of the main aquifer of the “Litorale Domizio-Agro Aversano NIPS” (Campania – southern Italy)



Alfonso Corniello, Daniela Ducci*

Department of Civil, Architectural and Environmental Engineering, Università di Napoli Federico II, P.le Tecchio 80, 80125 Naples, Italy

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ABSTRACT

The aim of the paper is the identification in a wide area located north of Napoli city (southern Italy) of different sectors and/or different sources of anthropogenic or natural contamination in groundwater, in order to guide more effective decontamination intervention and to establish long-term environmental measures. Local administrators and environmental agencies can follow the methods used for this first characterization and zonation of a wide region for planning more focused investigations.

The area includes a large part of the “Litorale Domizio-Agro Aversano” NIPS, recognized by the Italian State as a National Interest Priority Site, where there is a need to implement characterization and remediation activities. In this area the main aquifer is located in the Volturno river plain; the intensive agriculture and the presence of numerous dumping sites (both legal and illegal), has produced widespread contamination, with many wells showing very high nitrate concentrations and point source pollution (heavy metals, hydrocarbons, pesticides) has also been noticed.

Moreover, groundwater presents different kinds of “natural contamination” such as high fluoride concentration (almost everywhere > 1.5 mg/L) and high arsenic concentration in the zones related to volcanic formations and, in some sectors, high sulphates deriving from present and/or past hydrothermal conditions. Close to the rivers, lower nitrate content is related to reducing conditions. Low sulphate contents and high Fe and Mn contents corroborate the presence of a reducing zone.

The groundwater quality in the plain is influenced mainly by groundwater subsurface flows from the carbonate aquifers and by the proximity of volcanic districts, as stressed also by the statistical analysis. Indeed, the zonation of hydrochemical facies on the basis of the statistical analysis indicates clearly the different processes occurring in the aquifer along the groundwater flow path (contaminated areas, areas with reducing conditions, areas with carbonate influence, etc.).

The main results are in the proposition of a synergic use of different kinds of data for sustainable aquifer management. Indeed, it is possible to rehabilitate wide areas by means of education, legislation and long-term environmental measures, without recourse to expensive treatment processes.

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1. Introduction

Knowledge of the hydrogeochemical background of an aquifer suggests how to evaluate recent evolution and changes. Indeed, understanding natural chemical processes occurring in the aquifer is a key factor to define natural trends and hence the type and extent of real contamination.

In the last 15 years, the Italian State has identified 57 National Interest Priority Sites (NIPSSs), areas where characterization and remediation activities have to be implemented, six of which are in Campania region (southern Italy), for a total surface of about 1600 km², with different levels and sources of pollution (Napoli Orientale, Litorale Domizio-Agro Aversano, Napoli Bagnoli Coroglio, Litorale Vesuviano, Bacino idrografico del Sarno; Aree di Pianura, Litorale Domizio-Agro Aversano NIPS,

encompassing the plains of the Garigliano River and of the Volturno River and partially the Phlegrean Fields volcanic area, includes a large part of the polluted agricultural land belonging to more than 61 municipalities in the Naples and Caserta provinces. Indeed, human activities are the cause of widespread NO₃ contamination, with many wells showing NO₃ concentrations higher than 50 mg/L. Isotope techniques (¹⁴N/¹⁵N) applied at a small part of the aquifer (Acerra area in Corniello and Ducci, 2009) indicated the nitrate contamination as a cumulative result of intensive cropping and livestock, but also of leakage from the sewage network. Moreover, in this area the soil contamination is due also to legal and illegal dumping of waste, with hazardous consequences for groundwater quality (Bove et al., 2011; Grezzi et al., 2011).

Within the Litorale Domizio-Agro Aversano NIPS, attention has focused on the central and southern areas, taken up largely by the Volturno River Plain groundwater body and by a part of the Phlegrean Fields volcanic groundwater body (Fig. 1). The Garigliano

* Corresponding author.

E-mail addresses: corniell@unina.it (A. Corniello), daniela@unina.it (D. Ducci).

Conclusions

Different aspects of the chemical processes occurring in the main aquifer of the NIPS are discussed in this paper. Starting from the hydrogeochemical background and analysing recent hydrochemical data, corroborated by statistical analysis, we were able to evaluate the groundwater contamination condition of the aquifers. It was possible to distinguish anthropogenic contamination from natural contamination. Also the statistical grouping of hydrogeochemical data by hierarchical cluster analysis (HCA) and by principal component analysis (PCA) shows drastically different geochemical conditions, separating contaminated waters from the background.

The first consists mainly of high NO_3 concentrations affecting a very large area (480 km²), as a result of different activities, often illegal, in a densely inhabited area with urban and peri-urban settlements. Hence, nitrate sources in groundwater are a cumulative result of intensive cropping and livestock, but also of leakage from the sewage network, which is often old and/or illegal. Water treatment processes for reducing nitrate contents cannot be carried out over such large areas, where nitrate concentrations will decrease only through a slow transfer of groundwater to the sea and the progressive dilution effect of infiltration water and groundwater inflows. Nevertheless, this natural process has to be coupled with strict agricultural and municipal policies, limiting the access of nitrogen compounds into the aquifer, and identifying areas vulnerable to nitrate contamination (91/676/EEC).

Natural contamination is present in several zones of the NIPS and it is linked to different factors (the volcanic nature of the area, the presence of mineral groundwater or else of reducing environments etc.). For example, high sulphate groundwater is present in the Acerra area, and anomalous fluoride contents affect a large part of the Campanian Plain. High As is present in the vicinity of the Phlegrean Fields and the Somma-Vesuvius volcano groundwater bodies and high levels of Fe and Mn are detected in groundwater near the Volturno river. For these areas, affected by natural contamination the definition, on the basis of the hydrogeochemical features of the aquifer, of the Natural Background Levels (GWDD 2006/118/ EC) is crucial to relieve local administrators and environmental agencies of expensive mitigation measures.

In conclusion, in the main aquifer of the NIPS the contamination can be properly controlled without recourse to expensive treatment processes, but by means of education, legislation and long-term environmental measures required for sustainable aquifer management.

Alfonso Corniello, Daniela Ducci (2014)

Hydrogeochemical characterization of the main aquifer of the "Litorale Domizio-Agro Aversano NIPS" (Campania — southern Italy)

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Air pollution and air quality state in an Italian National Interest Priority Site. Part 1: the emission inventory

Paolo Iodice*, Adolfo Senatore

Department of Industrial Engineering, University of Naples Federico II, Via Claudio 21, Naples 80125, Italy

Abstract

In Campania region, southern Italy, a National Interest Priority Sites (NIPS) was identified: “Litorale Domitio-Agro Aversano” NIPS L.426/98, that includes a large part of the polluted agricultural land, belonging to more than 61 municipalities in the Naples and Caserta provinces. This paper represents a synthesis of a study developed for a LIFE project (LIFE11/ENV/IT/275–ECOREMED): “Implementation of Eco-Compatible Protocols for Agricultural Soil Remediation in Litorale Domizio-Agro Aversano NIPS”. As well known, the pollutants of the air may have an impact on the soil pollution; the contribution of the paper to this LIFE project is to provide the environmental characterization of the area, estimating the total annual emissions of the main air pollutants (CO, VOC, NOX and PM10) in the area under investigation, with municipal spatial disaggregation. The amounts of air pollutants emitted from various sources in this area were obtained through direct and continuous measures for the principal industrial systems, while for diffused sources the emissions were estimated on the basis of opportune activity indicators and fixed emission factors concerning specific emissive activities.

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Keywords: emission inventory; bottom-up approach; industrial pollution sources; COPERT methodology

1. Introduction

The past century witnessed a relevant increase in global pollution due to the high production and use of petroleum derived compounds which were carelessly released into the environment. As a consequence numerous organic contaminants are now present in soils and water of terrestrial polluted sites. Furthermore industrial plants, mining

* Corresponding author. Tel.: +390817683277; fax: +39081 2394165
E-mail address: paolo.iodice@unina.it

Conclusions

In the “Litorale Domitio-Agro Aversano” NIPS area a high level spotted soil contamination is due to the legal and outlaw industrial and municipal wastes dumping, with hazardous consequences also on the quality of the air and water table. The main objective of this study was to produce an air pollutants emissions inventory of this area, which expressly include a distribution in space for all the emissive sources, classified in different categories. Among these, two categories of emission sources were taken into account in great detail: mobile sources (meaning the road traffic) and stationary sources (mainly industry and power plants). These sources, in fact, represent in many European country the lion part of the anthropogenic emissions for the contaminants considered in this paper: CO, NO_x, PM₁₀ and VOC. The analysis of these results show clearly that in the NIPS area a considerable part of total emissions is due to contribution of road traffic. The road transport sector, in fact, contribute for about 83% and 41% of CO and VOC total emissions respectively, while regarding the total emission of NO_x and PM₁₀ it's responsible for about 28% and 39% of these pollutants. The results of the environmental pressure were analyzed to produce maps of this area with spatial disaggregation of municipal type, in which the different communes are aggregated for similar pollution levels. Atmospheric emission inventory so obtained is therefore an important tools for studying air quality and to set up possible remediation plans in the zones of this area characterized by nonattainment of the limit values established by legislation. The creation of this spatially distributed emission inventory with a relatively high resolution, in fact, is part of a bigger project aiming at the development of air quality and meteorological modelling tools for the NIPS area. Lastly, starting from these tools, it will be possible to formulate remediation actions.

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Air pollution and air quality state in an Italian National Interest Priority Site. Part 2: the pollutant dispersion

Paolo Iodice*, Adolfo Senatore

Department of Industrial Engineering, University of Naples Federico II, Via Claudio 21, Naples 80125, Italy

Abstract

In Campania region, southern Italy, a National Interest Priority Sites (NIPS) was identified: “Litorale Domitio-Agro Aversano” NIPS L.426/98, that includes a large part of the polluted agricultural land, belonging to more than 61 municipalities in the Naples and Caserta provinces. This second paper represents an analysis developed for a LIFE project (LIFE11/ENV/IT/275–ECOREMED): “Implementation of Eco-Compatible Protocols for Agricultural Soil Remediation in Litorale Domizio-Agro Aversano NIPS”. The contribution of this second paper to the above-mentioned LIFE project consists in the appraisal of the air quality state in this NIPS area, estimating the pollutant concentrations of the main air pollutants (CO, VOC, NO_x and PM₁₀) in the area under investigation due to the principal industrial systems (namely punctual sources) and to the main diffused sources. All entropic activities which determine emissions in the atmosphere, in fact, depending on the distance from the areas under examination, could contribute to the soil qualification. The assessment of the air quality to local scale was carried by integrating the data of emission inventory in the NIPS area, that was estimated and reported in the first paper (Part 1), with elaborations of a Gaussian dispersion model.

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Keywords: air pollution; emission inventory; air quality state; gaussian dispersion model

1. Introduction

In Campania region, Southern Italy there were identified four National Interest Priority Sites (NIPSS), for a total surface of about 200.000 ha, with different levels and sources of pollution (Napoli Orientale, Litorale Domitio-Agro

* Corresponding author. Tel.: +390817683277; fax: +39081 2394165
E-mail address: paolo.iodice@unina.it

Conclusions

The aim of this paper was to provide the environmental characterization of the “Litorale Domitio-Agro Aversano” NIPS area for a LIFE project (LIFE11/ENV/IT/275–ECOREMED), estimating the air quality state to local scale through the use of a dispersion model. The pollutants covered by this analyses are: carbon monoxide (CO), nitrogen oxides (NO_x), particulate matter (PM₁₀) and volatile organic compounds (VOC). The results obtained in this study supply a valid environmental programming instrument and an important tool for studying air quality and to set up possible remediation plans in the zones of the investigated area that are characterized by nonattainment of the limit values established by legislation; starting from these maps and these tools, it will be possible to formulate maintenance and remediation actions. In fact, the same procedures and simulation models can be used to examine strategies oriented to the air quality improvement; so new emissive background will be defined according to the adoption of new environmental laws and to the virtual implementation of low environmental impact technologies in the several analysed fields (transports, productive activities, energetic efficiency, etc.). However, future changes in pollutant emissions and in the air quality will be affected intensely by the evolution in anthropogenic emissions, that are always regulated by economic growth, environmental policy, and future application of emissions controls. Lastly, the emission inventory and this environmental characterization must be considered as a dynamic instrument since both the updating of many information and the data reliability and detail are in continuous evolution and improvement.

Paolo Iodice, Adolfo Senatore (2014)

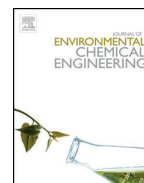
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Simulated solar photocatalytic processes for the simultaneous removal of EDDS, Cu(II), Fe(III) and Zn(II) in synthetic and real contaminated soil washing solutions



Suëllen Satyro^a, Marco Race^b, Raffaele Marotta^{c,*}, Marcia Dezotti^a, Danilo Spasiano^c, Giuseppe Mancini^d, Massimiliano Fabbicino^b

^a Federal University of Rio de Janeiro, COPPE – Chemical Engineering Program, Centro de Tecnologia, Cidade Universitária, Bloco G, sala 115, Rio de Janeiro, Brazil

^b Department of Civil, Architectural and Environmental Engineering, University of Naples “Federico II”, p.le V. Tecchio 80, 80125 Naples, Italy

^c Department of Chemical Engineering, Materials and Industrial Production, University of Naples “Federico II”, p.le V. Tecchio 80, 80125 Naples, Italy

^d Department of Industrial Engineering, University of Catania, v.le A. Doria 5, 95125 Catania, Italy

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ABSTRACT

Metal contamination of natural soil is a global problem. In many cases the contamination is due to anthropogenic activities, and, sometimes, it comes from illegal waste disposal due to uncontrolled industrial development. One of the ways of solving metal soil contamination is by soil washing using a chelating biodegradable agent (EDDS). However, the resulting liquid wastes that contain the extracted metals and chelating agents have to be submitted to further treatments for a complete detoxification before being discharged into the environment. The simultaneous removal of EDDS and three metals (Cu, Fe and Zn) from both synthetic waters (home prepared) and real contaminated soil washing mixtures at neutral pH has been investigated, a lab-scale, considering four artificial solar driven photocatalytic technologies (TiO₂/hν/N₂, TiO₂/hν/air, Fe(III)-EDDS/hν/air and Fe(III)-EDDS/hν/H₂O₂/air). The soils were sampled in the Province of Naples (South of Italy) in a zone infamously known for its high incidence of cancer mortality. The results indicate that both the type and the sequence of photocatalytic technologies that need to be applied should be chosen prudently considering both the nature and the content of the soil washing solutions.

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Introduction

The metal contamination of natural soils is a worldwide concern because of the negative effect that metals could have on living beings [1]. In order to face the problem, several remediation techniques, based on physical, chemical, and even biological processes, have been proposed [2,3]. Among these techniques, soil washing certainly plays a primary role because of its proven efficiency for various soil characteristics and metal types [4,5]. As is well known, soil washing is an off-site treatment that includes the removal of contaminants from the solid phase, using an appropriate washing solution, and a subsequent treatment of the liquid phase containing the extracted metals, for its complete

detoxification [6]. Although in the past 20 years many compounds have been tested as washing agents [4,5], the most frequently used ones today are those belonging to aminopolycarboxylate chelants groups (APCs) [2,7,8]. Most of the studies concerning the use of APCs processes have been carried out in aqueous solutions containing ethylenediaminetetraacetic acid (EDTA) because of its easy availability and relatively low cost [9,10]. Unfortunately, EDTA is quite persistent in the environment as it is poorly biodegradable [8]. Therefore, more and more often ethylenediaminedisuccinic acid (EDDS) is proposed as a safe and environmentally friendly replacement for EDTA in soil washing processes [11–13].

Although the S,S-stereoisomeric form of EDDS is considered to be easily biodegradable, the biodegradability of the complexes formed between S,S-EDDS and the heavy metals extracted during the washing process is still under discussion [14]. This is why it is extremely important to find an appropriate technique for exhausted EDDS washing solution detoxification. In this context

* Corresponding author. Tel.: +39 817682968; fax: +39 815936936.

E-mail address: rmarotta@unina.it (R. Marotta).

Conclusions

The results demonstrate that for the removal of EDDS and copper, zinc and iron metals from synthetic solutions and real soil washing mixtures a different photocatalytic treatment is necessary.

For the field scale, prior the photocatalytic processes, consideration must be given to the real washing solution, because treatments aimed to remove the residual turbidity are required.

The EDDS removal degrees, obtained using $\text{TiO}_2/\text{hv}/\text{N}_2$ or $\text{TiO}_2/\text{hn}/\text{air}$ processes on the real solutions ($[\text{EDDS}]_0$ 0.36 mM, TiO_2 load = 100 mg L⁻¹), are close to 70–80% after 3 h of treatment, while shorter reaction times (10 min) are necessary to reach the same percentage conversion degrees for synthetic contaminated water with $\text{TiO}_2/\text{hn}/\text{air}$, Fe(III)-EDDS/hn/air and Fe(III)-EDDS/hn/H₂O₂/air processes. Of all the investigated metal species, only cupric ions can be removed by photoreduction to zero-valent copper through the $\text{TiO}_2/\text{hn}/\text{N}_2$ process for both synthetic and real aqueous solutions. The results indicate that both the type and the sequence of photocatalytic technologies that need to be applied to simultaneously remove EDDS and metals, such as copper, iron and zinc, from soil washing mixtures, should be chosen prudently on the basis of the nature and the content of the soil washing solutions. Before directly exploiting natural sunlight by carrying out the photocatalytic experiments under outdoor conditions, further investigations, using artificial solar radiation on real soil washing waters are strongly recommended in order to choose the best sequence of photocatalytic steps in order to achieve the concentration limits established in the national regulations.

Suëllen Satyro, Marco Race, Raffaele Marotta, Marcia Dezotti, Danilo Spasiano, Giuseppe Mancini, Massimiliano Fabbricino (2014)

Simulated solar photocatalytic processes for the simultaneous removal of EDDS, Cu(II), Fe(III) and Zn(II) in synthetic and real contaminated soil washing solutions

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 Removal of EDDS and copper from waters by TiO₂ photocatalysis under simulated UV–solar conditions

 Suéllen Satyro^a, Raffaele Marotta^{b,*}, Laura Clarizia^b, Ilaria Di Somma^c, Giuseppe Vitiello^{b,d}, Marcia Dezotti^a, Gabriele Pinto^e, Renato F. Dantas^f, Roberto Andreozzi^b
^a Federal University of Rio de Janeiro, COPPE – Chemical Engineering Program, Centro de Tecnologia, Bloco G, sala 115, Cidade Universitária, Rio de Janeiro, Brazil

^b Department of Chemical Engineering, Materials and Industrial Production, University of Naples “Federico II”, p.le V. Tecchio 80, 80125 Naples, Italy

^c Istituto di Ricerche sulla Combustione, Centro Nazionale delle Ricerche IRC-CNR, p.le V. Tecchio 80, 80125 Naples, Italy

^d CSGI – Consorzio interuniversitario per lo sviluppo dei Sistemi a Grande Interfase, Italy

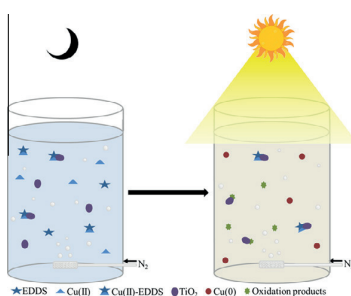
^e Department of Biology, University of Naples “Federico II”, 80139 Naples, Italy

^f Department of Chemical Engineering, University of Barcelona, Martí i Franquès 1, 08028 Barcelona, Spain

HIGHLIGHTS

- Simultaneous EDDS oxidation and Cu(II) reduction through TiO₂ solar photocatalysis.
- Evaluation of the influence of several operating conditions on system reactivity.
- The oxidation of EDDS proceeds mainly through the interaction with positive holes.
- Simplified reaction pathways for EDDS photocatalytic oxidation are proposed.
- The process is capable to reduce the ecotoxicity of the Cu/EDDS solution.

GRAPHICAL ABSTRACT



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ABSTRACT

The TiO₂ photocatalytic oxidation of the *N,N*-ethylenediamine-disuccinic acid and Cu(II) ions photoreduction were investigated in acidic solutions. The experimental results indicated a conversion of 100% for both EDDS and Cu(II) species whereas the mineralization degree was quite small (24%). The influence of several experimental variables, like purging gas, counter ion nature, pH, TiO₂ type, photocatalyst load, initial concentration of cupric ions, radiation source (natural or artificial), was investigated. For almost equimolar feed ratios of reactants, EDDS was not totally removed whereas Cu(II) species were completely reduced. An analysis of the data collected indicated a Cu(II)/EDDS molar consumption ratio close to two.

The presence of oxygen decreased the photoreduction process of Cu(II) species, whereas the initial concentration of Cu(II) ions and the counter ion (excepted for the chloride ions) did not affect the photocatalytic process. Ecotoxicity tests (*Pseudokirchneriella subcapitata* and *Lemna minor*) on treated samples indicated a marked decrease of the ecotoxicity for very prolonged reaction times.

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1. Introduction

Many “*in situ*” and “*ex situ*” treatment techniques are available to accomplish the difficult task of cleaning soils polluted by heavy

* Corresponding author. Tel.: +39 0817682968.

 E-mail address: rmarotta@unina.it (R. Marotta).

Conclusions

The results showed the possibility to use EDDS as sacrificial agent in the TiO_2 -photocatalytic process under inert atmosphere for Cu(II) reduction. The data showed a conversion of 100% for both species whereas the mineralization degree is small (24%). Chemical intermediates, formed during the process, are capable to contribute to the complete reduction of metallic ions present in the solution. Different types of TiO_2 can be used with small differences, with the only exception of rutile. The initial Cu(II) concentrations and the counter ions, with the exception of chloride ions, do not affect the system reactivity. It has been also demonstrated the possibility to remove copper from the solution under outdoor conditions. In presence of natural radiation, instead of artificial one, the rates of EDDS and Cu(II) removals are about four times slower.

The ecotoxicity assessment showed the efficiency of the process to reduce the toxicity of the starting solution. On the basis of the results collected during the present investigation it can be stated that the photo-oxidation of EDDS proceeds mainly through its direct interaction with positive holes on the catalyst surface. Chelated cupric ions seem to be the only copper form capable of reduction through reactions with photoelectrons.

Suéllen Satyro, Raffaele Marotta, Laura Clarizia, Ilaria Di Somma, Giuseppe Vitiello, Marcia Dezotti, Gabriele Pinto, Renato F. Dantas, Roberto Andreozzi (2014)

REMOVAL OF EDDS AND COPPER FROM WATERS BY TiO_2 PHOTOCATALYSIS UNDER SIMULATED UV-SOLAR CONDITIONS.

Chemical Engineering Journal Volume 251, 1 September 2014, Pages 257–268

Research Article

***Methylobacterium populi* VP2: Plant Growth-Promoting Bacterium Isolated from a Highly Polluted Environment for Polycyclic Aromatic Hydrocarbon (PAH) Biodegradation**

**Valeria Ventrino,¹ Filomena Sannino,¹ Alessandro Piccolo,¹
Valeria Cafaro,² Rita Carotenuto,² and Olimpia Pepe¹**

¹ DIA-Dipartimento di Agraria, Università degli Studi di Napoli Federico II, Via Università 100, 80055 Portici, Italy

² Dipartimento di Biologia, Università degli Studi di Napoli Federico II, Complesso Universitario Monte S. Angelo, Via Cintia 4, 80126 Napoli, Italy

Correspondence should be addressed to Olimpia Pepe; olipepe@unina.it

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The use of microorganisms to accelerate the natural detoxification processes of toxic substances in the soil represents an alternative ecofriendly and low-cost method of environmental remediation compared to harmful incineration and chemical treatments. Fourteen strains able to grow on minimal selective medium with a complex mixture of different classes of xenobiotic compounds as the sole carbon source were isolated from the soil of the ex-industrial site ACNA (Aziende Chimiche Nazionali Associate) in Cengio (Savona, Italy). The best putative degrading isolate, *Methylobacterium populi* VP2, was identified using a polyphasic approach on the basis of its phenotypic, biochemical, and molecular characterisation. Moreover, this strain also showed multiple plant growth promotion activities: it was able to produce indole-3-acetic acid (IAA) and siderophores, solubilise phosphate, and produce a biofilm in the presence of phenanthrene and alleviate phenanthrene stress in tomato seeds. This is the first report on the simultaneous occurrence of the PAH-degrading ability by *Methylobacterium populi* and its multiple plant growth-promoting activities. Therefore, the selected indigenous strain, which is naturally present in highly contaminated soils, is good candidate for plant growth promotion and is capable of biodegrading xenobiotic organic compounds to remediate contaminated soil alone and/or soil associated with plants.

1. Introduction

The accumulation of large amounts of persistent chemicals in the soil from urban, industrial, and agricultural activities is an increasingly important worldwide problem. In Italy, the ex-industrial site of ACNA (Aziende Chimiche Nazionali Associate) in Cengio (Savona, Italy) was contaminated by different classes of organic compounds and is on the list of national priorities for environmental reclamation.

Among the most common pollutants in contaminated environments, polycyclic aromatic hydrocarbons (PAHs) are fused-ring aromatic compounds that exist in nature as a

result of anthropogenic polluting events such as waste combustion, industrial treatment, and petroleum processing [1]. PAHs have been recognised to be mutagenic, carcinogenic, and cytotoxic to humans and animals [2]; therefore, their presence in contaminated soils represents a significant risk to the environment due to their intrinsic chemical stability, lower solubility, and high recalcitrance to different types of degradation [3]. For this reason, the United States Environmental Protection Agency (US EPA) considers PAHs to be priority pollutants for remediation.

Numerous physical and chemical technologies, such as soil washing, have been developed to remove PAHs from the

Conclusions

The effectiveness of the selective ecological strategy employed in this study allowed for the isolation of indigenous strains that are naturally present in highly contaminated soils. The strain *M. populi* VP2 demonstrated multiple plant growth promotion activities because it was able to produce IAA and siderophores and solubilise phosphate; interestingly, VP2 was able to produce biofilms in the presence of phenanthrene and alleviated PHE stress in tomato seeds. To our knowledge, this is first report describing the simultaneous occurrence of multiple plant growth-promoting activities and the potential biodegradation of xenobiotic organic compounds of industrial origin in *M. populi* VP2. Therefore, this selected strain could be a good candidate to employ in bioremediation strategies to remediate contaminated agricultural soil and may be useful in microbe-assisted phytoremediation.

Ventorino V., Sannino F., Piccolo A., Cafaro V., Carotenuto R., Pepe O. (2014)
Methylobacterium populi VP2: plant growth-promoting bacterium isolated from a highly polluted environment for polycyclic aromatic hydrocarbon (PAH) biodegradation
The Scientific World Journal, Article ID 931793 p. 1-11; DOI: 10.1155/2014/93179

LECTURES

XXXI Convegno Nazionale Società Italiana Di Chimica Agraria. 16-17 Settembre 2013, Napoli, Italia

MOBILITY AND BIOAVAILABILITY OF POLLUTANTS IN PILOT-SCALE FIELDS UNDER BIOREMEDIATION

Claudia Rocco¹, Dario Monaco², Paola Adamo¹, Salvatore Di Rosa³, Ida Duro⁴, Angela Vetromile³, Maria Di Rosa³, Mariano Peri³, Massimo Fagnano^{1,4}

1 Dipartimento di Agraria, Università di Napoli Federico II, Portici, Italy; 2 Dipartimento di Scienze e tecnologie, Università di Napoli Parthenope, Napoli, Italy 3 ARPAC – Agenzia Regionale per la Protezione Ambientale della Campania, Napoli, Italy; 4 CIRAM - Università di Napoli Federico II, Napoli, Italy;

The past century witnessed a relevant increase in global pollution due to the high production and use of petroleum derived compounds which were carelessly released into the environment. As a consequence numerous organic contaminants (PAHs) and potentially toxic elements (PTEs) are now present in soils and water of terrestrial polluted sites, which represent a relevant environmental concern due to their potential accumulation in the food chain. In Campania region, southern Italy, were identified five National Interest Priority Sites (NIPs), for a total surface of about 200.000 ha, with different levels and sources of pollution. The NIPs “Litorale Domitio-Agro Aversano (NIP L. 426/98) includes a large part of the polluted agricultural land, belonging to more than 61 municipalities in the Naples and Caserta provinces and the main pollution source is due to legal and outlaw industrial and municipal wastes dumping. The consequences of this, have been the abandonment of wide agricultural areas and the impairment of the image of population, economic activities and agricultural products.

The project LIFE ECOREMED “Implementation of eco-compatible protocols for agricultural soil remediation in Litorale Domizio-Agro Aversano NIPs”, intends to define an operative protocol for agriculture-based bioremediation of contaminated agricultural soils in the above described NIPs, including the use of biomasses for renewable energy production. In this framework, the C1 action aims to: 1) investigate pollutants mobility/bioavailability before, during and after the applied bioremediation processes; 2) test the effects of applied bioremediation processes on soil chemical and biological properties; 3) investigate pollutants mobility/bioavailability as influenced by changes in soil properties associated with bioremediation.

The long stability of pollutants in soils undergoing bioremediation and phytostabilization can be predicted for selected environmental scenarios by conducting simple leaching tests and more detailed chemical extractions and by direct soil analysis using advanced spectroscopic techniques. Knowing what kind of compounds and molecular bonds prevail between pollutants and soil constituents, allows prediction of their possible fate in soil-plant system.

In the first 6 months of activity the C1 research team established soil sampling and analytical protocols, carried out samplings with mapping and performed preliminary characterization of soil pollution.

7th International Conference on Environmental Engineering and Management - Integration Challenges for Sustainability - 18 - 21 September 2013, Vienna, Austria

TIO₂ PHOTOCATALYTIC COPPER REMOVAL FROM AQUEOUS SOLUTIONS CONTAINING CU(II) AND ETHYLENEDIAMINEDISUCCINIC ACID (EDDS)

Suéllen Satyro^{1,2*}, Laura Clarizia², Iliaria Di Somma³, Raffaele Marotta², Renato F. Dantas⁴, Marcia Dezotti¹, Roberto Andreozzi²

¹*Federal University of Rio de Janeiro, COPPE – Chemical Engineering Program, Centro de Tecnologia, Bloco G, sala 115, Cidade Universitária, Rio de Janeiro, Brazil, E-mail: *: satyro@gmail.com (S. Satyro).*

²*Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università di Napoli "Federico II", p.le V. Tecchio 80, 80125 Naples, Italy.*

³*Istituto di Ricerche sulla Combustione, CNR, p.le V. Tecchio 80, 80125 Naples, Italy.*

⁴*Department of Chemical Engineering, University of Barcelona, Martí i Franquès 1, 08028 Barcelona, Spain.*

Soils polluted by metals are widespread across the world. Many in-situ and ex-situ treatment techniques are available to accomplish the difficult task of cleaning polluted soils. Soil washing, an ex-situ technique, in which chelating agents are used, is indicated as one of the most suitable process to achieve this goal. The treatment is generally carried out in a closed reactor in which the soil removed from the site is contacted with the chelating agent. At the end of the treatment, the soil is separated from the extracting solution containing the metals and is returned on the site.

EDTA resulted from many studies as the most suited among the possible chelating agents capable of removing, for example, between 45 and 100 % of Pb or 47 and 98 % of Cu from various contaminated soils. Although EDTA has been one of the most used chelating agent for metal removal from solid matrices, due to its capability to ensure very high efficiency, many concerns have been raised in the past relating to its low biodegradability and consequent persistence in the environment. In fact, even if the most part of the chelating agent is removed from the soil before it returns to the field, some little amounts always remain in and its persistence may result into metal complexes leaching deep into the soil and contaminating groundwater. To overcome the difficulties connected with the use of EDTA, in recent years, the easily biodegradable isomer [S,S]EDDS has been proposed to replace it in soil washing. It is important to stress that [S,S]EDDS degrades better than the mixture of the two isomers (S,S) and (R,R). However, some indications are also reported in the literature that the [S,S]EDDS complexes of Cu, Ni, Co and Hg resulted not biodegradable.

It is clear that once the metals have been extracted from the soil matrix, it is necessary to recover them from the aqueous solution. Some reports indicate that the treatment of aqueous streams containing complexed metals with chelating agents employing traditional techniques such as precipitation is generally unsuitable due to the stability of complexes. Therefore, the possibility

to destroy the organic species (and the complexes) by means of TiO_2 photocatalysis has been proposed in the past for the case of EDTA. Similar problems for metal recovery can be expected when EDDS is used as chelating agent. However, no previous investigations, at the best of Authors' knowledge, have been published on EDDS/metal complex removal through TiO_2 photocatalysis. It is of particular interest the case of the extracting solution of EDDS in the presence of cupric ions, since it is well known that the latter one can be removed from solution after a photocatalytic reduction to zero-valent state made possible by an organic species undergoing, under de-aerated conditions, and an oxidation process (sacrificial photocatalysis). Hence, the present investigation aimed at evaluating the possibility of recovering copper from an aqueous solution in which initially cupric ions and EDDS molecules are present by using sacrificial photocatalysis.

To determine the total EDDS concentration in the solution, the analytical procedure proposed in the literature was adopted. A modification of this procedure allowed also measuring the concentration of total cupric ions in the reacting solution. At $\text{pH}=2.0$, preliminary results indicated that the system copper/EDDS was not interested by a direct photolysis whereas no indications about adsorption of the two species were found during experiments without TiO_2 under illumination. Successive runs, under de-aerated conditions, on solutions containing cupric ions (1mM), EDDS (0,20mM) and TiO_2 showed a marked reactivity increasing as the TiO_2 load was raised (Figure 1-a, 1-b).

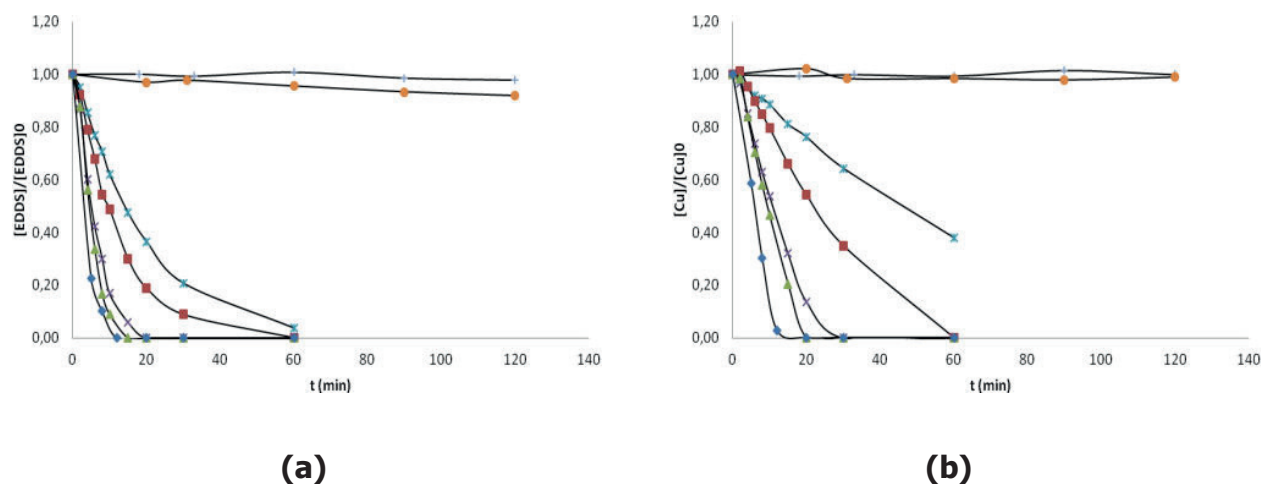


Figure 1: EDDS (a) and copper (b) removals at dark (+) in presence of TiO_2 , directly photolysis (●) in presence of copper, and photocatalysis with different loads of TiO_2 (25 (*), 50 (■), 75 (×), 100 (▲) and 500 (◆) ppm), at $\text{pH} 2$. $[\text{EDDS}]_0 = 0,20\text{mM}$; $[\text{Cu(II)}]_0 = 1.00 \text{ mM}$.

The samples collected during some runs were concentrated through lyophilization and submitted to HPLC analysis. The identification of the peaks observed in the chromatograms was done by comparing the retention times and UV spectra with those of selected standards. At the end of this work it was possible to state that oxalacetic acid and glyoxalic acids were present in the reacting solution during the investigated process. An attempt at identifying the reaction pathways through which these species could form was also done in agreement with the literature.

Geophysical Research Abstracts Vol. 16, EGU2014-11272, EGU General Assembly 2014.

DISTRIBUTION PATTERNS AND SOURCES OF METALS AND PAHS IN AN INTENSELY URBANIZED AREA: THE ACERRA–POMIGLIANO-MARIGLIANO CONURBATION (ITALY).

Albanese S., Lima A., Rezza C., Ferullo G., De Vivo B.

Dipartimento di Scienza della Terra, dell'Ambiente e delle Risorse - Università Federico II di Napoli

The main objective of the URGE (URban GEOchemistry) project is to define, map and interpretate the geochemical baseline patterns of potentially harmful elements and compounds in the soils of 12 European urban areas using shared procedures for both sampling and analytical techniques. In Italy, in the framework of the URGE project, the north-eastern sector of the Napoli metropolitan area, namely the Acerra-Pomigliano-Marigliano conurbation, has undergone a geochemical characterization based on 145 soil samples collected over an area of 90 sq km. This area has been selected on the basis of the results obtained from previous regional studies [1, 2, 3] and because of the presence on its territory of an historical industrial settlement (formerly devoted to plastic materials and synthetic fibres production) which was partly dismantled and partly converted to a power plant fuelled by palm oil. Furthermore, in March 2009 also an incinerator came into operation in the northern sector of the study area. The main objective of the study carried out for the Acerra-Pomigliano-Marigliano conurbation was to define the local geochemical baselines for both 53 elements (among which the toxic ones) and some organic compounds, including PAHs and OCPs. The study also aimed at supporting epidemiological researches at local scale and at establishing a record of the actual environmental conditions to evaluate the future impact of the incinerator on both the territory and the public health. Results obtained showed that Pb, Zn and V exceed the trigger limits established by the Italian Environmental law (D.Lgs. 152/2006) especially in correspondence with the most densely populated areas of the conurbation and where the traffic load is higher (Road junctions and fast lanes). Furthermore, most of the soils collected in the surroundings of the urbanized areas resulted to be generally enriched in Cu, Co, Cd, Be, Ni and P suggesting the presence of a relevant influence on their chemistry of an agricultural intensive land use. PAHs distribution pattern showed anomalous values across the whole study area. Especially, Benzo[a]pyrene values exceeds the trigger limits established by the Italian Environmental law (D.Lgs. 152/2006) in most of the analyzed soils and the diagnostic ratios calculated among several PAHs compounds suggested that the biomass burning in the rural sector of the study area could be a relevant source of pollution. The palm oil fuelled power plant in the northern sector of Acerra could not be excluded as a source of PAHs in the environment.

“International PhD Winter School organized by Italian Society of Agricultural Chemistry, Piacenza, 17-20 February 2014.”

MOBILITY AND BIOAVAILABILITY OF POLLUTANTS IN SOILS FROM ‘TERRA DEI FUOCHI’ (CAMPANIA REGION)

Claudia Rocco¹, Paola Adamo¹, Salvatore Di Rosa², Ida Duro³, Angela Vetromile², Massimo Fagnano^{1,3}

¹Dipartimento di Agraria, Università di Napoli Federico II, Portici, Italy;

²ARPAC – Agenzia Regionale per la Protezione Ambientale della Campania, Napoli, Italy;

³CIRAM - Università di Napoli Federico II, Napoli, Italy;

This work was carried out within the LIFE project ECOREMED *Implementation of eco-compatible protocols for agricultural soil remediation in Litorale Domizio-Agro Aversano RIPS (ex-NIPS L. 426/98)*, Campania region (Southern Italy). The area, commonly known as ‘Terra dei Fuochi’, is characterized by a diffuse land abuse mainly through legal and illegal activities of wastes dumping and incineration. The LIFE project intends to define an operative protocol for agriculture-based bioremediation of polluted soils, including the use of biomasses for renewable energy production.

This study was aimed to characterize the potentially toxic elements (PTE) pollution in terms of fractionation of total content among main soil geochemical forms and main pools or fractions available to plants.

Four abandoned agricultural sites were chosen in the districts of Giugliano (NA), Teverola, Trentola Ducenta and Castel Volturno (CE). From each site, soil samples, according to a grid of 10x10m cells, were collected. Pseudototal content of 16 PTE defined by Italian legislation (DL 152/2006) was measured by *acqua regia*. EU-MTP sequential extractions, EDTA 0.05 mol l⁻¹ pH7 and leaching test UNI EN ISO 12457-2/2004 were applied to define forms, phytoavailability and mobility of elements in soil.

Copper, Pb, Zn and Cr were the main pollutants exceeding the Italian legal limits (respectively 150, 100, 150, 150 mg/kg). Berillium, Sn and V, also above the limits (in order 2, 1, 90 mg/kg), were naturally enriched in soils according to Ispra 2010 (baselines for Be 6, Sn 4, V 150 mg/kg).

A very low mobility characterizes all pollutants, likely due to the general alkaline pH and fine texture of the studied soils. Nevertheless, the potentially phytoavailable quantity (as assessed by EU-MTP and EDTA) was for some pollutants a consistent fraction of the total (for Cu 48-65%), indicating a potential effectiveness of the phytoextraction remediation techniques.

GnosisGIS 2014 International Society ‘for Geospatial Health - 8th International Symposium on Geospatial Health “What’s New ... A Global Health Observation System” - New Orleans, Louisiana October 31 - November

LEAD CONCENTRATION IN SOIL VS GEOGRAPHIC POPULATION

De Vivo Benedetto¹, Albanese Stefano¹, Lima Annamaria¹, Pindozi Stefania², Capolupo Alessandra², Boccia Lorenzo²

¹ *Dipartimento di Scienze della Terra, dell’Ambiente e delle Risorse, University of Naples Federico II, Naples Italy*

² *Department of Agriculture, University of Naples Federico II, Naples Italy*

Campania region has always been known for the beauty and prosperity of its landscapes. Unfortunately, nowadays, it is in an extremely critical environmental situation. In fact, although it occupies the 18th position in the national ranking of the death rate, it occupies the 1st place in the annual report of male cancer mortality rate and the 3rd position in the national report of female cancer death rate. This situation could be explained by a combination of geogenic and anthropogenic pollution. Tap waters are quite well controlled, but, so far, no systematic monitoring on soils and air pollution has been achieved. Recently, accurate studies, with a nominal sampling density of about 5 x 5 km on the entire region and 1 x 1 km on the north - western part of the National Interest Priority Site (NIPS) “Litorale Domizio-Agro Aversano”, have been carried out on soils of the entire Campania region by some of authors of this abstract.

The study is focused on Lead (Pb) distribution on the overall territory due to its relation exceedence of this elements with the increasing of cancer incidence. In the soils of the NIPS “Litorale Domizio-Agro Aversano”, are present Pb anomalous high concentrations; in the same area have been as well individuated different illegal waste disposals. The Pb distribution maps, elaborated by means of multifractal IDW method, show a higher concentration in the north - western part of the NIPS and some subordinately smaller ones in the remaining areas of the NIPS. Based on such results, using remote sensing images to 5m (RapidEye) and by applying eCognition software, were derived the urban areas and was estimated the total population through a statistical modeling methods based on the relationship between people and dwelling units.

The geographical correlation between the Pb anomalies and population density has enabled us to identify areas with higher and lower human health risk.

International Symposium on Amphibian and Reptilian Endocrinology and Neurobiology 2014 (ISAREN)", November 7-9 at National Institute for Basic Biology, Okazaki, Japan

LIZARD SPERMATOGENESIS AS SOIL REMEDIATION BIOSENSOR: LIFE 11 ENV/IT/275 ECOMERED PROJECT, C2C SUB-ACTION

Giulia Guerriero¹, Gaetano Ciarci¹

¹Dipartimento di Biologia, Università di Napoli Federico II, Napoli, Italy

Recent developments in applied research have sought to incorporate novel operative protocol for agriculture-based restoration of contaminated agricultural soils, multi-functionality and landscape identity in the NIPS (National Interest Priority Site). Topics of LIFE 11 ENV/IT/ 275 ECOMERED project include, in C2c sub-action, the bio-monitoring of oxidative damage and characterization of reproductive health status of selected vertebrate and invertebrate species. The gonadal tissue, with abundance of highly unsaturated fatty acids, high rates of cell division, and variety of testis enzymes results very vulnerable to the overexpression of reactive oxygen species (ROS). Our approach highlights the importance to assess, before and after remediation in one testis gonadectomy of i.e. barcoded lizards, the oxidative damage starting from the level of ROS using ESR spectroscopy and to analyze the steroid receptors gene regulation of antioxidant stress enzymes. It also deals with of the advantages to follow testis histological variation and the gene expression of an antioxidant under steroid control, the major selenoprotein expressed by germ cells in the testis, the phospholipid hydroperoxide glutathione peroxidase (PHGPx/GPx4). GPx4, in particular, represents the pivotal link between sperm quality, species preservation and soil bioremediation indicator establishing a connection between the disrupters effect in the organism and its environment.

Proc. AGU Fall Meeting, San Francisco (CA, USA), 15-19 Dec. 2014, Paper # B33B-0176.

THE ROLE OF SOIL HYDROLOGIC HETEROGENEITY FOR MODELING LARGE-SCALE BIOREMEDIATION PROTOCOLS.

Palladino, M., G. Speranza, P. Di Fiore, B. Sica, P. Nasta, and N. Romano

Department of Agriculture, Division of Agricultural, Forest and Biosystems Engineering - University of Naples Federico II, Via Università n. 100, 80055 Portici, Italy

The major aim of the EU-Life+ project EcoRemed (Implementation of eco-compatible protocols for agricultural soil remediation in Litorale Domizio-Agro Aversano NIPS) is the implementation of operating protocols for agriculture-based bioremediation of contaminated croplands, which also involves plants extracting pollutants being then used as biomasses for renewable energy production. The study area is the National Interest Priority Site (NIPS) called Litorale Domizio-Agro Aversano, which is located in the Campania Region (Southern Italy) and has an extent of about 200,000 ectars. In this area, a high-level spotted soil contamination is mostly due to the legal or outlaw industrial and municipal wastes, with hazardous consequences also on the quality of the groundwater. An accurate determination of the soil hydraulic properties to characterize the landscape heterogeneity of the study area plays a key role within the general framework of this project, especially in view of the use of various modeling tools for water flow and solute transport simulations and to predict the effectiveness of the adopted bioremediation protocols. The present contribution is part of an ongoing study where we are investigating the following research questions: a) Which spatial aggregation schemes seem more suitable for upscaling from point to block support? b) Which effective soil hydrologic characteristic schemes simulate better the average behavior of larger scale phytoremediation processes? c) Allowing also for questions a) and b), how the spatial variability of soil hydraulic properties affect the variability of plant responses to hydro-meteorological forcing?

XIV Colòquio Anual de Engenharia Química. 12-14 November 2014

PHOTOCATALYTIC PROCESSES APLIED ON THE METAL AND EDDS REMOVAL FROM A SOIL WASHING WASTE

S. Satyro¹, M. Race², I. Di Somma³, R.F. Dantas⁴, m. Dezotti¹, r. Andreozzi⁵

¹ Federal University of Rio de Janeiro, Chemical Engeneering Program

² University of Naples "Federico II", Department of Civil, Architectural and Environmental Engineering

³ Istituto di Ricerche sulla Combustione, CNR

⁴ University of Campinas, Faculty of Technology

⁵ University of Naples "Federico II", Department of Chemical Engineering, Materials and Industrial Production

ABSTRACT – The soil contamination is a global problem connected with illegal waste disposal due to the uncontrolled industrial development. These disposals are normally done with waste enriched by metals. One of the ways to solve the metal soil contamination problem is the soil washing. It uses a chelating agent (EDDS, EDTA i.e.) that complexes with metallic ions and carries them out. But in the end remains an aqueous solution with metals and organics at high concentration. Some reports indicate that the treatment of this solution employing traditional techniques, such as precipitation, is generally unsuitable due to the complexes stability. Therefore, the possibility to destroy the organic species (and the complexes) by means of TiO₂ photocatalysis has been proposed in the past for the case of EDTA. Hence, the present investigation aims to evaluate the possibility to remove Cu, Fe and Zn from synthetic and real soil washing solutions through photocatalytic processes.

4. CONCLUSIONS

The results demonstrated that for the EDDS and metals removal, from synthetic solutions and real soil washing mixtures, it is necessary different photocatalytic treatments. The EDDS removal degrees, by using TiO₂/hv/N₂ or TiO₂/hv/O₂ processes on the real solutions, are close to 70 – 80 % after 3 hours of treatment, while shorter reaction times (10 minutes) are requested to reach the same percentage conversion degrees for synthetic contaminated waters through TiO₂/hv/O₂, Fe(III)-EDDS/hv/O₂ and Fe(III)-EDDS/hv/H₂O₂/O₂ processes.

Among the investigated metal species, only cupric ions can be removed by photoreduction to zero-valent copper through TiO₂/hv/N₂ process for both synthetic and real aqueous solutions.

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CHEMICAL CHARACTERIZATION AND SPATIAL DISTRIBUTION OF POLLUTANTS IN SOIL BIOREMEDIATION PLANNING

Paola Adamo^{a,*}, Claudia Rocco^a, Dario Monaco^b, Salvatore Di Rosa^c, Angelo Riccio^b, Elena Chianese^b, Ida Duro^d, Nunzio Fiorentino^{a,d}, Massimo Fagnano^{a,d}

^aDipartimento di Agraria, Università di Napoli Federico II, Portici, Italy;

^bDipartimento di Scienze e tecnologie, Università di Napoli Parthenope, Napoli, Italy

^cARPAC – Agenzia Regionale per la Protezione Ambientale della Campania, Napoli, Italy;

^dCIRAM - Università di Napoli Federico II, Napoli, Italy;

*Autore di riferimento:

The past century witnessed a relevant increase in global pollution due to the high production and use of petroleum derived compounds which were carelessly released into the environment. As a consequence numerous organic contaminants (PAHs) and potentially toxic elements (PTEs) are now present in soils and water of terrestrial polluted sites, which represent a relevant environmental concern due to their potential accumulation in the food chain.

In Campania region, southern Italy, were identified five National Interest Priority Sites (NIPs), for a total surface of about 200.000 ha, with different levels and sources of pollution. The NIPs “Litorale Domitio-Agro Aversano (NIPS L. 426/98) includes a large part of the polluted agricultural land, belonging to more than 61 municipalities in the Naples and Caserta provinces and the main pollution source is due to legal and outlaw industrial and municipal wastes dumping. The consequences of this, have been the abandonment of wide agricultural areas and the impairment of the image of population, economic activities and agricultural products.

The project LIFE ECOREMED “Implementation of eco-compatible protocols for agricultural soil remediation in Litorale Domizio-Agro Aversano NIPS”, intends to define an operative protocol for agriculture-based bioremediation of contaminated agricultural soils in the above described NIPS, including the use of biomasses for renewable energy production.

In this paper, the behaviour and distribution patterns of PTEs, heavy hydrocarbons and several PAHs priority pollutants, were evaluated in 891 soil samples collected in three expected polluted rural sites, to plan and test innovative agriculture-based soil restoration techniques. The three sites have been used in the past for the temporary storage of urban wastes, or subject to illicit dump of unknown material. The chemical analysis of soil samples allowed to assess the baseline pollution levels, prior to any intervention. The sampling protocol showed large dishomogeneities in soil pollutant spatial distribution, even at scale as small as 3.3 meters, pointing out that variability could emerge at very short spatial scales.

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ECOSYSTEM SERVICES AND BIOREMEDIATION OF POLLUTED AREAS

Pindozzi Stefania¹, Cervelli Elena¹, Capolupo Alessandra¹, Okello Collins¹⁻², Fiorentino Nunzio¹, Fagnano Massimo¹, Boccia Lorenzo¹

¹ Department of Agriculture, University of Naples Federico II, Naples Italy

² Gulu University, Department of Biosystems Engineering, P.O. Box 166, Gulu, Uganda

In many areas of the world there are contaminated areas due to illegal actions. Naples and the whole Campania region, in South of Italy, are under the pressure of mass media caused by the discover of criminal acts and are now suffering the damage of their image in tourism, culture and agriculture, in addition to problems related to public health.

The European Project LIFE/ENV/IT/275 Ecoremed has implemented a protocol for the bioremediation of contaminated soils in Campania region. The cultivation of no food crops is purposed as buffer crops waiting for the characterization of the areas, favoring the uptake of the mineral contaminants and the biodegradation of organic compounds, reducing risk for leaching and run off of harmful contaminants that would occur on bare soils.

Basing on environmental and socio-economic factors, through a GIS software and decision support software (ArcGIS/ILWIS), areas for which it is realistic to assume a land use change (LUC) have been identified. Literature data has been used to assess the current value (€/ha) of the benefits people obtain from ecosystems (Ecosystem Service-ES). Then three scenarios have been hypothesized, one of land degradation and two of land use change into energy crops (Poplar and Giant reed), the first converting only meadow and pasture areas and the second including all agricultural areas, uncultivated areas and non-irrigated arable land.

Results show that areas susceptible of LUC constitute about the 3% of the total study area and their current ES value is around 1.8% of the total. According to second and third scenario, areas convertible to non-food crops are about the 1.20% and 2.7 % of the study area, respectively. The ES value of the abandonment scenario going down to 1.45%, whereas the ES value for the second and the third scenario grow up to 4.5% and 6%, respectively.

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SOIL HYDROLOGIC CHARACTERIZATION FOR MODELING LARGE SCALE SOIL REMEDIATION PROTOCOLS.

Romano, N., M. Palladino, P. Di Fiore, B. Sica, G. Speranza

Department of Agriculture, Division of Agricultural, Forest and Biosystems Engineering - University of Naples Federico II, Via Università n. 100, 80055 Portici, Italy

In Campania Region (Italy), the Ministry of Environment identified a National Interest Priority Sites (NIPS) with a surface of about 200,000 ha, characterized by different levels and sources of pollution. This area, called Litorale Domitio-Agro Aversano includes some polluted agricultural land, belonging to more than 61 municipalities in the Naples and Caserta provinces. In this area, a high level spotted soil contamination is moreover due to the legal and outlaw industrial and municipal wastes dumping, with hazardous consequences also on the quality of the water table. The EU-Life+ project ECOREMED (Implementation of eco-compatible protocols for agricultural soil remediation in Litorale Domizio-Agro Aversano NIPS) has the major aim of defining an operating protocol for agriculture-based bioremediation of contaminated agricultural soils, also including the use of crops extracting pollutants to be used as biomasses for renewable energy production. In the framework of this project, soil hydrologic characterization plays a key role and modeling water flow and solute transport has two main challenging points on which we focus on. A first question is related to the fate of contaminants infiltrated from stormwater runoff and the potential for groundwater contamination. Another question is the quantification of fluxes and spatial extent of root water uptake by the plant species employed to extract pollutants in the uppermost soil horizons. Given the high variability of spatial distribution of pollutants, we use soil characterization at different scales, from field scale when facing root water uptake process, to regional scale when simulating interaction between soil hydrology and groundwater fluxes.

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