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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
REMIEDIATION 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 2015-2017: 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
B1-ENVIRONMENTAL CHARACTERIZATION OF THE AREA	D. Ducci	hydrogeology
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
C2. BIOMONITORING OF RIQUALIFICATION ACTIONS IN PILOT FIELDS.	S. Giordano	environmental botany
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
C3 GROUNDWATER MONITORING	A. Corniello	applied geology
C4. MONITORING OF ENVIRONMENTAL QUALITY OF THE PROCESSES OF ENERGETIC CONVERSION OF BIOMASSES	S. Pindoizzi	agricultural engineering
C5 ENVIRONMENTAL EFFECTS OF LAND USE CHANGE	L. Boccia M. Rigillo	engineering territory; city planning
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



PAPERS





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Science of the Total Environment

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Photogrammetry for environmental monitoring: The use of drones and hydrological models for detection of soil contaminated by copper


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HIGHLIGHTS

- Soil sampling and analysis to investigate copper concentration is very expensive.
- A method aimed to increase the effectiveness of investigation is proposed.
- The method involves photogrammetry, hydrology and wetlands prediction indices.
- High resolution DEM (30 mm) has been generated.
- Prediction indices are able to detect areas of Cu accumulation at plot scale.

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ABSTRACT

Campania Region of Southern Italy has a complex environmental situation, due to geogenic and anthropogenic soil pollution. Some of the pollutants such as copper are mobilized in the organic matter. It has been shown that wetlands provide physical as well as biogeochemical barriers against pollutants. Therefore, the objective of this study was to introduce and test an innovative approach able to predict copper accumulation points at plot scales, using a combination of aerial photos, taken by drones, micro-rill network modelling and wetland prediction indices usually used at catchment scales. Data were collected from an area measuring 4500 m² in Trentola Ducenta locality of Caserta Province of southern Italy. The photos processing with a fifth generation software for photogrammetry resulted in a high resolution Digital Elevation Model (DEM), used to study micro-rill processes. The DEM was also used to test the ability of Topographic Index (TI) and the Clima-Topographic Index (CTI) to predict copper sedimentation points at plot scale (0.1–10 ha) by comparing the map of the predicted and the actual copper distribution in the field. The DEM obtained with a resolution of 30 mm showed a high potential for the study of micro-rill processes and TI and CTI indices were able to predict zones of copper accumulation at a plot scale.

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1. Introduction

Currently, Campania Region, in South Italy, is facing one of the most critical environmental problems due to agricultural soil pollution by accidental contamination. Unfortunately, the overall situation is heterogeneous and complex. Between the years 1998 and 2008, six of the 55 National Interest Priority Site (NIPS) gazetted in Italy were located in Campania Region (Vito et al., 2009). Of the six NIPS, Domitian Coast Flegreo and Agro Aversano were selected as most important in Campania Region (Law no. 426 of 1998). In addition, the National Institute of

Health has included these NIPS areas among the 44 Italian regions with high levels of cancer risk, due to the different and numerous pollutants found in soil such as heavy metals.

High concentrations of heavy metals in Campania Region are a result of a combination of geogenic pollution caused by natural phenomena, and anthropogenic pollution due to voluntary or accidental activities (Cicchella et al., 2005). Geogenic pollution is essentially linked to the processes of parent rock genesis that are extremely rich of metallic elements, due to volcanic activities and related events, such as hot springs and fumaroles (De Vivo et al., 1995). Anthropogenic pollution is mainly related to industrial activities, which produce high concentrations of cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), lead (Pb), nickel (Ni), and zinc (Zn) (Filippelli et al., 2012). Motor vehicle traffic also results in high concentrations of Cd, Cr, Cu, Ni, Pb, selenium (Se) and Zn in the areas near driveways (Albanese and Cicchella, 2012). Use of inorganic pesticides and chemical fertilizers could result in soil

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Conclusions

In this paper, a novel approach that combines photogrammetric technique with hydrological models was tested, (Merot et al., 2003; Gascuel-Oudoux et al., 1998) in the prediction of accumulation sites of trace elements, that can be mobilised adhering to organic matter. In this case, the approach was used to predict copper accumulation sites in an experimental field, and it turned out to be very promising. Specifically it considerably reduces the soil sampling requirements, making it necessary to take samples only in the areas where copper sedimentation points are expected.

Geostatistics was confirmed as the method to be used to spatialize hydrological models (Castrignanò et al., 2011). Copper concentration observed in the field test does not exceed the range values reported by Albanese et al. (2007).

In conclusion the method proposed for the detection of critical sampling points for the characterization of polluted soils, seems to be robust, rapid and most economic compared to the traditional techniques for the characterization of the soil with the ordinary mesh of 5 ×5m.

Therefore, it appears that it could play a key role in future development of environmental monitoring techniques.

For example, it could be used as a model for the development of similar methods for detecting other heavy metals or the parasites that live in the wetlands.

Moreover, another possible field of investigation deals with management of fertilizing activities for the prediction of nutrient in the soil.

Capolupo A., Pindozi P., Collins Okello, Fiorentino N., Boccia L. (2015)

PHOTOGRAMMETRY FOR ENVIRONMENTAL MONITORING: THE USE OF DRONES AND HYDROLOGICAL MODELS FOR DETECTION OF SOIL CONTAMINATED BY COPPER

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Chemical Engineering Journal

A kinetic study of the simultaneous removal of EDDS and cupric ions from acidic aqueous solutions by TiO₂-based photocatalysis under artificial solar light irradiation and deaerated batch conditions


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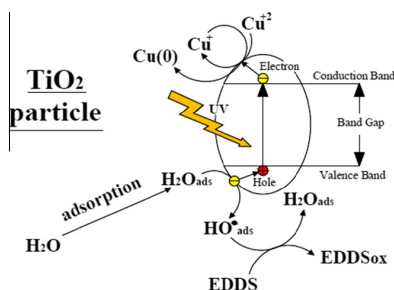
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HIGHLIGHTS

- A reaction network for photocatalytic Cu⁺⁺ reduction and EDDS oxidation is built.
- A kinetic model is developed based on the reaction network built.
- The model is used on a first pool of data to estimate the unknown parameters.
- The model is successfully used to simulate a second pool of data.

GRAPHICAL ABSTRACT



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Water decontamination

ABSTRACT

The removal of cupric ions from aqueous solutions containing *N,N*-ethylenediamine-disuccinic acid (EDDS) is carried out in batch conditions to simulate a possible treatment of water streams coming from soil washing treatment units for heavy metal decontamination. The reduction of cupric ions to zero-valent copper and the oxidation of EDDS species is observed with the achievement of low degrees of mineralization.

A mathematical model has been developed to simulate and predict the concentration profiles of both total EDDS and cupric ions under specified experimental conditions. A series of experimental investigations have been carried out and the results have been used to build a reaction network. Kinetic models have been developed to describe the system behavior in a variety of operating starting conditions (such as different photocatalyst load, cupric ions and EDDS starting concentrations, pH). One of the mathematical models proposed has allowed to estimate the best numerical values of the unknown kinetic constants through an optimization process. A good alignment with the values reported in literature for similar reactions has also emerged for some kinetic constants. Model validation has been carried out successfully. The mathematical model proposed could be useful for the design of a photo-reactor, capable of purifying the solutions coming from soil washing procedure.

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1. Introduction

Cleaning of soils polluted by heavy metals may be carried out by adopting either “in-situ” or “ex-situ” treatment techniques [1].

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Conclusions

An attempt has been done to simulate the results collected during an experimental campaign on the removal of cupric ions from aqueous solution containing also EDDS species by means of TiO_2 photocatalysis. Low degrees of mineralization have been observed along with a reduction to zerovalent state of cupric ions.

Mathematical models have been developed on the basis of a simplified reaction network built following the experimental findings to describe the system behavior at varying the operating starting conditions (photocatalyst load, cupric ions and EDDS starting concentrations, pH).

The adoption of a proper optimization procedure has allowed to find suitable estimates for unknown kinetic constants or some of which a good agreement has been observed with the values reported in literature for similar reactions.

The best results in terms of percentage standard deviations on the components and simplicity have been observed using a reduced model (Model 1.2.2.1). In this model have been ruled out all the reactions between (i) free cupric ions in solution with photoelectrons on the surface of the photocatalyst and (ii) adsorbed and protonated EDDS with photogenerated positive holes.

A model validation has been successfully carried out on Model 1.2.2.1 using the data from two experiments not included in the pool considered for kinetic constants optimization. The validation has been achieved by running the model without any further adjustment of kinetic parameters.

*Di Somma I., Clarizia L., Satyro S., Spasiano D., Marotta R., Andreozzi R. (2015)
A KINETIC STUDY OF THE SIMULTANEOUS REMOVAL OF EDDS AND CUPRIC IONS FROM ACIDIC AQUEOUS SOLUTIONS BY
TiO₂-BASED PHOTOCATALYSIS UNDER ARTIFICIAL SOLAR LIGHT IRRADIATION AND DEAERATED BATCH CONDITIONS
Chemical Engineering Journal 270 (2015) 519–527*

Chemical characterization and spatial distribution of PAHs and heavy hydrocarbons in rural sites of Campania Region, South Italy

D. Monaco¹ · A. Riccio¹ · E. Chianese¹ · P. Adamo² · S. Di Rosa³ · M. Fagnano^{2,4}

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Abstract In this paper, the behaviour and distribution patterns of heavy hydrocarbons and several polycyclic aromatic hydrocarbon (PAH) priority pollutants, as listed by the US Environmental Protection Agency, were evaluated in 891 soil samples. The samples were collected in three expected polluted rural sites in Campania (southern Italy) as part of the LIFE11 ECOREMED project, funded by the European Commission, to test innovative agriculture-based soil restoration techniques. These sites have been selected because they have been used for the temporary storage of urban and building waste (Teverola), subject to illicit dumping of unknown material (Trentola-Ducenta), or suspected to be polluted by metals due to agricultural practices (Giugliano). Chemical analysis of soil samples allowed the baseline pollution levels to be determined prior to any intervention. It was found that these areas can be considered contaminated for residential use, in accordance with Italian environmental law (Law Decree 152/2006). Statistical analysis applied to the data proved that average mean concentrations of heavy hydrocarbons could be as high as 140 mg/kg of dry soil with peaks of 700 mg/kg of dry soil, for the Trentola-Ducenta site; the median concentration of analytical results for hydrocarbon (HC) concentration

for the Trentola-Ducenta and Giugliano sites was 63 and 73.4 mg/kg dry soil, respectively; for Teverola, the median level was 35 mg/kg dry soil. Some PAHs (usually benzo(a)pyrene) also exceeded the maximum allowed level in all sites. From the principal component analysis applied to PAH concentrations, it emerged that pollutants can be supposed to derive from a single source for the three sites. Diagnostic ratios calculated to determine possible PAH sources suggest petroleum combustion or disposal practice. Our sampling protocol also showed large dishomogeneity in soil pollutant spatial distribution, even at a scale as small as 3.3 m, indicating that variability could emerge at very short spatial scales.

Keywords Heavy hydrocarbons · PAHs · Soil pollution · Waste disposal · Small-scale sampling · Campania rural areas

Introduction

Even though disposal at landfills has steadily declined and the percentage of waste and energy recovery has significantly grown in recent years, in 2008 the EU-27 countries generated more than 2.6 billion tonnes of wastes, of which 98 million tonnes was hazardous (Eurostat 2011). This amounts to about 6 t of solid waste for every man, woman and child. Such a large production of waste inevitably feeds into illegal dumping and inappropriate practices (e.g. burning of agricultural residues). Recently, the European Commission, through the European Soil Data Centre, conducted a project to collect data on contaminated sites from national institutions in Europe using the European Environment Information and Observation Network for soil (EIONET-SOIL). There was estimated to be local soil contamination at 2.5 million potentially contaminated sites, of which about 342,000 have already

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Conclusions

This study allowed characterization of soil pollutant distribution in three sites in the so-called Land of Fires area in the southern Italian region of Campania. Soil samples were analysed to survey pollution levels for both HC and PAH concentrations.

The results of our investigation, on one of the most controversially debated polluted regions in Italy, showed a worrying scenario for rural areas subject to known unauthorized waste disposal and burning. In all cases, the dumping of waste contaminated the sites considered here, above Italian legal limits. In most cases, the maximum admissible Italian law limit for HCs (50 mg/kg d.w., according to Law Decree 152/2006) was exceeded, such that these areas can be considered contaminated for residential or recreational use.

Our hierarchical sampling protocol, based on 'topsoil' layer (0–30-cm depth) and 'subsoil' layer (30–60-cm depth), showed large dishomogeneity in soil pollutant spatial distribution, even at a scale as small as 3.3 m. As a consequence, it is reasonable to imagine a leopard-spot distribution of soil pollutants, whose detection and health hazard diagnosis suggests the importance of more detailed soil surveys and samplings than those performed so far.

Due to extensive wide area involved (about 2400 km²), it is reasonably unworkable to use our hierarchical sampling protocol to evaluate the soil pollution level at such a high sampling density and the application of industrial processes for soil restoration. To reduce population exposure, combat unemployment and boost the local economy, the location and control of contaminant source emissions will be decisive, starting with a large programme of bio- and phytodepuration compatible with the contamination condition.

*Monaco D., A. Riccio, E. Chianese, P. Adamo, S. Di Rosa, M. Fagnano (2015)
CHEMICAL CHARACTERIZATION AND SPATIAL DISTRIBUTION OF PAHS AND HEAVY HYDROCARBONS IN RURAL SITES OF
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Environ Sci Pollut Res (2015) 22:14993–15003 DOI 10.1007/s11356-015-4733-y*



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Biomonitoring of atmospheric pollution by moss bags: Discriminating urban-rural structure in a fragmented landscape



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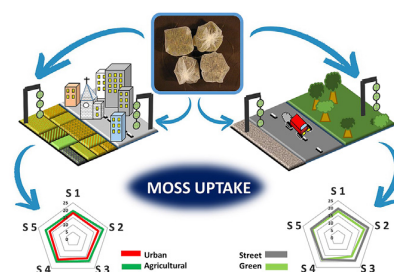
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HIGHLIGHTS

- Moss bag sensitivity was tested in an urban-rural fragmented landscape.
- Moss uptakes were overall higher in agricultural than in urban sites.
- Mosses were able to discriminate between front road and matching green sites.
- Traffic and intensive agriculture are the major pollution sources in the study area.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper we investigated the possibility to use moss bags to detect pollution inputs - metals, metalloids and polycyclic aromatic hydrocarbons (PAHs) - in sites chosen for their different land use (agricultural, urban/residential scenarios) and proximity to roads (sub-scenarios), in a fragmented conurbation of Campania (southern Italy). We focused on thirty-nine elements including rare earths. For most of them, moss uptake was higher in agricultural than in urban scenarios and in front road sites. Twenty PAHs were analyzed in a subset of agricultural sites; 4- and 5-ringed PAHs were the most abundant, particularly chrysene, fluoranthene and pyrene. Overall results indicated that investigated pollutants have a similar spatial distribution pattern over the entire study area, with road traffic and agricultural practices as the major diffuse pollution sources. Moss bags proved a very sensitive tool, able to discriminate between different land use scenarios and proximity to roads in a mixed rural-urban landscape.

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1. Introduction

Campania (southern Italy, one of the 20 administrative districts of Italy) experienced in the last century profound changes in land use, as a massive urbanization and increase of industrial

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Conclusions

Results of the present survey indicate *Hypnum cupressiforme* moss bags as a very sensitive tool to detect airborne element and PAH inputs in a landscape characterized by a jeopardized structure in which agricultural and urban/residential sites are strictly mixed together. Particularly, through the exposure scheme adopted for elements, we were able to discriminate different pollution levels in agricultural and urban scenarios and green and street subscenarios.

In general, agricultural sites showed higher moss uptake than urban ones, as well as moss suspended at street sites, directly facing the vehicular traffic. On the basis of moss uptake, the whole study area is homogeneously polluted. Agricultural practices and road traffic appear to be the major diffuse pollution sources over the whole study area, both producing polluted particulate matter that mosses are able to entrap.

The impact of agricultural practices, indicated by our survey at a regional scale, seems in line with a global trend; agriculture indeed, has been recently reported as the leading source of particulate matter (specifically PM_{2.5}) in Europe, with a contribution of 40% or higher in many European countries (Lelieveld et al., 2015).

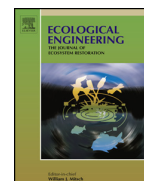
Such a detailed information, up to a very small land scale, would never be possible by using monitoring stations, also considering the large set of pollutants here analyzed (i.e., 39 chemical elements and 20 PAHs). Therefore, moss bags should be considered as a valid candidate for a qualitative appraisal of atmospheric pollution for regulatory purposes.

Capozzi F., Giordano S., Di Palma A., Spagnuolo V., De Nicola F., Adamo P. (2016)
BIOMONITORING OF ATMOSPHERIC POLLUTION BY MOSS BAGS: DISCRIMINATING URBAN-RURAL STRUCTURE IN A
FRAGMENTED LANDSCAPE
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Ecosystem services and bioremediation of polluted areas


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ABSTRACT

Contaminated areas represent a crucial concern in contemporary planning all over the world. The absence of shared value for such areas leads to abandonment and soil sealing specially if such areas have lost their agricultural potential. 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 (Poplar and Giant reed) is proposed as buffer crops waiting for the characterization of the areas. This facilitates the uptake of the mineral contaminants and the biodegradation of organic compounds reducing the risk for leaching and the run off of harmful contaminants that would occur on bare soils.

The study discusses a new approach to land use change (LUC) assessment based on environmental and socio-economic factors, evaluated through GIS tool and decision support software (ArcGIS/ILWIS). Literature data have been used to assess the current value of the ecosystem services (ES) provided by such crops (€/ha/year) and the benefits that people obtained from ecosystems. Three scenarios have sorted out and compared through multicriteria analysis. Moving from the deep knowledge of the environmental condition of the territory the study shows the alternative ES values of the land use change starting from no-change scenario to energy crops (Poplar and Giant reed), to abandonment. Results show that is possible to assess an increase of the ES value, both in case of a private and public action, also referring to the opportunities for farmers income in the short and medium-long period.

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1. Introduction

Ecosystem services (ES) are crucial for providing condition for human well-being, qualitative livelihoods and efficiency for the human habitat (Costanza et al., 1997, 1998; Millenium Ecosystem Assessment (MEA), 2005; TEEB Foundations, 2010; de Groot et al., 2012; Comino et al., 2014). Changes in ES influence all components of the human well-being (Balmford and Bond, 2005; Farber et al., 2002; Salles, 2011), so that the early assessment of the ES change may effectively support decision makers in planning (Marulli and Mallarach, 2005; Busch et al., 2012) and in programming policies for improving social well-being (Daily et al., 2009; Deutsch et al., 2003).

Further the capacity of evaluating the monetary values of ES (Costanza et al., 1997), although ignores more intangibles services (Viglizzo et al., 2012; von Haaren et al., 2014), makes the ES one of the key elements of the planning processes (Bennett et al., 2009; Frank et al., 2012) and of the decision analysis, leading towards new methodologies in terms of planning alternatives.

The Millennium Ecosystem Assessment (MEA, 2005) definition for ES describes it as the implementation of a set of effective benefits for both natural and urban environment. Thanks to the MEA studies (2003, 2005), ES has become a popular research topic and it acts as conceptual framework for many scientific projects so that various ES classification strategies, mapping methodologies and evaluations proposals have been provided at global, regional and local scales (Daily and Matson, 2008; Fisher and Turner, 2008; de Groot, 2006; Tianhong et al., 2010). Further, the evaluation of ES in economic terms became an increasingly popular approach both to assess alternative scenarios in land use change and to demonstrate the economic value of biodiversity conservation (Bayon and Jenkins, 2010; Chan et al., 2006; Costanza et al., 1997; de Groot et al., 2002; Fisher et al., 2009; Ghazoul, 2007; Ridder, 2008; Wallace, 2007; Schneiders et al., 2012).

Abbreviations: ANP, analytic network process; DEM, digital elevation model; ES, ecosystem services; LUC, land use change; MC-SDSS, Multicriteria-Spatial Decision Support Systems; NIPS, National Interest Priority Sites; PDO, protected designation of origin; SIR, Regional Interest Site; AV, added value.

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Conclusions

The study put into evidence the benefits of bio-remediation in the management of contaminated sites located in the agricultural areas. Bioremediation techniques, integrated with policies and measures, are a key opportunity that can be site-specifically appraised as a crucial concern in planning due to it reduces human and environmental risks.

According to this, the monetary evaluation of ES helps to facilitate the social awareness of the value of maintaining vegetated soils in case of polluted areas even if it is not yet assessed the increasing monetary value of bio-remediation in risk reduction. Vice versa the study does not take into account the reduced monetary value due to the strong intensification of land use for energy crops and no food crops (such as in Scenario 2).

It generally leads to a decline in biodiversity (i.e. future framework of Schneiders, 2012) so that the future development of the study could be oriented to foreseen and design mitigations actions to ensure sustainable use. More “weak-ness” in LUC is the change of water consumption due to the increase of permanent crops, the reducing of natural competition of non-crop plants, the increase of the phytophagous insects, etc. (Swift et al., 2004; Zhang et al., 2007).

Furthermore, the massive LUC of Scenario 2 corresponds to the significant reduction of the value of agricultural land and farmer’s incomes. Such single farmer reduction of incomes could be balanced by the social benefit of the ES monetary value, quantified by the study proposed methodology. In fact the ES monetary value increase is almost 600 D /ha that is consistent with the decrease of the farmers’ incomes. The worst scenario is the Scenario 3 – Abandonment that is the most presumable in absence of public action. Here it will observe both the reduction of the farmers’ incomes and the reduction of the ES value.

Planning could play a crucial role in providing shared actions and private needs. Beside, the approach can be easily replicated.

*Cervelli E., Pindozi S., Capolupo A., Okello Collins, Rigillo M. e Boccia L. (2016)
ECOSYSTEM SERVICES AND BIOREMEDIATION OF POLLUTED AREAS
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Air pollution monitoring using emission inventories combined with the moss bag approach


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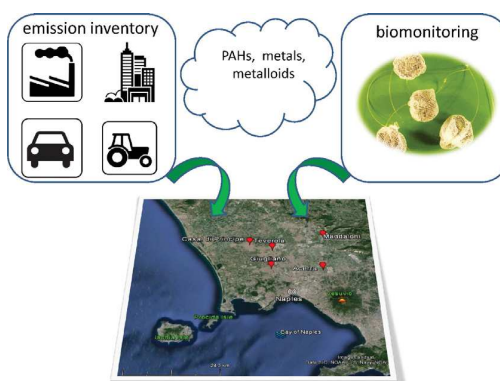
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HIGHLIGHTS

- Emission inventory and moss biomonitoring were at once used to assess air pollution.
- The road transport contributed most of the emissions of CO, NO_x, PM₁₀, Cu, Pb, and Zn.
- Emission inventory and moss accumulation evidenced similar spatial patterns for Pb.
- The two approaches indicated the same most polluted municipality.
- Both approaches monitored point and diffuse source pollution.

GRAPHICAL ABSTRACT



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ABSTRACT

Inventory of emission sources and biomonitoring with moss transplants are two different methods to evaluate air pollution. In this study, for the first time, both these approaches were simultaneously applied in five municipalities in Campania (southern Italy), deserving attention for health-oriented interventions as part of a National Interest Priority Site. The pollutants covered by the inventory were CO, NO_x, particulate matter (PM₁₀), volatile organic compounds (VOCs), and some heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Se, and Zn). The biomonitoring survey was based on the use of the devitalized moss *Hypnum cupressiforme* transplanted into bags, following a harmonized protocol. The exposure covered 40 agricultural and urban/residential sites, with half of them located in proximity to roads. The pollutants monitored were Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Se, and Zn, as well as total polycyclic aromatic hydrocarbons (PAHs) only in five sites. Using the emission inventory approach, high emission loads were detected for all the major air pollutants and the following heavy metals: Cr, Cu, Ni, Pb and Zn, over the entire study area. Arsenic, Pb, and Zn were the elements most accumulated by moss. Total PAH postexposure contents were higher than the preexposure values (~20–50% of initial value). Moss uptakes did not differ substantially among municipalities or within exposure sites. In the five municipalities, a similar spatial pattern was evidenced for Pb by emission inventory and moss accumulation. Both approaches indicated the same most

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Conclusions

The uniqueness of this study lies in the combined use of the two widely used methods for evaluating air pollution: the inventory of emission sources and biomonitoring by moss transplants. Combined analysis of the different data sets clearly shows that for the investigated municipalities in Campania, a considerable part of total emissions is due to road traffic.

When the emission inventory is based on a reliable and constant-over-time single pollution source, as in the case of lead, the two data sets produce almost coincident outputs, whereas those contaminants showing multiple and scattered sources, variable in time, produce less overlapping outputs.

Therefore, according to a harmonized protocol, the combined use of the atmospheric emission inventory and moss bags is an important tool to study air quality and set up possible remediation plans. This could be particularly useful in areas of alleged pollution, to support the monitoring of attainment of limit values established by legislation.

In areas with high pollution, the creation of a spatially distributed emission inventory and the establishment of a regular biomonitoring network using moss bags could be part of a project to develop and improve the modeling of air quality.

Indeed, the comparison between the two data sets (i.e., emission inventory and biomonitoring) could prove a valuable resource to reveal suspected point source pollution (where denser data points are needed) and for the simultaneous detection of contaminants not monitored by automatic devices and eluding the records of emission inventories.

It is believed that this study will help engineers and research biologists to face the challenges of air pollution monitoring.

*Iodice P., Adamo P., Capozzi F., Di Palma A., Senatore A., Spagnuolo V., Giordano S. (2016)
AIR POLLUTION MONITORING USING EMISSION INVENTORIES COMBINED WITH THE MOSS BAG APPROACH
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Copper and zinc removal from contaminated soils through soil washing process using ethylenediaminedisuccinic acid as a chelating agent: A modeling investigation



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ABSTRACT

This study demonstrated that soil washing using ethylenediaminedisuccinic acid (EDDS) as a chelating agent was efficient at removing copper and zinc from real polluted soils. Only the exchangeable and reducible fractions of Cu and Zn were extracted by EDDS. Intra-particle diffusion was the main rate controlling step in this extraction of heavy metals from the solid matrix. Different contributions were found by applying the Weber and Morris intraparticle diffusion model resulting from the different roles of superficial and intra-particle diffusive processes. The diffusion coefficients of the Cu/EDDS and Zn/EDDS complexes in real contaminated soils were estimated using simplified diffusive models (based on Crank's and Vermeulen's approximations). The relationship between the grain size and diffusion coefficient was also evaluated. In particular, the intraparticle diffusion coefficients increased with increasing the particle size, thus indicating that the smallest granulometric fractions are characterized by a higher percentage of micropores than the largest fractions.

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1. Introduction

During the last 20 years, the contamination of soils and sediments with heavy metals (HMs) has become a worldwide concern due to their high toxicity of most species and their ability to accumulate in living tissues [1,2].

In agricultural areas, HMs contamination, even if not related to specific health hazards, compromises the optimal use of the land, may reduce economic output [3], and modifies the existing equilibrium among natural components [4]. In these zones, the remediation interventions are needed that remove the contamination without affecting the original structure and composition of the soil.

In many cases, especially if the pollution is of anthropogenic origin, very high concentrations of HMs may occur in portions of

the contaminated areas leading to so-called "hot spots" [5]. The remediation of these hot spots requires specific processes. Soil washing is a promising strategy if the applied extracting agent minimally changes the original solid matrix original characteristics and does not leave toxic residues in the treated soil [6]. Moreover, feasible treatment methods and safe disposal of the washing solution should be available [7,8].

For these reasons, biodegradable organic chelants with low environmental persistence are highly recommended [9]. The most common chelating agents, such as ethylenediaminetetraacetic acid (EDTA), are poorly biodegradable and quite persistent in the environment. An alternative, the [S,S]-stereoisomer of ethylenediaminedisuccinic acid (EDDS), has recently received attention in the literature as it is both safe and environmentally-friendly [10–15]. For example, the use of EDDS for soil reclamation does not

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Conclusions

The present investigation demonstrated the effectiveness of removing copper and zinc from polluted soils through a soil washing process using EDDS as a chelating agent.

The results provided evidence that the intra-particle diffusion is the main rate controlling step in the extraction of heavy metals from the solid matrix.

The soil washing process allows the efficient extraction of only the Cu (100%) and Zn (80.9%) exchangeable and reducible fractions.

The Weber plots exhibited multi-linearity thus indicating that the diffusive process develops in the pores of progressively smaller sizes.

The diffusion coefficients of the Cu-EDDS and Zn-EDDS complexes in real contaminated soils were calculated using the Crank's approximation (for short contact times, <1 h) and Vermeulen's approximation (for long contact times, >1 h).

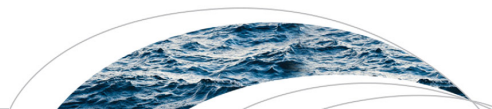
Both models provided a good fit to the experimental data and the best calculated pore diffusion coefficients were consistent with those reported in the literature.

The "apparent" diffusion coefficients of the Cu-EDDS and Zn-EDDS species increase with increasing particle size, ranging from 10^{-18} to $10^{-19} \text{m}^2 \text{s}^{-1}$ for particle diameters smaller than 30 mm and to $10^{-13} \text{m}^2 \text{s}^{-1}$ for diameters higher than 5 mm.

The obtained results suggest that soil washing with chelating agents under the adopted experimental conditions is limited by the intra-particle diffusion process.

Due to the very small pore sizes of the sampled soils, the proposed process represents a promising alternative for soil remediation, as these two heavy metals otherwise would not be available for the removal using less intense techniques.

*M. Race, R. Marotta, M. Fabbri, R. Andreozzi, Cortese L., Giudicianni P., Pirozzi F. (2016)
COPPER AND ZINC REMOVAL FROM CONTAMINATED SOILS THROUGH SOIL WASHING PROCESS USING
ETHYLENEDIAMINEDISUCCINIC ACID AS A CHELATING AGENT: A MODELING INVESTIGATION
Journal of Environmental Chemical Engineering 4 (2016) 2878-2891*



Water Resources Research

RESEARCH ARTICLE

10.1002/2015WR016979

Key Points:

- Uncertainty associated to parameterization of layered soil profiles
- Grouping available layered soil profiles into suitable textural groups
- Quantification of epistemic errors

Supporting Information:

- Supporting Information S1

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Use of a flux-based field capacity criterion to identify *effective* hydraulic parameters of layered soil profiles subjected to synthetic drainage experiments

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Abstract This study explores the feasibility of identifying the *effective* soil hydraulic parameterization of a layered soil profile by using a conventional unsteady drainage experiment leading to field capacity. The flux-based field capacity criterion is attained by subjecting the soil profile to a synthetic drainage process implemented numerically in the Soil-Water-Atmosphere-Plant (SWAP) model. The *effective* hydraulic parameterization is associated to either *aggregated* or *equivalent* parameters, the former being determined by the geometrical scaling theory while the latter is obtained through the inverse modeling approach. Outcomes from both these methods depend on information that is sometimes difficult to retrieve at local scale and rather challenging or virtually impossible at larger scales. The only knowledge of *topsoil* hydraulic properties, for example, as retrieved by a near-surface field campaign or a data assimilation technique, is often exploited as a proxy to determine *effective* soil hydraulic parameterization at the largest spatial scales. Comparisons of the *effective* soil hydraulic characterization provided by these three methods are conducted by discussing the implications for their use and accounting for the trade-offs between required input information and model output reliability. To better highlight the epistemic errors associated to the different *effective* soil hydraulic properties and to provide some more practical guidance, the layered soil profiles are then grouped by using the FAO textural classes. For the moderately heterogeneous soil profiles available, all three approaches guarantee a general good predictability of the actual field capacity values and provide adequate identification of the *effective* hydraulic parameters. Conversely, worse performances are encountered for the highly variable vertical heterogeneity, especially when resorting to the “*topsoil-only*” information. In general, the best performances are guaranteed by the *equivalent* parameters, which might be considered a reference for comparisons with other techniques. As might be expected, the information content of the soil hydraulic properties pertaining only to the uppermost soil horizon is rather inefficient and also not capable to map out the hydrologic behavior of the real vertical soil heterogeneity since the drainage process is significantly affected by profile layering in almost all cases.

1. Introduction

Accurate predictions of moisture fluxes are a primary concern in managing land and water resources, relying on hydrology computer models that adequately describe water flow and solute transport in soil, which is inherently a highly heterogeneous porous medium. Viewing the porous domain as a layered profile, made up of a number of different soil horizons, is undoubtedly a suitable, albeit simplified, way to explain the natural vertical heterogeneity of soils. Moreover, it is strategically important for the model to properly characterize nonlinear soil hydraulic functions for each horizon, namely the soil water retention (WRF) and hydraulic conductivity functions (HCF), commonly described by unimodal relationships linking the volumetric soil water content, θ ($L^3 L^{-3}$), to the soil matric pressure head, h (L), and to the unsaturated hydraulic conductivity, K ($L T^{-1}$), respectively.

Generally speaking, a model can only be a simplified, virtual representation of a real phenomenon and attempts to mimic as closely and consistently as possible the description of a complex process. In our specific case, the process entails water dynamics and storage in a layered profile. Indeed, a layered soil profile exhibits considerable textural and structural vertical contrasts which, in turn, cause large variations in the relevant soil hydraulic properties. Water movement through the vadose zone is generally described in detail

Conclusions

While soil water content at field capacity, hFC, is a key hydraulic variable even in comprehensive hydrologic models (e.g., for the calculation of actual transpiration fluxes), to our knowledge, there is still little recognition of how important its determination is in the cases of layered soil profiles, which are the rule rather than an exception in real world cases.

The proposed procedure to obtain the effective WRF and HCF of an actual layered soil profile, through identification of field capacity with a synthetic unsteady drainage experiment, sheds light on the following major aspects of the effective soil hydraulic parameterization problem:

1. From the comparisons between the outcomes of the three methods evaluated in this study, it is illusory and misleading to state that the actual soil hydrologic response of a multilayer soil profile can be easily synthesized by the behavior of an ideally uniform soil column if input data with adequate information content are not incorporated.
2. Albeit promising, the “topsoil-only” soil hydraulic parameterization, which retrieves the hydraulic information only from the uppermost soil layer, provides results that are prone to large epistemic uncertainty, especially in the cases of highly vertical heterogeneity in the soil profile.
3. The equivalent (obtained from inverse modeling) and aggregated (obtained from geometrical scaling) soil hydraulic parameterizations would be ideal, but under the restraining condition of availability of soil hydraulic characterization at plot scale. The equivalent soil hydraulic functions lead to the best performances in terms of estimating an effective field capacity value even for soil profiles whose horizons have highly contrasting properties and can mimic an actual drainage process in a fairly large number of the cases considered. The reliability of aggregated hydraulic parameters does not prove so inadequate under field conditions (at least for the unsteady drainage processes examined here), but can be seriously undermined if the basic hypothesis of soil porosity similarity among the soil layers is substantially violated.

The findings of this study, based on a database of 84 existing soil profiles, support the concept that small scale process theory and local property observations can be employed for large-scale hydrologic modeling provided that the effective soil hydraulic parameters are properly identified. Future investigations will focus on testing these outcomes in a bucket model for large-scale modeling applications.

Comparisons among the three effective methods, and especially between the equivalent and aggregated soil hydraulic parameterizations, show that empirical scaling of soil heterogeneity (as implemented in this study by the geometrical scaling method) provides poorer performances than scaling of soil moisture dynamics regulated by such soil heterogeneity (as implemented in this study by the inverse modeling method).

Nasta P. and Romano N. (2016)

USE OF A FLUX-BASED FIELD CAPACITY CRITERION TO IDENTIFY EFFECTIVE HYDRAULIC PARAMETERS OF LAYERED SOIL PROFILES SUBJECTED TO SYNTHETIC DRAINAGE EXPERIMENTS.

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Solar photocatalytic processes for treatment of soil washing wastewater

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HIGHLIGHTS

- Solar photocatalytic sequential treatment of soil washing effluents.
- Efficient removal of copper, zinc, EDDS and TOC from effluents.
- A plate solar collector with a multitubular reactor is used.
- Procedure for the estimation of illuminated area of the solar photoreactor.
- The ecotoxicity of the soil washing effluents is noticeably reduced.

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ABSTRACT

In the present work the use of a sequence of two solar photocatalytic processes was investigated for the removal of copper, iron, zinc and ethylenediaminedisuccinic acid (EDDS), used as chelating agent, from real soil washing effluents. Removal efficiencies of 93.5% (copper), 99.6% (iron), 99.4% (zinc), 97.2% (EDDS) and 80.7% (TOC) were achieved through outdoor solar photocatalytic treatments using parabolic trough collectors and carried out in Naples (Italy, N 40°50', E 14°12') in the period June–July 2015. These removal efficiencies were achieved for an incident UVA solar energy per unit volume ($Q_{i,n}$) of 580 kJ·L⁻¹, calculated by taking into account the irradiated surface area of the photoreactor estimated in the present work (9.79×10^{-2} m²) and the solar irradiance measurements collected during the experiments.

The results suggest that the two-step solar process adopted can be proposed as a useful solution to the problem of heavy metals and chelating organic agents removals from soil washing.

The ecotoxicological assessment, using different living organisms (*Daphnia magna*, *Vibrio fischeri*, *Pseudokirchneriella subcapitata*, *Lepidium sativum* and *Caenorhabditis elegans*), showed a noticeable decrease of the ecotoxicity of the soil washing effluents after the two-step photocatalytic process.

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1. Introduction

Ex-situ soil washing processes based on the use of biodegradable chelating agents for heavy metals removal are very promising for the treatment of contaminated soils [1].

A major disadvantage of using these processes is that wastewater effluents containing extracted heavy metals and residual chelating agents must be decontaminated by appropriate methods.

Consequently, spent soil washing effluents can not be directly discharged neither into civil sewer nor in surface waters.

Conventional technologies, such as adsorption on activated carbon or precipitation, have been demonstrated to be ineffective in treating these effluents since the presence of chelating agents inhibits the separation of heavy metals from aqueous solutions due to a high thermodynamic stability of metal-chelant complexes.

For this purpose, different physical [2,3], chemical [4–6], or integrated physico-chemical [7] processes have been recently proposed to enhance the removal of heavy metals and chelating agents from wastewater effluents before their release into the environment. Among the processes proposed for treating soil washing solutions, solar driven photocatalytic systems can be

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Conclusions

A sequence of two solar TiO₂-photocatalytic processes was tested to remove copper, iron, zinc, and EDDS from real soil washing wastewater at neutral pH conditions.

The results collected from experimental runs demonstrate that iron and zinc are mainly removed by precipitation as insoluble hydroxides during the first step (TiO₂-photocatalysis with oxygen) whereas the second one (TiO₂-sacrificial photocatalysis) is necessary to reduce cupric ions to zero-valent copper which precipitates from the solution.

The ecotoxicological results indicate that natural solar photocatalytic processes are able to reduce noticeably the ecotoxicity of the soil washing effluents with respect to the untreated solutions.

In conclusion, it can be stated that soil washing, followed by solar photocatalytic treatment of wastewater produced, can be proposed as a suitable and environmentally safe removal process for metal-contaminated hot spot soils for which generally other approaches fail.

*Onotri L., Race M., Clarizia L., Guida M., Alfè M., Andreozzi A., Marotta R. (2016)
SOLAR PHOTOCATALYTIC PROCESSES FOR SOIL WASHING WASTEWATER TREATMENT
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Composite vs. discrete soil sampling in assessing soil pollution of agricultural sites affected by solid waste disposal



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ABSTRACT

The choice of an appropriate sampling scheme is a crucial step in the process of soil pollution assessment and risk management. In agricultural systems, where soil is mixed by ploughing, the bulking of discrete samples to obtain composite samples improves soil sampling precision, unless strong concentration gradients exist. In this case, the compositing may significantly underestimate the risk posed by the contaminants. In this paper, the degree and spatial variability of soil pollution by potentially toxic elements in three agricultural sites, subjected to unauthorized waste disposal, were assessed applying a soil sampling scheme based on a two-level grid resolution. On the first level, a regular low-resolution 10×10 m grid was defined. On the second level, each grid was subdivided into nine high-resolution 3.33×3.33 m subplots. Discrete soil samples were taken from each 3.33×3.33 m plot. Composite soil samples were made bulking aliquots from the discrete soil samples. Soil samples were collected at 0–30 and 30–60 cm depths to evaluate vertical variations. When statistical analyses were applied to composite data and various pollution indices were calculated, only one site appeared to be slightly polluted by Cu and Zn, with mean contents of 131 and 95 mg kg^{-1} and peaks of 275 and 174 mg kg^{-1} . When the same analysis and indices were applied to discrete soil data a much worse scenario emerged. The slightly polluted site became highly polluted by Cu (mean and max of 276 and 1707 mg kg^{-1}) and Zn (174 and 972 mg kg^{-1}), and slightly polluted by Sb and As (max of 15 and 30 mg kg^{-1}). Plots classified as unpolluted on the basis of composite data revealed metals above legal limits. Pollution always interested both the 0–30 and 30–60 cm depth soil samples, with the deeper samples showing only in few cases higher values than the surface samples. The adopted two-level soil sampling scheme succeeded to show dishomogeneity in soil pollutant spatial distribution, with pollution hot spots emerging only when sampling was done at a very short spatial scale.

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1. Introduction

The determination of potentially toxic elements (PTEs) total or 'pseudototal' content in soil is considered a valuable preliminary aid in establishing the risks for biota and human health, assuming that pollutants transference to water resources or biota are correlated with the contamination level (Adamo and Zampella, 2008). In contrast, relevant paradigms in environmental monitoring, risk assessment and remediation feasibility are the natural levels of PTEs in soil, the spatial variability of soil pollution, the mobility and bioavailability of pollutants to microorganisms, plants, animals and humans. In agricultural land,

contamination of soil with PTEs represents a serious risk to human and animal health due to the potential accumulation of pollutants in the food chain (Wuana and Okieimen, 2011). Moreover, in all parts of the world, agriculture is a primary sector of economy playing a key role in food security and rural environment sustainability, and any abandonment or change of land use would result in increased environmental pressures and deterioration of valuable farm habitats with serious economic and social consequences (Washa et al., 2014). Hence, the adequate choice of sampling scheme, assessment of the level and geographical extend of soil contamination and consequently the adoption of the most appropriate remediation strategy, is of vital importance in croplands (de Abreu et al., 2012, Loska et al., 2003).

Although field soil sampling is a crucial step in the description of the type, patterns and spatial distribution of soil pollution, its study has lagged behind in relation to soil analysis techniques. According to Markert (1995) the uncertainty arising from representative soil

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Conclusions

In this study, a two depths soil sampling scheme based on a two level grid resolution, a regular 10×10 m low-resolution grid and a 3.33×3.33 m high resolution grid, was applied in three agricultural sites suspected of heavy metal(loid)s pollution by waste disposal, dumping and incineration. This approach was chosen to investigate the spatial distribution patterns of pollutants in soil and to highlight the difficulties to appropriately assess the degree of soil pollution and the detection of pollution foci when large scale and composite sampling is applied.

In the studied sites, we did not find any high and diffuse soil pollution, as expected. Only in one site (GI) the soil contained PTEs (Cu, Zn, Sb and As) well above Italian legal limits and local natural backgrounds. A large dishomogeneity in soil pollutant spatial distribution emerged from comparison of data taken at high and low resolution level.

The degree of soil pollution, as assessed by pollution indices, worsen passing from composite 10×10 m to discrete 3.33×3.33 m scale of sampling. Pollution foci were detected only when soil was discretely sampled at the 3.33×3.33 m scale. Unpolluted 10×10 m plots were found to contain metals above legal limits when sampled at 3.33×3.33 m scale.

These results arise comprehensible doubts on the soil pollution monitoring based on a large scale and composite soil sampling introducing a great deal of variability and uncertainty in the evaluation of results from different investigations. This applies to our study area known as the 'Land of Fires', where most of the soil data actually available have been taken at a large (1×1 km) or at a very large (5×5 km) scale and mostly collecting composite soil samples. According to our results the uncertainty of these data might be very high, with potential underestimation of pollution degree and omission of pollution foci.

Appropriate soil sampling and pollution assessment are crucial for assessing soil volumes requiring remediation as well as for estimating the adverse health effects in humans who may be exposed to chemicals in contaminated soil. In this study, for example, on the base of the 10×10 m data, only 40 and 15% of GI and TD soil need to be cleaned up to a depth of 60 cm.

These volumes would increase if calculation is done considering the 3.33×3.33 m scaled soil samples. Environmental risk assessment, based on the total concentration of PTEs in soil, would have produced different probable levels of risk if CS or DS data were used.

High resolution soil sampling is very expensive and arduous when monitoring soil contamination over large areas has to be done. An appraisal of the site history aimed to identify past and present potential contaminating activities and preliminary geophysical measurements might help to define the most appropriate sampling scheme.

When a high spatial variability is suspected, it might be advisable to make a preliminary composite sampling at low-resolution, and only in the areas where the composite samples exceed the threshold/background values, proceed with a high-resolution sampling.

Rocco C., Duro I., Di Rosa S., Fagnano M., Fiorentino N., Vetromile A., Adamo P. (2016)
 COMPOSITE VS. DISCRETE SOIL SAMPLING IN ASSESSING SOIL POLLUTION OF AGRICULTURAL SITES AFFECTED BY SOLID WASTE DISPOSAL
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How effective is bimodal soil hydraulic characterization? Functional evaluations for predictions of soil water balance

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Summary

To overcome some drawbacks of the unimodal relations commonly used to describe soil hydraulic properties (SHPs), previously we developed bimodal lognormal relations that have the following main features: (i) they are closed-form expressions, (ii) they have a sound theoretical basis and provide a more general conceptualization of soil and (iii) they improve the description of both the water retention (WRF) and hydraulic conductivity (HCF) functions. Nevertheless, the reliability of soil hydraulic analytical relations is often tested only at the curve fitting level. Comparisons between unimodal and bimodal soil hydraulic relations are more effective and informative when performed within a functional evaluation approach. We use the HYDRUS-1D package to quantify and compare soil moisture dynamics and storage regimes for hydrological processes at both the event and annual time-scales when the soil domain is characterized by either unimodal or bimodal hydraulic properties. Seven soil samples taken from a previous study were used in numerical simulations of drainage or infiltration processes; there were large relative discrepancies in terms of simulated soil water storage. A subsequent test that involved simulations of soil water budget for the period 2000–2012 was implemented for a peach-orchard field by a conventional scaling method. This test also enables soil spatial variation to be taken into consideration. Two different scenarios enable the epistemic uncertainty to be evaluated when different hydraulic models are considered for soil with weak or strong bimodality. With Willmott's refined index of agreement, discrepancies in soil water storage were about 15% (weak bimodality) or more than 30% (strong bimodality).

Highlights

- Main aim of this study is the assessment of epistemic uncertainty in modelling soil water dynamics.
- We make functional evaluations for both event-based and long-term hydrological processes.
- Disregard of bimodal soil hydraulic behaviour can lead to large epistemic errors.
- Better predictions of soil hydraulic properties should be sought in future research.

Introduction

Quantification of the hydrological balance requires information on how soil reacts when subjected to initial and boundary conditions. Such behaviour is commonly described by relations between soil water content, θ , and hydraulic conductivity, K , versus matric pressure head, h . They represent the so-called soil hydraulic properties, namely the functions of water retention, $\theta(h)$ (WRF), and hydraulic conductivity, $K(h)$ (HCF).

For ease of comparison or use in computer models of hydrological balance, soil hydraulic properties are conveniently described by

analytical expressions whose parameter values depend on the specific soil type under study (Nimmo, 1997). The most widely used soil hydraulic parametric expressions are the unimodal Brooks and Corey (uBC), van Genuchten–Mualem (uVGM) or Kosugi (uKOS) relations, which all describe the soil-pore system with a unimodal pore-size distribution (PSD) (Brooks & Corey, 1964; van Genuchten, 1980; Kosugi, 1996). The unknown parameters are estimated by classical nonlinear regression techniques with a sufficient number of soil-water retention, $h-\theta$, and hydraulic conductivity, $h-K$, data points obtained from laboratory or field experiments. Allowing for the extensive literature on unimodal hydraulic relations, the reader is directed to the papers by Kosugi *et al.* (2002) or Assouline & Or (2013) for further information on these unimodal models and their basic features.

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Conclusions

From our assessment of three popular bimodal soil hydraulic relations with both parametric and functional evaluations, we draw the following conclusions:

- In spite of the additional water retention information required, the benefit of using bimodal analytical expressions in numerical simulations of soil hydrological processes is considerable even for weak bimodality in the porous domain. The three bimodal relations tested are as easy to implement as their unimodal counterparts, but require a few extra parameters that provide sufficient mathematical flexibility to distinguish inter-aggregate pores (structural macropores) and intra-aggregate pores (textural micropores). Bimodal parametric expressions improve the estimation of soil hydraulic conductivity and reduce prediction uncertainty, in spite of the large cross-correlations among the model parameters.
- One-dimensional infiltration into a uniform soil profile can be more sensitive to bimodality than one-dimensional drainage. The relative errors in some numerical simulations could be rather large, especially when the bPD and bROM bimodal models are compared with the uKOS and uVGM unimodal models, respectively. In contrast, the mixed bimodal model (bRS) shows minor discrepancies when compared with its corresponding unimodal expression.
- Functional evaluations of an annual water budget at the field scale demonstrate that appropriate characterization of the soil is essential for reliable results and for larger spatial and temporal extents, in which discrepancies might be smoother and epistemic uncertainty small.

Romano N. and Nasta P. (2016)

HOW EFFECTIVE IS BIMODAL SOIL HYDRAULIC CHARACTERIZATION? FUNCTIONAL EVALUATIONS FOR PREDICTIONS OF SOIL WATER BALANCE

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Simultaneous removal of heavy metals from field-polluted soils and treatment of soil washing effluents through combined adsorption and artificial sunlight-driven photocatalytic processes

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HIGHLIGHTS

- Removing heavy metals from a real contaminated soil using EDDS.
- Sequence of photochemical and adsorption processes for soil washing effluents.
- Kinetic and equilibrium models for soil washing and adsorption processes.
- Ecotoxicological assessment of the soil washing effluents.

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ABSTRACT

This paper proposes a process for reducing the content of copper and zinc in polluted soils and a combined photocatalytic-physical process for the treatment of the soil washing effluents. For this purpose, real soil samples were taken from the “Land of Fires”, a region in Southern Italy which is known for its high incidence of cancer mortality. Ethylenediamine-*N,N*-disuccinic acid (EDDS) was used to extract the heavy metals from the contaminated soil. The soil washing effluents were treated through a sequence of photocatalytic and adsorption processes to lower the concentration values of metals (Cu, Zn, Fe and Mn) below the limits of national legislation for discharge in municipal sewers and to remove the EDDS from the soil washing solutions. Ecotoxicological tests, using different living organisms (*Daphnia magna*, *Vibrio fischeri*, *Pseudokirchneriella subcapitata* and *Lepidium sativum*), were performed on the soil washing effluents before and after the treatments to assess the effects of the proposed combined process on the ecotoxicity of the soil washing solutions.

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1. Introduction

Soil washing is one of the most promising “ex-situ” techniques for cleaning of soils contaminated by toxic metals [1]. Different organic agents can be used to extract the metals from the polluted soils. Ethylenediaminetetraacetic acid (EDTA) is the most commonly used chelating agent, due to its ability to form stable complex species with several metals [2]. Unfortunately, EDTA is quite persistent in the environment due to its poor biodegradability. Therefore, ethylenediaminedisuccinic acid (EDDS) has recently been proposed as a safe and environmentally-friendly substitute for EDTA in soil washing processes [3]. However, a proper

treatment of the exhausted soil washing solutions containing the chelating agent and the extracted metals is necessary before these effluents can be discharged into the environment. The treatment of metal-chelating agent leachate using traditional techniques, such as precipitation or adsorption, is generally unsuitable due to the thermodynamic stability of the metal-organic complexes [4]. The possibility of destroying the organometallic complexes by simultaneously removing the chelating agent (i.e. EDDS, EDTA) and the metals through heterogeneous and homogeneous photocatalytic chemical processes has been recently proposed [5–7]. However, these studies are restricted to synthetic solutions or real soil washing solutions at a low trisodium EDDS salt-to-metal molar ratio (i.e. MR = 0.6), whereas chelating agent-to-metal molar ratios greater than 1 have been often suggested in the literature in order to achieve higher metal extraction from field-polluted soils [8].

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Conclusions

The removal of heavy metals from field-contaminated soils, sampled from the “Land of Fires” located in the province of Naples in Italy, was achieved through soil washing with aqueous solutions at EDDS-to-metal molar ratios larger than 1.

The soil washing process succeeded in reducing the heavy metal concentration in the sampled soils to levels that comply with Italian regulations. However, the process generated effluents containing the chelating agent and metals at concentrations exceeding the sewer discharge limits established by Italian legislation.

An increase in the solution to- soil ratio slightly improved Zn extraction percentage from 40% to 55% after 96 h of soil washing, whereas its influence on Cu extraction was negligible. In order to comply with the Italian regulatory requirements, a combination of artificial sunlight-driven photocatalytic (photo-Fenton-like) and adsorption (on activated carbon) techniques was adopted.

The processes proved to be very effective in completely removing EDDS and reducing the concentrations of copper, zinc, iron and manganese to values (0.4, 0.95, 0.24 and 1.13 mg L⁻¹ respectively) within the Italian regulatory limits, without adding additional reagents and adjustment of the pH value of the soil washing effluent.

However, the ecotoxicological tests carried out on the untreated and treated soil washing effluents using living organisms belonging to highly diverse taxonomic groups (bacteria, alga, crustacean and seed), gave conflicting outcomes.

The different sensitivities, as measured in the treated soil washing effluents, may be ascribed to the complexity of the chemical matrix and to the by-products, such as some carboxylic acids, formed during the photocatalytic treatment.

The metal–organic species could have different bioavailability among the organisms tested, also giving rise to synergistic and/or cumulative effects, which may explain the different responses obtained across the species tested.

Satyro S., Race M., Di Natale F., Erto A., Guida M., Marotta R. (2016)

SIMULTANEOUS REMOVAL OF HEAVY METALS FROM FIELD-POLLUTED SOILS AND TREATMENT OF SOIL WASHING EFFLUENTS THROUGH COMBINED ADSORPTION AND ARTIFICIAL SUNLIGHT-DRIVEN PHOTOCATALYTIC PROCESSES

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Photocatalytic processes assisted by artificial solar light for soil washing effluent treatment

Suéllen Satyro¹ · Marco Race² · Raffaele Marotta^{3,4} · Márcia Dezotti¹ · Marco Guida⁵ · Laura Clarizia³

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Abstract Contaminated soil has become a growing issue in recent years. The most common technique used to remove contaminants (such as metals) from the soil is the soil washing process. However, this process produces a final effluent containing chelating agents (i.e., ethylenediaminedisuccinic acid, also known as EDDS) and extracted metals (i.e., Cu, Fe, and Zn) at concentrations higher than discharge limits allowed by the Italian and Brazilian environmental law. Therefore, it is necessary to develop further treatments before its proper disposal or reuse. In the present study, soil washing tests were carried out through two sequential paths. Moreover, different artificial sunlight-driven photocatalytic treatments were used to remove Cu, Zn, Fe, and EDDS from soil washing effluents.

Metal concentrations after the additional treatment were within the Brazilian and Italian regulatory limits for discharging in public sewers. The combined TiO₂-photocatalytic processes applied were enough to decontaminate the effluents, allowing their reuse in soil washing treatment. Ecotoxicological assessment using different living organisms was carried out to assess the impact of the proposed two-step photocatalytic process on the effluent ecotoxicity.

Keywords Soil washing effluent · Metal removal · Sacrificial photocatalysis · “Land of Fires” · Soil remediation

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Introduction

Heavy metal pollution of soils and sediments is a global concern due to the negative impact of such metals on living organisms (Järup 2003). Hence, different remediation techniques based on physical, chemical, and even biological processes have been proposed to remove metals from contaminated soils (Mulligan et al. 2001). Among the chemical techniques, the soil washing using organic chelating agents is one of the most promising “ex situ” processes (Voglar and Lestan 2012), even though the extracting agents can persist in the environment at unacceptable levels. Recently, the attention has been focused on soil washing processes adopting more readily biodegradable substances, such as (S,S)-ethylenediamine-N,N'-disuccinic (EDDS), for heavy metal removal from polluted soils (Dermont et al. 2008). The main disadvantage of such processes is the subsequent need to remove heavy metals extracted from contaminated soils and residual chelating agent from soil washing effluents before any reuse and/or discharge into the aquatic environment. Normally, adsorption or precipitation processes are ineffective for treating these effluents due to the presence of chelating

Conclusions

Combined photocatalytic processes (TiO_2 -based) can be used for the simultaneous removal of heavy metals, such as Cu and Zn, from effluent produced in washing process of polluted soil when EDDS is used as organic chelate.

It was demonstrated that it is possible (i) to use artificial solar light on the photocatalytic treatment of the effluent produced by the first washing and (ii) to reuse this effluent for further rewashing. Ecotoxicity assessments on final effluents also showed the efficiency of photocatalytic treatment in reducing levels of ecotoxic effects for three living organisms tested.

*Satyro S., Race M., Marotta R., Dezotti M., Guida M., Clarizia L. (2016)
PHOTOCATALYTIC PROCESSES ASSISTED BY ARTIFICIAL SOLAR LIGHT FOR SOIL WASHING EFFLUENT TREATMENT
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Investigation of Groundwater Systems at different scale: the case study of the Volturno River Plain (Campania, Italy)

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ABSTRACT

This hydrogeological study has been performed in the framework of a LIFE + project (LIFE11/ENV/IT/275 – ECOMED). The study area is a large flat area (> 1500 km²) located in Campania region (Southern Italy). In the first phase, completed in 2014, the study consisted in the synergetic approach among different scientists to attain to the environmental characterization of the whole area. The second phase, started in 2015, was focused on the hydrogeological characterization of small sites (from 3000 m² to 4500 m²), and it included a detailed investigation survey, based on boreholes drilling, slug tests, pumping tests, hydrogeochemical monitoring, etc. The site-scale study showed the important role of small lenses of impervious materials together to the differences in the flowpath for groundwater above and under impervious materials and the flowpath at regional scale. Finally, the hydrogeochemistry gave important results about the groundwater quality and the contamination state.

KEY WORDS: Groundwater systems, NBL, groundwater pollution, groundwater monitoring,

INTRODUCTION

The study was developed in the framework of the LIFE + project (LIFE11/ENV/IT/275) ECOMED. The aim of the project is the definition of an operative protocol for agriculture-based bioremediation of contaminated agricultural soils in the NIPS "Litorale Domitio-Agro Aversano", and the verification of the effects of this protocol in three polluted pilot areas, of small dimension.

The study area is located in southern Italy, in the Campania region (Fig. 1). It is a large flat area (> 1500 km²) extending from the boundaries of the city of Naples to Latium region. Area is surrounded by carbonatic mountains, with a population of about 1,400,000 inhabitants (Ducci et al., in press).

In this area, the soil contamination is spotted and prevalently due to the legal and outlaw industrial and municipal wastes dumping, with hazardous consequences also on the groundwater quality.

The agricultural activities could be compromised threatening the supply chains of PDO products such as the "Mozzarella di Bufala Campana", with high economic, social costs for the population. Moreover, there is a general perception of health risks, due to the contamination of human food, water and air (Ducci et al., in press).

HYDROGEOLOGICAL SETTING

The flat coastal area is crossed by the Garigliano river and the Volturno river (Fig. 1). It is a Quaternary tectonic depression filled by alluvial and volcanic deposits. The graben is bounded by the Mesozoic carbonatic ridges of the southern Apennines (N and E) and by the Roccamonfina volcano (NE). Tuffs and pyroclastic deposits, emitted by the Phlegraean Fields during the Late Pleistocene-Holocene, occur in the subsoil of the plain and outcrop in the hills of the Phlegraean Fields (Corniello & Ducci, 2014).

The area encompasses only one whole Groundwater Body (GWB) of the Campania region (as defined in Sogesid, 2005): the Garigliano Plain (GAR); and parts of the GWBs of the lower part of the Volturno river (BVR), the eastern Plain of Naples (NAP) and the Phlegraean Fields (FLE) (Fig. 2).

The BVR GWB includes shallow aquifers, not continuous, constituted by alluvial and pyroclastic deposits, overlying the tuffs (Campanian Ignimbrite). The main aquifer is confined or

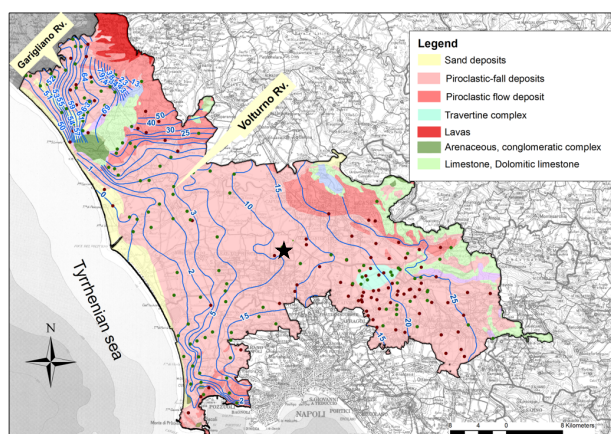


Fig. 1 – Hydrogeology of the study area, in blue the piezometric levels (m a.s.l.) of the main aquifer. Points indicate the monitoring network, in red the sample points exceeding the nitrate reference value (50 mg/L). Star indicates the pilot site of "Teverola".

Conclusions

In conclusion, the hydrogeological and hydrogeochemical characterization at regional scale is useful to:

1. delineate the main GW flow directions;
2. individuate the hydrogeochemical patterns of the study area;
3. distinguish between natural and anthropogenic pollution using NBLs.

The hydrogeological characterization at site scale is essential to:

1. reconstruct the most reliable hydrostratigraphical schemes also using the 3d models;
2. highlight the local GW flow and the differences with the GW flow at regional scale;
3. detect relationships between deep and shallow aquifers;
4. implement an accurate GW flow model as support for a future solute transport model.

Sellerino M., Corniello A. & Ducci, D. (2016)

INVESTIGATION OF GROUNDWATER SYSTEMS AT DIFFERENT SCALE: THE CASE STUDY OF THE VOLTURNO RIVER PLAIN (CAMPANIA, ITALY).

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Monitoring chronic and acute PAH atmospheric pollution using transplants of the moss *Hypnum cupressiforme* and *Robinia pseudoacacia* leaves


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HIGHLIGHTS

- Relations between PAH contents in *H. cupressiforme* and *R. pseudoacacia* were studied.
- *R. pseudoacacia* was able to accumulate LMW and HMW PAHs while moss prevalently HMW.
- Locust tree combined chronic PAH inputs, while moss reflected PAH recently emitted.

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ABSTRACT

Few studies are focused on correlations between the concentrations of PAHs in mosses and other bio-indicator plant species. This study was carried out to investigate the potential of the joint use of devitalized *H. cupressiforme* transplants and *R. pseudoacacia* leaves as cost effective biomonitors for the assessment of PAHs in the air. The test was performed in a land historically devoted to agriculture, where recurrent waste burnings randomly occur, especially in the season we chose for the investigation. The presence of 20 PAHs was assessed following EPA 3550 C 2007 and EPA 8270 D 2014 protocols. *R. pseudoacacia* was able to accumulate both LMW and HMW PAHs, while moss prevalently collected the latter. It is suggested that *R. pseudoacacia* combined chronic pyrogenic and petrogenic PAH inputs, while moss transplants reflected PAH depositions from recent pyrogenic events. Our approach revealed long and short-term pollution footprints, with *R. pseudoacacia* recording the chronic input of PAH compounds loaded along its vegetative growth, and moss bags reflecting acute pollution inputs occurred during the exposure duration.

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1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are listed by US Environmental Protection Agency and the EU Directive 2004/107/EC (US EPA, 1997; EU, 2005) among the contaminants of emerging environmental concern. These compounds consist of two to seven condensed aromatic rings; they can be of anthropogenic origin (mainly from fossil fuels burning), but they can also originate from natural sources such as volcanic eruptions and wild fires (Simonich and Hites, 1995). The transport pathways of PAHs in the

atmosphere depend on their physical-chemical properties. The most volatile (with low molecular weight and number of rings - LMW) remain in gaseous phase after their emission, while the heavier (high molecular weight and number of rings - HMW) are adsorbed on solid particulate matter. Due to the different partitioning between these two phases, lighter PAHs could be long range transported, while those with a higher molecular weight are generally deposited nearer to their emission sources (Thomas, 1986). Besides, environmental conditions such as temperature, UV radiation and wind dispersion can also affect their transport and persistence in the ambient air.

To by-pass the difficulty of direct measures of PAHs in the air by conventional devices, many researchers proposed the use of vegetation to monitor the occurrence of such compounds (e.g.

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Conclusions

The experiment carried out in this study demonstrated the potential of devitalized *H. cupressiforme* transplants and *R. pseudoacacia* leaves as cost-effective biomonitors for the evaluation of PAH presence in the air. Our approach suggests long- and short-term pollution footprints, with *R. pseudoacacia* recording the chronic input of PAH compounds loaded along its vegetative growth, and moss transplants reflecting acute pollution inputs during the exposure duration. In future studies, a similar trial, comparing the two biomonitors with passive samplers would be useful to substantiate these outcomes.

Robinia pseudoacacia was able to accumulate and store both LMW and HMW PAHs, while moss prevalently accumulated the latter. In agreement with their specific morphological and physiological characteristics, and according to PAH profile and specific diagnostic ratios, *R. pseudoacacia* combined chronic pyrogenic and petrogenic PAH inputs, while moss transplants reflected PAH depositions from recent pollution events, pyrogenic in our survey.

Moss bags exposed for 6 weeks confirm to be suitable biomonitors to detect pollution inputs, even considering PAHs. Although their use represents the only option in biomonitoring when suitable autochthonous species are lacking, longer or subsequent exposures would be tried to attempt the reconstruction of chronic PAH pollution.

Therefore, at the state, the joint use of autochthonous trees and moss transplants should be preferred to obtain a more comprehensive environmental information.

Further studies are needed to understand the different PAH accumulation dynamics of higher plants and moss transplants (devitalized and alive) and to explore the possibilities (e.g. different plant species, seasonality, land use) of their joint use in view of the proposal of a reproducible biomonitoring protocol.

Capozzi F., Di Palma A., Adamo P., Spagnuolo V., Giordano S. (2017)

MONITORING CHRONIC AND ACUTE PAH ATMOSPHERIC POLLUTION USING TRANSPLANTS OF THE MOSS HYPNUM CUPRESSIFORME AND ROBINIA PSEUDACACIA LEAVES

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Pyrolysis for exploitation of biomasses selected for soil phytoremediation: Characterization of gaseous and solid products

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ABSTRACT

Biomasses to be used in the phytoremediation process are generally selected to match agronomic parameters and heavy metals uptake ability. A proper selection can be made greatly effective if knowledge of the properties of the residual char from pyrolysis is available to identify possible valorization routes. In this study a comparative analysis of the yields and characteristics of char obtained from slow pyrolysis of five uncontaminated biomasses (*Populus nigra*, *Salix alba*, *Fraxinus oxyphylla*, *Eucalyptus occidentalis* and *Arundo donax*) was carried out under steam atmosphere to better develop char porosity. Moreover, the dependence of the properties of solid residue on the process final temperature was studied for *E. occidentalis* in the temperature range of 688–967 K. The results demonstrate that, among the studied biomasses, chars from *P. nigra* and *E. occidentalis* have to be preferred for applications regulated by surface phenomena given their highest surface area (270–300 m²/g), whereas char from *E. occidentalis* is the best choice when the goal is to maximize energy recovery.

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1. Introduction

Interest in creating biobased energy and materials supply chains has grown over the last few decades, especially for biomasses grown on contaminated or physically degraded lands unsuitable for ordinary food production (Fagnano et al., 2015; Shortall, 2013). When the contamination is represented by bioavailable potentially toxic elements (PTEs) the cultivation of specific biomasses becomes even more appealing as, under well suited conditions, the specific biomasses are able to remove contaminants from the soil through a process known as phytoremediation (Fiorentino et al., 2013; Barbosa et al., 2015), thus preserving food safety and agricultural landscape in polluted areas and improving soil ecological services.

The European LIFE ECOREMED project is now implementing an eco-compatible protocol for soil restoration through phytoremediation in Litorale Domitio - Agro Aversano NIPS (South Italy, Campania region). A key goal of the project is the selection of proper vegetal species to be used in the process. They are generally selected to match different desired parameters, such as absence

from the trophic chain, high biomass production, ability to uptake heavy metals, high growing rate, high adaptability to the climatic conditions, and high resistance to biotic and abiotic stresses. Based on these criteria, the ECOREMED project selected five biomasses, namely *Populus nigra*, *Salix alba*, *Fraxinus oxyphylla*, *Eucalyptus occidentalis* and *Arundo donax*. To implement phytoremediation properly, a plan for the safe disposal of the contaminated plant material after harvesting is required. Composting and compaction have been proposed as postprocessing treatments, as both are capable of greatly reducing the volume of the harvested biomass (Ghosh and Singh, 2005). Nevertheless, the high solubility of heavy metals in the leachate from these processes warrants additional treatments to ensure their appropriate collection and disposal.

A more appealing approach consists of utilizing of the contaminated plant material as feedstock in a biobased energy and/or material supply chain. Pyrolysis can be explored as a possible thermal treatment capable of producing, in the absence of molecular oxygen, a solid residue (char) suitable for application in several fields (as a fertilizer, activated carbon, etc.) and a liquid (bio-oil) and gaseous products that can be exploited for energy applications. Depending on the thermal conditions and the vapor residence time applied in the process, different types of pyrolysis exist: slow, fast, and flash pyrolysis. A lower process temperature and heating rate

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Conclusions

The dependence of the properties of solid residue on the process final temperature was studied for *E. occidentalis* in the temperature range of 688–967 K. Tests on *E. occidentalis* char at increasing final temperatures show that:

- The fixed carbon content reached its maximum at 873 K, due to the onset of char oxidation reactions at higher temperatures.
- The HHV followed the same trend as fixed carbon content. Careful control of pyrolysis temperature is mandatory when steamassisted pyrolysis is conducted with the aim of exploiting the char energy content. In this case, the management of ash was a problem, given the high concentration of inorganics in the char residue.
- The char surface becomes alkaline in nature at low temperature. Mild thermal treatment ($T < 794$ K) should be conducted if neutrality is desired.
- The char BET surface has a nonmonotonous trend with temperature; at 688 K, the char still had a compact structure, whereas the highest value occurred at 794 K.

The comparative analysis between the chars derived from *P. nigra*, *S. alba*, *F. oxyphylla*, *Eucalyptus occidentalis*, and *A. donax* shows that the chemical nature of the biomass had a relevant role in the determination of char yield and properties as summarized in the following:

- Char yield depend on the content of lignin as well as of alkali and earth alkali metals. Under the pyrolysis conditions used in this work, a linear correlation has been observed between the yield of the organic fraction of char obtained at 600 °C and the product between lignin content, cellulose content and the content of both alkali and earth alkali ions.
- All the produced chars, especially *P. nigra* char, has an O/C value lower than 0.2, revealing a high degree of aromaticity and maturation.
- All the chars were alkaline in nature, due to the presence of alkali and alkaline earth metal ions. In particular, the *S. alba* and *F. oxyphylla* chars had the highest content of exchangeable cations (Na, K, and Ca).
- The *P. nigra* and *E. occidentalis* chars exhibited the highest HHV, in agreement with the fixed carbon content and the lowest ash content. Moreover, the highest char yield obtained for *E. occidentalis* determined its highest ER value in the corresponding char
- Type II isotherms characterized all the chars and are associated with narrow slit pores including pores in the micropore region. The *P. nigra* and *E. occidentalis* chars seemed to be the most promising in terms of specific surface area.

In conclusion, the results of this study reveal that *E. occidentalis* char is the most appealing to be tested for energy applications, *P. nigra* should be considered for carbon sequestration in soils and for use as a sorbent of undesired species in fluid stream and *F. oxyphylla* and *S. alba* could be applied in agronomic applications as nutrients source. Future developments of this study will deal with the analysis of the distribution of PTE in the pyrolysis product of the contaminated biomasses. Furthermore the stability of the heavy metals concentrated in the char residue will be assessed.

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Geochemical and Pb isotopic characterization of soil, groundwater, human hair, and corn samples from the Domizio Flegreo and Agro Aversano area (Campania region, Italy)

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ABSTRACT

A geochemical survey was carried out to investigate metal contamination in the Domizio Littoral and Agro Aversano area (Southern Italy) by means of soil, groundwater, human hair and corn samples. Pb isotope ratios were also determined to identify the sources of metals. Specifically, the investigation focused on topsoils ($n = 1064$), groundwater ($n = 26$), 25 human hair ($n = 24$) and corn samples ($n = 13$). Topsoils have been sampled and analysed in a previous study for 53 elements (including potentially harmful ones), and determined by ICP-MS after dissolving with aqua regia. Groundwater was analysed for 72 elements by ICP-MS and by ICP-ES. Samples of human hair were prepared and analysed for 16 elements by ICP-MS. Dried corn collected at several farms were also analysed for 53 elements by ICP-MS. The isotopic ratios of $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ in selected topsoil ($n = 24$), groundwater ($n = 9$), human hair ($n = 9$) and corn ($n = 4$) samples were analysed from both eluates and residues to investigate possible anthropogenic contamination and geogenic contributions. All data were processed and mapped by ArcGis software to produce interpolated maps and contamination factor maps of potentially harmful elements, in accordance with Italian Environmental Law (Legislative Decree 152/06). Results show that soil sampling sites are characterized by As, Cd, Co, Cr, Cu, Hg, Pb, Se, and Zn contents exceeding the action limits established for residential land use (RAL) and, in some cases, also the action limits for industrial land use (IAL) as established by Legislative Decree 152/06. A map of contamination factors and a map showing the degrees of contamination indicate that the areas in the municipalities of Acerra, Casoria and Giugliano have been affected by considerable anthropogenic-related pollution. To interpret the isotopic data and roughly estimate proportion of Pb from an anthropogenic source we broadly defined possible natural and anthropogenic Pb end-member fields based on literature data. For example, we summarized data for Vesuvius and Campi Flegrei volcanic rocks, gasoline, and aerosol deposits.

Lead isotope data show mixing between geogenic and anthropogenic sources. Topsoil, groundwater, human hair and corn samples show a greater contribution from geogenic sources like the Yellow Tuff (from Campi Flegrei) and volcanic rocks from Mt. Vesuvius. Aerosols, fly ash and gasoline (anthropogenic sources) have also been contributors. In detail, 46% of the topsoil residues, 96% of topsoil leachates, 88% of groundwater, 90% of human hair, and 25% of corn samples indicate that >50% percent of the lead in this area can be ascribed to anthropogenic activity.

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1. Introduction

This paper presents the results of a comprehensive geochemical study of the Domizio Littoral and Agro Aversano area (Southern Italy) based on analyses of topsoil, groundwater, vegetable (corn) and human hair samples, conducted in order to determine the impact of human activities on the environment. Preceding studies have documented the

heavy metal pollution of topsoils across this area (Albanese et al., 2011; Bove et al., 2011; Grezzi et al., 2011; Lima et al., 2012) as well as an increased rate of cancer mortality compared to the regional average (Senior and Mazza, 2004). Many studies in recent years have focused on environmental issues using isotope ratios of lead. (Ayuso et al., 2013; Ayuso and Foley, 2016; Chen et al., 2016; Galušková et al., 2014; Jiao et al., 2015; Kumar et al., 2013). The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio is the most commonly used as tracer of environmental pollution sources because it can be precisely determined (Komárek et al., 2008). A detailed study of Pb isotope ratios was used as a key method to discriminate and apportion

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Conclusions

Results of this study for geochemical and isotopic characterization of various media, with support of GIS and GEODAS software, suggest a complex interplay of geogenic and anthropogenic sources.

The results of geochemical analyses of topsoil, groundwater, human hair and corn samples show that the presence of Tl and V can be attributed to a geological source.

The numerous agricultural practices in this area could have caused the environmental contamination of Cu. Heavy metal pollution is concentrated in specific areas: Acerra, Casoria, Giugliano in Campania municipalities, as indicated by the high concentration values of several elements such as Hg, Ni, Pb, Se, Sb, Zn. Industrial activities and presence of illegal waste management practices may have greatly contributed to the contamination of Sb, Pb, Hg, Zn and Pb as indicated by the variations of the Pb isotopes ratios in topsoil, groundwater, human hair and local vegetables.

We suggest that most of the Pb present in our samples comes from anthropogenic activities.

Most of the samples imply the contribution of aerosols and fly ash as a source of lead.

Topsoil, groundwater, human hair and corn samples show a greater contribution by geogenic sources, such as yellow tuff and Mt. Vesuvius volcanic and aerosols.

Overall, 46% of topsoil (corresponding the solid residues), 96% of topsoil (corresponding the leachate), 88% of groundwater, 90% of human scalp hair, and 25% of corn samples show that N50% percent of the lead found in the area is related to anthropogenic sources.

We also conclude that groundwater samples and corn samples can be related to pesticides and thus are a natural effect of intense and long lasting agricultural activities in this area.

In the next phase, we are going to study in more detail the potential hazards to human health caused by contamination, either anthropogenic or of natural origin, at the study site.

Rezza C., Albanese S., Ayuso R., Lima A., Sorvari J., De Vivo B. (2017)

GEOCHEMICAL AND Pb ISOTOPIC CHARACTERIZATION OF SOIL, GROUNDWATER, HUMAN HAIR, AND CORN SAMPLES FROM THE DOMIZIO FLEGREO AND AGRO AVERSANO AREA (CAMPANIA REGION, ITALY).

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Tracking the route of phenanthrene uptake in mosses: An experimental trial



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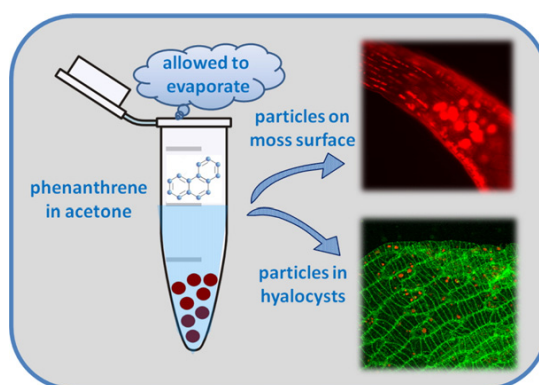
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HIGHLIGHTS

- Phenanthrene uptake was investigated by fluorescence microscopy in four mosses.
- Phenanthrene was selected since it is one of the most abundant in the atmosphere.
- The compound was prevalently intercepted and up-taken in particulate form.
- The four mosses showed different uptake ability.
- Evidence of a physical more than a chemical uptake emerged.

GRAPHICAL ABSTRACT



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 Fluorescence microscopy

ABSTRACT

In recent decades, mosses have been used as native species or as transplants in monitoring a wide range of pollutants from inorganic (i.e. metals and metalloids) to organic contaminants (mainly polycyclic aromatic hydrocarbons-PAHs). To implement the use of mosses as biomonitors of PAHs, one important issue is the study of the interactions between these compounds and moss tissues. In this study we investigated the mode of phenanthrene uptake in four moss species (*Amblystegium humile*, *Plagiomnium affine*, *Hypnum cupressiforme* and a clone of *Sphagnum palustre*) and its movements from air to plant surface and within the biomonitors, using fluorescent and confocal microscopy. The target compound, partitioned between gas and particulate phase depending on air conditions, was selected since it is one of the most abundant PAHs released into the atmosphere. Our findings support the hypothesis that phenanthrene aggregates in particles and in this form it is chiefly intercepted and uptaken onto moss surfaces, albeit with different frequency in the four species, with *S. palustre* > *H. cupressiforme* > *P. affine* = *A. humile*. Phenanthrene enters the dead, empty hyalocysts of *S. palustre*. Specific surface area and composition, frequency and distribution of binding groups may also explain the different ability of phenanthrene uptake by the four moss species.

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Conclusions

Fluorescence microscopy proved a good tool to investigate the mode of interaction and uptake of PAHs, especially phenanthrene, in mosses, due to their auto-fluorescence.

Phenanthrene shows hydrophobic properties (high octanol–water partition coefficient, $\log K_{ow} = 4.5$), displaying a fairly low solubility in water.

Our findings do not support the hypothesis of phenanthrene entry into the aqueous compartments of the cell, such as vacuoles and the cytoplasm. Instead, at least in the conditions used for our experimental set-up, we support the hypothesis that phenanthrene forms micron-sized particle aggregates already in the stock solution and that it is uptaken by mosses in this form.

Phenanthrene particles were deposited on the leaf surface of mosses, and in some cases (*P. affine*) entrapped by the rhizoids; only in *S. palustre* did phenanthrene particles enter the empty, dead hyalocysts through the pores present on the leaf surface.

In addition, surface characteristics, differing in the four mosses investigated, may play an important role in the uptake and retention of phenanthrene.

Therefore we support the concept of a physical rather than chemical uptake of this and similar compounds in mosses.

Our findings showed a different ability of the tested species in the uptake and retention of phenanthrene particles, confirming *S. palustre* and *H. cupressiforme* as good bioaccumulators; therefore, this laboratory experiment is only the first phase to elucidate the route of phenanthrene uptake, but it does represent a key step for selecting the appropriate moss species to use in field studies.

Spagnuolo V., Figlioli F., De Nicola F., Capozzi F., Giordano S. (2017)

TRACKING THE ROUTE OF PHENANTHRENE UPTAKE IN MOSESSES: AN EXPERIMENTAL TRIAL

Science of the Total Environment 575 (2017) 1066–1073

LECTURES

7th International Workshop on Biomonitoring of Atmospheric Pollution (BIOMAP) - June 14-19, 2015 - Lisbon, Portugal.

BIOMONITORING RESEARCH OF HEAVY METALS AND PAHS IN THE AIR OF AGRICULTURAL LANDSCAPE OF ITALY'S CAMPANIA REGION.

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In recent years the Campania region, one of the most fertile Italian agricultural landscapes has been under the attention of media because for decades its soils were illegally used to dump potentially lethal toxic wastes, as result of waste crisis.

Moreover, with time people began setting fire to the dumps, making matters worse. Public opinion claims that this situation is the cause of increase of some cancers rates and shorter lifespan of people living in this area.

Authoritative researchers have recently suggested that Campania region could be a perfect field study for a biomonitoring research programme, as their poisoned fields could serve as a giant experiment in the new science of 'exposomics'. In pilot sites of "Litorale Domizio-Agro Aversano" NIPS, recognized by the Italian State as a National Interest Priority Site in Campania, the Life ENV-IT ECOREMED project is working to implement eco-compatible protocols for agricultural soil remediation.

In this framework we present the data from a first biomonitoring survey to detect inorganic (metals and metalloids) and organic (PAHs) pollutants in the air using moss transplants.

The methodology applied follows a harmonised protocol of exposure in which devitalised moss *Hypnum cupressiforme* was used to prepare sub-spherical moss bags that were exposed in the sites of interest for six weeks starting on March 2014.

The exposure design was set taking into account the inventory of known emissions to the atmosphere, and the diffuse urbanization of the area in which agricultural and urban/residential sites are strictly intermingled and was applied to five municipalities, Acerra, Casal Di Principe, Giugliano, Maddaloni, Teverola.

Results for metals and metalloids indicate that all the investigated area is highly homogeneous, and for most of analysed elements the uptake rates were higher in agricultural sites compared to urban/residential ones.

The highest uptakes were measured for Pb, Zn, Cu, major pollutants in the soils of the area, the last one with large application in agricultural practices. Limited PAH uptakes were evidenced with the most represented components, pyrene and benzo(b)fluoranthene following a similar trend in soils. Comparison with previous monitoring surveys indicates moss uptake rates largely lower than those measured in the urban area of Naples city.

Geophysical Research Abstracts Vol. 17, EGU2015-14736-1 (EGU General Assembly 2015, 12-27 April 2015, Vienna, Austria. Oral presentation)

DETERMINING PRIORITIES OF A REMEDIATION PLAN AT URBAN SCALE BY ASSESSING THE RISK OF METALS AND POPS FOR LOCAL POPULATION: THE ACERRA-POMIGLIANO-MARIGLIANO CONURBATION CASE STUDY IN ITALY.

Albanese S., Lima A., Rezza C., Qi S., Qu C., Wei C., De Vivo B.

In the framework of the URGE (Urban Geochemistry) project aiming at depicting the environmental conditions of several cities in Europe, the north-eastern sector of the Naples metropolitan area (Italy), namely the Acerra-Pomigliano-Marigliano area (with ~160.000 inhabitants), has undergone a geochemical characterization based on topsoil sampling (145 samples over an area of 90 sqkm).

The conurbation includes 6 municipalities (Acerra, Pomigliano D'Arco, Castello di Cisterna, Bruscianno, Mariglianella and Marigliano) and considering the total extension of the urbanized areas (18-20 sqkm) the average population density could be corrected to 6-7000 inhabitants/sqkm. Soils of the area are mostly originated by the pedogenesis of the original pyroclastics produced by the Mt. Somma-Vesuvius volcano on the south-western side of the study area.

The area has been selected because of both the presence of an historical industrial settlement on it (mainly devoted to plastic materials and synthetic fibers production) and of an incinerator which came into operation in March 2009. The main objective of the study was 1) to define the local geochemical baselines both for 53 elements (among which the toxic ones) and for some organic compounds, including PAHs, PCBs and OCPs and 2) to assess the environmental risk generated by polluted soils. Furthermore, the study aimed at supporting epidemiological researches and at establishing a record of the environmental status quo ante to evaluate in the future the impact of the incinerator on life quality and on health of local population.

Obtained results showed that most of the urbanized areas of the Acerra-Pomigliano-Marigliano conurbations are characterized by concentrations of Pb, Zn and V exceeding the intervention limits established by the Italian Environmental law (D.Lgs. 152/2006).

Agricultural soils, in the surroundings of the urbanized areas, are enriched in Cu, Co, Cd, Be and Ni, and the probable presence of illegal waste disposals in the area should be considered as a source for them. In the area where the incinerator has been built Se, Hg, Cu, Cd and Sb baselines are generally higher than in the rest of the territory. Benzo(a)pyrene, benzo(g,h,i)perylene and indeno(123-cd)pyrene are the most concentrated PAHs in urbanized areas and they are characterized by concentrations exceeding the Italian guidelines.

AIIA 2015 Mid term conference “New frontiers of biosystem and agricultural engineering for feeding the planet”. (Salerno).

BIOMONITORING RESEARCH OF HEAVY METALS AND PAHS IN THE AIR OF AGRICULTURAL LANDSCAPE OF ITALY’S CAMPANIA REGION.

E. Cervelli; S .Pindozi; A. Capolupo; M. Rigillo; L. Boccia

The paper discusses a field study on the topics of the Land Use Change (LUC) applied to the Ecosystem services (ES).

Specially, the study focuses on the assessment of the value of ES through different option in LUC according to progressive findings of the European Project LIFE/ENV/IT/275 Ecoremed that has implemented a protocol for the bioremediation of contaminated soils in Campania region.

The cultivation of no food crops (Poplar and Giant reed) is proposed as buffer crops waiting for the characterization of the areas.

This facilitates the uptake of the mineral contaminants and the biodegradation of organic compounds reducing the risk for leaching and the run off of harmful contaminants that would occur on bare soils. The study aims at testing a proposal in approaching Land Use Change (LUC) adding socio-economic factors to the environmental topics.

The research experience evaluated ES economic value through GIS tool and decision support software (ArcGIS/ILWIS), using literature data to assess the current value of the ES provided for such crops (t/ha/year) as benefits that people obtained from ecosystems. Some key scenarios have sorted out and compared through multicriteria analysis.

Those scenarios are based on a large data set produced within the Life project activity. Moving from the deep knowledge of the environmental condition of the territory the study shows the alternative ES values of the Land Use Change starting from no-change scenario (Poplar and Giant reed), to abandonment.

The discussion gives evidence that is possible to asses an increase of the ES value, both in case of a private and public action.

Proc. EGU General Assembly, Vienna, 12-17 April, Geophysical Research Abstracts, vol. 17, EGU2015-7007, ISSN: 1607-7962.

MONITORING AND MODELING OF WATER FLOW AND SOLUTE TRANSPORT IN THE SOIL-PLANT-ATMOSPHERE SYSTEM OF POPLAR TREES TO EVALUATE THE EFFECTIVENESS OF PHYTOREMEDIATION TECHNIQUES.

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

This work is part of a series of studies being carried out within the EU-Life+ project Ecoremed (Implementation of eco-compatible protocols for agricultural soil remediation in Litorale Domizio-Agro Aversano NIPS).

The project refers to Litorale Domizio-Agro Aversano that has been identified as National Interest Priority Site (NIPS) and includes some polluted agricultural land belonging to more than 61 municipalities in the Naples and Caserta provinces of the Campania Region.

The major aim of the project is to define an operating protocol for agriculture-based bioremediation of contaminated agricultural soils, also including the use of plant extracting pollutants to be used as biomasses for renewable energy production.

This contribution specifically address the question of evaluating the effectiveness of phytoremediation actions selected by the project in the pilot area of Trentola-Ducenta and will provide some preliminary results of monitoring and modeling activities.

A physical and hydraulic characterization has been carried out in this area where poplar trees were planted. Monitoring of water flow, root water uptake and solute transport in the soil-plant-atmosphere is under way with reference to two trees using capacitance soil moisture and matric potential sensors located at three different soil depths, whereas plant water status and evapotranspiration fluxes are indirectly estimated using fast-responding stem dendrometers.

European Conference on Environmental Applications of Advanced Oxidation Processes, EAAOP-4. 21 - 24 october 2015, Athens - Greece.

SOLAR PHOTOCATALYTIC PROCESSES FOR SOIL WASHING WASTEWATER TREATMENT

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The use of biodegradable chelating agents(EDDS) for removing heavy metals from soils is a very promising ex-situ process for the treatment of contaminated soils . The main drawback of the soil washing is the need of a successive treatment of the wastewater which contains the extracted heavy metals and chelating agents.

The studies on the possibility to decontaminate EDDS containing soil washing effluents are restricted to synthetic solutions or real soil washing solutions but using exclusively artificial solar radiation.

The present investigation proposes, for the first time, an integrated “ outdoor“ photocatalytic process for lowering the high concentration of copper, iron and zinc and EDDS present in soil washing wastewaters to values below the limits defined by the Italian legislation for discharge in civil sewers.

The effluents were produced through a soil washing process using EDDS as chelating organic agent.

The polluted soils were taken from the “Land of Fires,” an area in Campania region, Southern Italy, near Naples, known for its high incidence of cancer mortality also due to a marked presence of toxic residues in the environment. The “ outdoor“ runs under sunlight were carried during the spring 2015 at University of Naples (Italy, local latitude 40° 50 00 N, longitude 14°12 00 W) by means of a solar tubular collector supported by an aluminium structure. The unit comprised 8 parallel borosilicate glass tubes (i.d. 4 mm, length 34.6 cm and width 6 mm) connected by plastic junctions.

An experimental campaign was carried out “ indoor” , by using a simulated solar radiation (sodium vapour lamp), aiming at the establishment of an optimal sequence of photocatalytic processes capable to ensure the highest efficiency of removal Cu, Zn, Fe and EDDS. The best choice resulted to be firstly the removal of Fe, Zn and EDDS through a TiO₂-photocatalysis with oxygen, followed by a photocatalytic step under inert atmosphere (sacrificial TiO₂-photocatalysis) for the abatement of the residual metals, particularly Cu, and organics (scheme 1) concentration in 16 kJ/L and Cu content after 35kJ/L below the limits permitted by the actual Italian legislation. In general, removal efficiencies of 100% for Fe, Zn and EDDS, and over 65% for Cu were achieved after 25.4 kJ/L of accumulated energy by means of solar tubular reactor. The high removal efficiency reached with the photocatalytic processes suggests that the system could be proposed as useful solution for removing some heavy metals and chelating agents from soil washing wastewater. Ecotoxicological tests were carried out to evaluate the ecotoxicity of the soil washing wastewaters before and after the solar photocatalytic treatment.

The ecotoxicological assessment was performed on four different target organisms: a bacterium (*Vibrio fischeri*), a green microalga (*Pseudokirchneriella subcapitata*), a crustacean (*Daphnia magna*) and a seed (*Lepidium sativum*). Preliminary ecotoxicity test showed the efficiency of the photocatalytic system to modify the toxicity of the soil washing effluents.

8th Euregeo, 15-17 June 2015, Barcelona, Spain.

GEOCHEMICAL CHARACTERIZATION, ISOTOPIC APPROACH AND ENVIRONMENTAL RISK ASSESSMENT IN THE DOMIZIO FLEGREO AND AGRO AVERSANO AREA (CAMPANIA REGION)

Rezza C., Albanese S., Ayuso R., Lima A., De Vivo B.

The LIFE11ENV/IT/000275 project has the aim to define an operative protocol for agriculture-based bioremediation of contaminated agricultural soils in the “Litorale Domizio-Agro Aversano” NIPS (National Interest Protection Site) and to identify geochemical indicators and eco-toxicological biomarkers to monitoring environmental quality.

Within such project a comprehensive geochemical environmental study has been carried focused on topsoil, groundwater, vegetable (corn) and human hair samples since former studies (Lima et al. 2012, Grezzi et al. 2011; Bove et al. 2011) pointed out the occurrence of an heavy metal pollution accross this area.

Lead isotopic analysis on different matrices have been carried out to discriminate among the contamination sources of Pb and to establish their geogenic and/or anthropogenic nature (Ayuso et al. 2008). In particular, our study concentrated on specific site affected by different pollution types: Teverola (Fondo Comunale), Trentola-Ducenta (Fondo Bove), Giugliano (Fondo Zaccaria), Castelvoturno (Soglitelle- Laghetti).

VIII EPOA II CIPOA 3 a 6 de Novembro de 2015 -Belo Horizonte – Brasil

SIMULTANEOUS REMOVAL OF EDDS, CU, FE AND ZN FROM SOIL WASHING WASTE THROUGH COMBINED PHOTOCATALYTIC TREATMENTS

S. Satyro¹; R. Marotta; M. Race; M. Dezotti; R. Andreozzi

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The metal contamination on the soil has different kinds of sources. One of the soil remediation techniques is the soil washing, which uses a chelating agent for extracting metals from the polluted soil, but it produces a liquid waste containing the metals and the chelating agent, being necessary to treat this waste for its complete detoxification.

This treatment could be by photochemical processes, since some metal complexes are photosensitive to sunlight irradiation and their photodecomposition may lead to metal precipitation and chelant destruction [SATYRO et al., 2014a]. In our previous paper [SATYRO et al., 2014b] it was demonstrated that the removal of different metals require distinct photochemical processes.

Then it was made an attempt to remove all the metals using a sequential of different photochemical treatments with the aim to achieve the Brazilian and the Italian metal limits established by each Country normative.

Combined photocatalytic treatments are highly efficient for the removal of Cu, Fe and Zn, allowing the proper disposal of the waste produced on the metal contaminated soil remediation as is required by the Brazilian and Italian Normative.

Microbial Diversity 2015 - THE CHALLENGE OF COMPLEXITY - 2015 SIMTREA, Società Italiana di Microbiologia Agraria-Alimentare e Ambientale, San Casciano Val di Pesa, Firenze, Italy

BACTERIAL STRAINS FROM THE “Terra dei Fuochi”: ISOLATION, SELECTION AND EFFECT ON THE DYNAMIC OF MICROBIAL POPULATIONS AFTER THEIR APPLICATION TO THE CONTAMINATED SOILS

Ventorino V., Ambrosanio A., Cafaro V., Di Donato A., Starace D., Pepe O.

Università degli Studi di Napoli “Federico II”, Italy

The environmental contamination due to accumulation in the soil of persistent organic xenobiotics substances chemicals such as hydrocarbons is a problem that is becoming increasingly important in the world.

Technologies based on the use of microorganisms able to degrade the organic pollutants, allow to accelerate the natural detoxification processes in the soil environment and represent an alternative method of environmental remediation compared to the harmful traditional methods.

The aim of this study was to isolate and select microorganisms potentially able to remove hydrocarbons from contaminated soils in the “terra dei fuochi” (Campania region, Italy) and also the dynamic of microbial populations after inocula application.

Selective and differential substrates to isolate new microorganisms were developed on the basis of contaminants identified in the pilot sites.

A total of ninety-six microbial strains were isolated and identified by polyphasic approach on the basis of their phenotypic, biochemical and molecular characterization.

Isolated strains were also tested for their ability to grow on selective minimal medium with a mixture of different PAHs as sole carbon source and characterized for their bioemulsifier production and the ability to grow in biofilm on hydrophobic surfaces.

Obtained results showed a wide range of bacterial species able to metabolize contaminants with potential use in soil remediation as well as to produce bioemulsion.

On the basis of all results, the two strains *Bacillus megaterium* EL5, able to degrade up to 30.4% of PAHs (phenanthrene) in 21 days, and *Bordetella petrii* EL12B, showing high emulsification properties (Emulsification Index=0,95) and able to degrade up to 70.7% of phenanthrene in 21 days, were selected to produce the bacterial formulate to use in in situ experiments.

PCR-DGGE as well as high-throughput sequencing were performed to highlighted the microbial dynamic and diversity in the contaminated soils before and after microbial inoculation.

Input Torino 2016 - 9th International Conference on Innovation in Urban and Regional Planning

THE BIOREMEDIATION OF POLLUTED AREAS AS AN OPPORTUNITY TO IMPROVE ECOSYSTEM SERVICES.

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The intensive urban development characterizes the European context, demonstrating existing dynamics generally orientated toward the increasing of urban population in cities and in the coastal areas, and the reduction of rural landscape (abandonment, underutilization, deterioration, pollution, inappropriate utilization, etc., of agricultural areas and marginal lands).

The main impact of such dynamics is the loss of territorial maintenance and the phenomenon of land abandonment (landslides, burning, wastes disposal, together with socio economic degradation).

This land downgrade, despite it not, necessarily, correspond to a severe soil pollution, could impulse to a land requalification, basically based on a land use change, passing from intensive agricultural use toward no-food cropped areas or (if possible) areas for recreational use.

European Community policies, jointly with industrial stakeholders in the field of the biomass production, could be an important support such conversion.

Due to the use of decision support software, the gradual evolutions of land use change (LUC) scenarios are conceivable. Scenarios comparison will be based both on a productivity criterion and on the evaluation of Ecosystem Services (ESs).

ESs indeed provide better condition for human well being, qualitative livelihoods and efficiency for the human habitat (Costanza, 1997).

Since the Millennium Ecosystem Assessment (MEA, 2003 and 2005) scholars consider ESs an essential topic for improve urban and peri-urban resilience and a key concept for updating the planning framework. Moreover ES are useful tools for the assessment of planning policies and of the outcome of the EU funds.

In Campania Region (Southern Italy), both PON Biopolis and the European LIFE/ENV/IT /275 Ecoremed projects work for providing scientific proofs in the using of no food crops to prevent marginalization or abandonment in large areas.

In such framework the aim of the study is to find out a set of consistent scenario for testing the impacts of LUC for such widespread polluted areas that could become an opportunity for a positive change of the ESs values, improving the biodiversity of the territory.

The here presented evaluation, made through the ESs approach are now under comparison with the first results of the LUC on the ecological networks and local wildlife.

AIIA 2016 “Smart Rural Buildings: Food, Security, Safety and Sustainability Improving knowledge for rural building design and management” - Bologna

GIS SUPPORTED TECHNIQUES FOR LAND USE CHANGE IMPACTS EVALUATION IN POTENTIAL ENVIRONMENTALLY SENSITIVE AREAS

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In recent centuries, the anthropogenic land use change caused extensive loss of habitat and is widely recognized as a major driver of the current biodiversity crisis (de Lima, Dallimer, Atkinson, Barlow, 2012).

One of the main transformation of the land use is caused by agriculture. Understanding how to minimize the impacts on biodiversity of the LUC not just limited to the peri-urban areas, but also to agricultural land is one of the main issues in land management.

Mitigation measures have to be devoted to contrast fragmentation and increasing insulation in more natural environments, avoiding, on the other hand, an increasing homogenization of the agricultural landscape.

This paper presents the evaluation of three LUC scenarios in a NIP Area of Campania Region (Cervelli et al., 2016), in terms of impacts on wildlife.

The work was developed within European LIFE/ENV/IT/275 Ecoremed projects. GIS applications techniques and Spatial Multicriteria Decision Analysis (Malczewskj, 2006) have identified the areas of 14 wildlife species-umbrella possible presence in landscape.

The evaluations were integrated through the use of sensitivity data, based on habitat assessments, territory permeability, species conservation and rarity, extended to more than 300 taxa.

The developed methodology allows the identification of potential conflict areas between LUC scenarios and species presence areas, in order to calibrate interventions and mitigation strategies. The methodology is, therefore, a support tool for the decision-maker, to define appropriate planning strategies aimed to ecological networks management, physical-territorial continuity among the natural environments maintenance, creation of a species mobility support systems, combating isolation and ensuring the maintenance of adequate biodiversity levels.

Purpose of the work is to contribute to the definition of positive LUC for NIP area, not only in economic terms, but as integrated development opportunities of the territory.

Rend. Online Soc. Geol. It., 39(1): 825 - 42nd IAH International Congress; Hydrogeology: Back to the future!" ROMA, 13-18/09/2015

INVESTIGATING GROUNDWATER SYSTEMS FROM REGIONAL SCALE TO SITE-SCALE

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This hydrogeological study has been performed in the framework of a LIFE + project (LIFE11/ENV/IT/275 - ECOREMED). The study area (> 1500 km²) is located in Campania region (Southern Italy) and it encompasses the plains of the Garigliano River and of the Volturno River and part of the volcanic district of the Phlegrean Fields.

There are widespread agricultural and livestock activities, and an intensive production of the "Mozzarella di Bufala Campana".

Soil and/or groundwater are affected by a widespread agricultural pollution and by a local contamination, caused by legal and illegal wastes.

Moreover, the population perceives this situation as at risk for the health, due to the possibility of contamination of the food products through soil and water, with high economic and social costs.

In the first phase, completed in 2014, the study consisted in the synergetic approach among different scientists to attain to the environmental characterization of the whole area; in the second phase, now running, the study is focused on the field activities in small areas (from 3000 m² to 4500 m²), agricultural or used as temporary storage of urban wastes, contaminated by metals (zinc, copper, etc.) and organic pollutants.

In the first phase, the aim of the hydrogeological part was the reconstruction for the whole area of the stratigraphic model, the identification of the groundwater bodies, the assessment of groundwater quality, the derivation of natural background levels (NBLs) and the definition of the pollution vulnerability of the aquifers.

In the second phase, the hydrogeological characterization of the sites includes a detailed investigation survey, based on boreholes drilling, slug tests, pumping tests, hydrogeochemical monitoring, etc. and it is partially carried out and it will continue up to the end of 2016. The main results achieved in this phase are:

1. the site-scale heterogeneous system shows the important role of small lenses of impervious materials: they act like confining materials for the underlying alluvial-pyroclastic sediments and support a phreatic groundwater;
 2. the flowpath is quite different for groundwater above and under impervious materials;
 3. the local-scale heterogeneity has an effect on the flowpath, in some cases it is different from the regional groundwater flow directed toward west;
 4. the first data about hydrogeochemistry show high values of arsenic and fluoride coinciding with the regional distribution, testifying a geogenic origin of these ions. Also for SO₄, Fe, Mn the changes are slight. For NO₃ some decrease has been recorded.
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Rend. Online Soc. Geol. It., Suppl. n. 1 al Vol. 40 (2016) 88° Congresso SGI, Napoli 2016 - Società Geologica Italiana, Roma 2016

NEW CONSIDERATIONS ABOUT NITRATE CONTENT IN GROUNDWATER OF THE ALLUVIAL-PYROCLASTIC AQUIFER OF THE CAMPANIAN PLAIN (SOUTHERN ITALY)

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The type of land use has an impact on groundwater quality. The application of manure, fertilizers and pesticides in agriculture is a primary source of groundwater pollution, especially diffuse pollution, that remains the most difficult to control.

Nitrate in groundwater is the most common type of diffuse pollution. Since the nineties, we registered in the alluvial-pyroclastic aquifer of the Campanian Plain very high nitrate contents (Cornielo & Ducci, 2014) both in the shallow aquifer and in the deeper aquifer confined or semiconfined by a thick layer of tuff (Ignimbrite Campana, about 39Ky B.P).

These high values were confirmed in the years 2000, up to 300 mg/L in the shallow aquifer and until 150 mg/L in the deeper aquifer. Isotopic studies carried out in a small sector of the area (Cornielo & Ducci, 2009) revealed that here high contents of nitrate were prevalently due to the farming and the buffaloes breeding.

In these areas, groundwater suffers from different pressures, being intensive agriculture and buffalo-breeding the most important, in addition to illegal dumping and municipal waste.

Moreover, in the coastal part near the Volturno mouth, a saltwater intrusion issue exists. Finally, these areas are affected by natural contamination and in different sectors high contents of fluoride, arsenic, sulphate, iron and manganese are present.

Moreover, in the last decade the area degraded its reputation and has been called the “Land of Fire” by the media for the widespread illegal burning of waste. Consequently the appeal of local food products has been reduced and has thrown the agricultural economy (the area is the Campania Felix of the Roman times) of the region into crisis.

In the framework of a detailed study of the hydrogeology of the Campanian Plain, we have updated the knowledge about the nitrate contents in groundwater.

In 2016 we started a hydrochemical monitoring of groundwater in wells, and in most of them we carried out isotopic analysis (¹⁵N/¹⁴N and the ¹⁸O/¹⁶O ratios of dissolved nitrate) with the aim to define the sources of nitrate contamination.

Indeed, a wide range of measures can be implemented to limit pollution: control of the sewerage systems, land use restrictions, obligatory treatment of industrial waste waters, and prohibition of the use of certain chemicals. Although the partial adoption of these measures in the last years, nitrate content in groundwater of many areas of the Campanian Plain seems remain very high.

Geophysical Research Abstracts Vol. 18, EGU2016-15747, 2016 - EGU General Assembly 2016

NITRATE CONTAMINATION RISK ASSESSMENT IN GROUNDWATER AT REGIONAL SCALE

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Nitrate groundwater contamination is widespread in the world, due to the intensive use of fertilizers, to the leaking from the sewage network and to the presence of old septic systems.

This research presents a methodology for groundwater contamination risk assessment using thematic maps derived mainly from the land-use map and from statistical data available at the national institutes of statistic (especially demographic and environmental data).

The potential nitrate contamination is considered as deriving from three sources: agricultural, urban and periurban. The first one is related to the use of fertilizers. For this reason the land-use map is re-classified on the basis of the crop requirements in terms of fertilizers.

The urban source is the possibility of leaks from the sewage network and, consequently, is linked to the anthropogenic pressure, expressed by the population density, weighted on the basis of the mapped urbanized areas of the municipality.

The periurban sources include the un-sewered areas, especially present in the periurban context, where illegal sewage connections coexist with on-site sewage disposal (cesspools, septic tanks and pit latrines).

The potential nitrate contamination map is produced by overlaying the agricultural, urban and periurban maps. The map combination process is very easy, being an algebraic combination: the output values are the arithmetic average of the input values.

The groundwater vulnerability to contamination can be assessed using parametric methods, like DRASTIC or easier, like AVI (that involves a limited numbers of parameters). In most of cases, previous documents produced at regional level can be used. T

he pollution risk map is obtained by combining the thematic maps of the potential nitrate contamination map and the groundwater contamination vulnerability map. The criterion for the linkages of the different GIS layers is very easy, corresponding to an algebraic combination.

The methodology has been successfully applied in a large flat area of southern Italy, with high concentrations in NO_3^- .

Rem Tech 2016

CHARACTERIZATION AND REMEDIATION OF DEGRADED AGRICULTURAL LANDS: THE ROLES OF VEGETATION.

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Alla luce della legislazione attuale un terreno viene definito inquinato in relazione ai rischi per l'ambiente e la salute umana che derivano dall'uso del sito.

Nel caso dei suoli agricoli in mancanza di una esplicita definizione normativa, è necessario analizzare i rischi sia diretti che indiretti.

Quelli diretti sono relativi alle ore di frequentazione da parte degli operatori agricoli.

Quelli indiretti, legati all'alimentazione con i prodotti ottenuti sul sito, sono determinati dalla biodisponibilità degli elementi potenzialmente tossici (EPT) ed in definitiva dal rischio di accumulo di sostanze tossiche nelle parti eduli dei prodotti agricoli.

Esistono diverse tecniche analitiche per determinare la frazione potenzialmente (es. EDTA) o prontamente biodisponibile (es. NH_4NO_3) degli EPT nei suoli, ma solo l'analisi della vegetazione ed in particolare delle specie iperaccumulatrici può dare la risposta definitiva sul rischio sanitario legato alla contaminazione degli alimenti prodotti sul sito.

Le tecniche di risanamento dei suoli agricoli quindi devono mirare a ridurre o annullare i rischi legati alla frazione biodisponibile degli EPT.

18th International Conference on Heavy Metals in the Environment. 12-15 September, Ghent, Belgium.

MICROSCOPICAL ANALYSIS OF PARTICULATE MATTER INTERCEPTED BY MOSS-BAGS IN URBAN, INDUSTRIAL AND AGRICULTURAL AREAS OF THREE EU COUNTRIES

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The particulate matter (PM) represents an important transport form of heavy metals in the atmosphere (WHO, 2013), recently recognized by the International Agency for Research on Cancer (IARC) as one of the pollutants most affecting human health and closely associated with increased cancer incidence (EEA, 2015).

High costs and technical constrains often hamper an adequate evaluation of airborne particulate load. The use of moss-bags represents a cost effective alternative to evaluate PM deposition. It consists of the exposure of mosses inside nylon bags according a rationale design with the aim to evaluate the air quality (Capozzi et al., 2016a; 2016b; Ares et al., 2012).

Mosses are in fact well-known biomaterials able to adsorb and entrap different type of airborne particles (Adamo et al., 2007; González et al., 2016).

According to the above considerations, the aims of this work were: 1) to describe the nature of PM adhering to leaf surfaces of the moss *Pseudoscleropodium purum* (Hedw.) M. Fleisch. after 12 weeks exposure in bags in urban, industrial and agricultural sites of Italy, Austria and Spain; 2) to relate PM size and relative chemical composition to site-specific land use; 3) to identify different markers of possible PM pollutant source.

Many studies highlighted the efficiency of moss exposed in bags to retain particulate matter, but only few of them are focused on a morphological/numerical/chemical characterization of particles.

This study represented a further confirmation of the close association between PM entrapped by moss surface and moss elemental uptake.

Different land uses appear to be associated to the deposition of specific particle size class and composition, with a commonly frequent soil dust contribution.

Morphological and chemical characterization of PM entrapped by mosses might be useful to track possible sources of air pollution.

BIT's 9th Annual World Congress of Industrial Biotechnology-2016, March 16-18 Seoul, Korea

ROLE OF BIOSENTINELS IN THE BIOREMEDIATION PROJECT LIFE 11 ENV/IT/275 ECOREMED-C2C SUB-ACTION

Guerriero G.

Researchers have enhanced their capacities in pollution risk management using soil biodiversity and bioindicators named “biosentinels” as an ordinary tool to attain sustainability.

International mechanisms for strategic advice, coordination and partnership development (i.e. global platform and forums) have been instrumental in progress in the development of policies and strategies and the advancement of knowledge and mutual learning.

Overall, LIFE 11 ENV/IT/ 275 ECOMERED project has been an important instrument for raising public and institutional awareness, generating political commitment and focusing and catalyzing research actions by a wide range of stakeholders at all levels.

Topics of C2c sub-action are the bio-monitoring of oxidative damage and characterization of reproductive health status of invertebrate and vertebrate biosentinels with special attention to the answer of one vertebrate, phylogenetic close to the mammalian, the lizard *Podarcis sicula*.

As known, 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 highlighted the importance to assess in one testis gonadectomy of barcoded biosentinel, before and after remediation, 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 disruptors effect in the organism and its environment.

Expected outcome and goals in progress will be to develop and implement bioinformatics and data management solutions for environmental genomics researcher platform and to sustain the microarray development to screen simultaneously the expression of genes in regarding the reproduction of selected biosentinel as tool of soil sustainability.

BIT's 9th Annual World Congress of Industrial Biotechnology-2016, March 16-18 Seoul, Korea

PROJECT LIFE 11 ENV/IT/275 ECOREMED-C2C SUB-ACTION: SOIL DECONTAMINATION ASSESSMENT BY RTQPCR OF GONADAL GPX4 IN THE BIOSENTINEL PODARCIS SICULA

Guerriero G., Rabbito D., Ciarcia G.

Important molecular achievements have been made during the last decades for bioremediation and its assessment in relation to soil potentiality as industry of life.

We focus our subaction of 11Env/IT/275 Ecoremed project work on the male seasonal breeder, the biosentinel *Podarcis sicula* starting from its phospholipid hydroperoxide glutathione peroxidase (gpx4, the gene encoding PHGPx) partial gene sequence previously deposited (GenBank JN689224.1).

Here, we report RTqPCR analyses performed on male gonadal tissues of specimens of barcoded lizard of one site of "the Land of Fires": Teverola (South Italy) collected before and after bioremediation. A significant increase of gene expression was assessed respect to unpolluted control before decontamination whereas a significant decrease was detect corresponding to Glutathione S-Transferase pollution index.

The data are discussed in relation to the potentiality of biosentinels highlighting the role of *Podarcis sicula* gonad and of gpx4 as biomarker of decontamination assessment.

Conclusions

The quantitative gpx4 expression in the biosentinel *Podarcis sicula* testis characterized by abundance of highly unsaturated fatty acids, high rates of cell division, and very vulnerable to the overexpression of reactive oxygen species (ROS), confirms its relation with the different level of Glutathione S-Transferase pre and post bioremediation as pollution index.

In conclusion, the RTqPCR of gonadal *Podarcis sicula* gpx4 gives a reliable response as biomarker for decontamination assessment of the Land of Fires sites.

IFAMA-WICaNeM World Forum and Symposium, Aarhus (Denmark), June 19th - June 23rd , 2016

THE REMEDIATION OF POLLUTED LAND IN CAMPANIA REGION: SOME ECONOMIC ASPECTS

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The results of the analysis shown below concerns the hypothesis of cultivation of giant reed (with and without irrigation) in the polluted soils, to use the biomass in the biogas supply chain and the poplar irrigated crop in buffer areas.

The latter choice was due to the current setting of the Campania Region RDP Rural Development Plain (Reg. EU 1305/2013). In fact, the traditional poplar crop system in polluted soils may not have public support for the establishment costs.

Concerning the use of polluted soils, it should be clarified that under current legislation, the biomass coming from those areas is considered a by-product (the main function of the crop in fact is considered the phyto-remediation), which can be placed in the possible supply chains for the exploitation for energy purposes.

Concerning giant reed crop without irrigation, the cumulative biomass production at the tenth year was 260 t per hectare, with a production value about 11,600 Euros per hectare, without public support (Figure 2). The costs was 11,700 Euros per hectare, with the prevalence of explicit costs (almost 90%). In particular, the most important item is represented by rentals.

The labor represents the most significant item among the opportunity costs, which constitutes 61%, this is also due to the decision to assign zero value to the polluted land. The NI was 1,200 Euros per hectare (average per year = 120 Euros), the profitability expressed by the PI was 0.93 (Figure 3), then 7% lower than the equilibrium level, corresponding in a labor remuneration of 10.60 €/h.

Concerning the giant reed cultivated with irrigation, the biomass production at the ten years was 490 t per hectare, with production value of almost 24,000 Euros per hectare, without public support (Figure 2). Even the cost of production grows to over 23,000 euro per hectares.

The cost structure was, also for this crop, dominated by the explicit component, especially by rentals. It should be noted that this crop had the highest values both in terms of total costs and production value among those analyzed in the present paper. The NI was 2.290 Euros at tenth year (average per year = 229 Euros).

The profitability was slightly above the equilibrium level (1.26) (Figure 3), corresponding to a remuneration of labor of 14.40 € / h.

The analyzed poplar plantation obtained a production value of 20,400 Euro per hectare, with a cost level of almost 20,200 Euro per hectare for 2/3 represented by the explicit component (Figure 2). Also in this case the most representative items are rentals, followed by technical means and labor cost. We must to emphasized that for this crop there are considered also the land cost, being hypothesized the realization in non-polluted soils.

The poplar had the highest net income among the crops analyzed, with 10.113 Euros (1.011 per year).

Basically, the poplar wood PI was in equilibrium (1.03), without public support, while with the support according to the RDP could achieve a profitability of 1.47, nearly 50% higher than the equilibrium level (Figure 3).

In general, for the crop analyzed, with current prices, the level of unitary profitability can be considered satisfactory, especially for the poplar with the grant of Rural Development Plan, which reduces the costs of the plant for farmers.

Those results are, however, also to be assessed in the light of the characteristics of agricultural farms in the Terra dei Fuochi area.

However, in terms of total net income per hectare the results of the crops analyzed are considerably distant from those achievable with highly intensive production systems, typical of the Terra dei Fuochi area. That generates a lost revenue for the farmers involved which currently are being considered by public institutions.

The balance of the FADN farms showed good economic performances, in terms of both profitability and net income per hectare⁴.

In fact, on average its production value per hectare was above 14,000 Euros per year, the net income was above 4,000 Euros per year, and the PI was far above the equilibrium level, both with public support (1.64) and without it (1.40).

As mentioned above, the functions hypothesized for the two crops analyzed were different. In fact, in polluted areas the function of the giant reed was associate the activity of phyto- purification production of biomass, capable to give revenues that could cover the production costs, at least.

Instead, the cultivation of poplar in the buffer areas could associate the production of wood and the creation of a physical barrier to protect the valuable productions in the soils around the waste dump with also landscape and environmental features.

There is a reason to suppose that the latter may constitute an important element of reassurance to consumers, affected by environmental scandals emphasized by media, about the healthiness of produced in the Terra dei Fuochi areas.

Therefore, while the giant reed could be a viable economic alternative in toto for the polluted soils, in the case of buffer areas the poplar could take an indirect economic function, consisting in the protection of the value of agricultural production in this area.

AIIA 2016 “Smart Rural Buildings: Food, Security, Safety and Sustainability Improving knowledge for rural building design and management” - Bologna

PREDICTING LAND USE CHANGE ON A BROAD AREA: DYNA-CLUE MODEL APPLICATION TO THE LITORALE DOMIZIO-AGRO AVERSANO

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The long-standing awareness of the environmental impact of land-use change (LUC) has led scientific community to develop tools able to predict their amount and to evaluate their effect on environment, with the aim supporting policy makers in their planning activities.

This paper proposes an implementation of the Dyna-CLUE model applied to the Litorale Domizio-Agro Aversano, an area of Campania region which needs interventions for environmental remediation.

Future land use changes were simulated in two different scenarios developed under alternative strategies of land management: scenario 1 is a simple projection of the recent LUC trend, while scenario 2 hypothesizes the introduction of alternative cultures, such as poplar (*Populus nigra* L.) and giant reed (*Arundo donax* L.), in addition to a less impactful urban sprawl, which is one of the main issues in the study area.

The overall duration of simulations was 13 years, subdivided into yearly time steps. CORINE Land Cover maps were used as baseline for land use detection in the study area.

Competition between different land use types is taken into account by setting the conversion elasticity, a parameter ranging from 0 to 1, according to their capital investment level (Verburg & Veldkamp, 2004).

Location suitability for each land use type is based on logit model. Since no actual land cover already exists for the alternative cultures investigated in scenario 2, a suitability map realized through a Spatial Multicriteria Decision Analysis (Cervelli et al., 2016) was used as a proxy for its land use pattern.

The comparison of the land cover in 2012 and scenario 1, evaluated through the application of Kappa statistics (Visser & de Nijs, 2006), showed a general tendency to expansion of built-up areas, with an increase of about 2.400ha (1.5% of the total surface), at the expense of agricultural land and those covered by natural vegetation. The comparison of the land cover in 2012 and scenario 2 showed a less significant spread of built-up areas, affecting approximately 750ha (0.5% of the total surface).

Moreover, the introduction of alternative crops on about 10.000ha the territory (6.8% of the total surface), would result in a significant decrease of arable land and a lower decrease of permanent crops, respectively equal to 6.800ha and 2.900ha.

This work highlighted the importance and the potential of predicting land-use change models as valid tools supporting decisions, especially in those region needing interventions aimed to environmental remediation, as in the case study examined in this paper.

Geophysical Research Abstracts, Vol. 18, EGU2016-16763, 2016 (EGU General Assembly 2017, 17-22 April 2017, Vienna, Austria. Poster presentation)

PB ISOTOPIC CONSTRAINS AND ENVIRONMENTAL RISK ASSESSMENT OF THE DOMIZIO FLEGREO AND AGRO AVERSANO AREA (CAMPANIA REGION, ITALY)

Rezza. C., Albanese S., Ayuso R., Lima A., Sorvari J., De Vivo B.

A comprehensive geochemical environmental study focused on topsoil, groundwater, vegetable (corn) and human hair samples has been carried out in the Domizio-Flegreo Littoral and Agro Aversano areas in Southern Italy, covering 1287 km² and including 90 municipalities.

Within the framework of the this study a focus was also carried on some specific sites (Teverola, Trentola-Ducenta, Giugliano, Castelvolturno and Acerra), that may have been affected by different sources of pollution (industrial and agricultural) and by the large presence of illegal buried waste disposals.

Among the industrial sites that are expected to contribute to the contamination of the region a car and a chemical factory producing polyester fibres could be taken into account together with an urban waste incineration plant that is in operation since 2009 within the Acerra municipality administrative area.

The research is based on 1064 topsoil samples, 27 groundwater samples, 24 samples of human hair and 13 corn samples taken in across the whole study area. Although samples were analysed for 53 elements at ACME Analytical Laboratories (Vancouver, Canada) by means of ICP-MS and ICP-ES after an aqua regia digestion, we focused on 15 key elements (As, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, Tl, V and Zn), for which the Italian Environmental Law 152/06 establishes trigger and action limits for both residential/recreational and industrial/commercial land use, based on the risks to human health.

All the chemical data were statistically treated and dot and interpolated maps were produced by means of the GeoDAS software.

Maps showing the distribution of contamination factors (1) (Hakanson,1980) for each key element were also created. In general, As, Pb, Cr, Cd and Hg resulted to be the most critical pollutants for the area. Furthermore, Pb isotopic analyses on soil, water, corn and hair were conducted in order to distinguish between possible sources of contamination and geogenic and/or anthropogenic contribution.

These studies were done at the Radiogenic Isotope Laboratory of the U.S. Geological Survey (Reston, VA, USA) following standard isotopic separations in Class 100 laboratories.

The samples were analyzed using an HR-ICP-MS and a FinniganMat (Spectromat) spectrometers. Notably, the Pb isotopic compositions of human hair generally matched the Pb isotopic values that were previously shown by others to represent the composition of aerosol (2) (Tommasini et al., 2000), implying that Pb originates from the anthropogenic activities in the area.

Further studies will include the determination of risks to human health caused by the elevated concentrations of the key elements in the environment and food items.

To start with, a preliminary conceptual model will be created that serves as a basis for a detailed regional risk assessments. The results will enable us to define specific risk management actions needed for the protection of human health in the study area.

XXXIV Convegno Nazionale della Società Italiana di Chimica Agraria, Perugia 5-7 Ottobre 2016

SPATIAL VARIABILITY, MOBILITY AND BIOAVAILABILITY OF POTENTIALLY TOXIC METALS IN AGRICULTURAL SOILS AFFECTED BY WASTE DISPOSAL

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Soil pollution by potentially toxic metals (PTMs) is a serious worldwide problem. Understanding the spatial distribution of pollutants and their mobility and bioavailability is crucial for environmental management and decision-making.

Not all EU countries have standard soil sampling guidelines imposed by law neither similar soil sampling protocols. Risk assessment is mostly based only on the total or “pseudototal” content of PTMs in soil. In this work (carried out within the LIFE11/ENV/IT/275-ECOREMED), in agricultural soils affected by waste disposal we studied: 1) the relevance of an appropriate sampling scheme to assess the PTMs pollution and 2) the feasibility and the effectiveness of a phytoremediation treatment, based on Eucalyptus planting assisted by compost and microorganisms.

For this purpose, in three pilot sites, the degree and spatial variability of soil pollution by PTMs, were assessed applying a soil sampling scheme based on a two-level grid resolution.

On the first level, a regular low-resolution 10x10 m grid was defined. On the second level, each grid was subdivided into nine high-resolution 3x3 m subplots.

Discrete soil samples were taken from each 3x3 m plot. Composite soil samples were made bulking aliquots from the discrete soil samples.

Soil samples were collected from two depths, 0-30 (topsoil) and 30- 60 cm (subsoil) to evaluate the vertical gradient. Among the studied sites only Giugliano (GI) was polluted, mostly by Cu and Zn. On the base of pollution indices, composite soil samples GI appeared to be slightly polluted (mean content of 131 and 95 mg kg⁻¹, for Cu and Zn respectively).

When the indices were applied to discrete soil data, the slightly polluted site became highly polluted by Cu (mean and max of 276 and 1707 mg kg⁻¹) and Zn (174 and 972 mg kg⁻¹), and slightly polluted by Sb and As (max of 15 and 30 mg kg⁻¹). Furthermore, a large inhomogeneity in soil pollutant spatial distribution emerged.

The readily and potentially bioavailable amounts of Cu and Zn in polluted soil samples, before and during the phytoremediation treatment, were investigated applying single (1M NH₄NO₃ and 0.05M EDTA pH 7) and sequential extractions (EU-BCR) and comparing the values with plant uptake.

The amount of both metals extracted by 1M NH₄NO₃ was from 0.1 to 7.9 % of respective total contents, while the amount extracted by 0.05 M EDTA ranged from 13 to 64 % of total content.

After one year from planting, a reduction of Cu and Zn bioavailable amounts was detected.

Plant uptake was not significantly correlated with single extractions and a general underestimation of 1M NH₄NO₃ bioavailable Zn in comparison with plant uptake was observed.

Both single and sequential extractions suggested a higher mobility of Zn respect to Cu in soil. Overall, in the study sites, the phytoremediation treatment was effective in reducing at least the mobile and plant available PTMs content of the soil.

Atti del XLV Convegno della Società Italiana di Agronomia Sassari, 20-22 Settembre 2016 (pg 34-35)

THE POTENTIAL OF NATIVE PLANTS TO ACCUMULATE HEAVY METALS FROM AN INDUSTRIAL POLLUTED SOIL: PRELIMINARY RESULTS

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With the development of urbanization and industrialization, soils were increasingly polluted by heavy metals (HM) threatening ecosystems, surface and ground waters, food safety and human health. Phytoremediation can be potentially used for the risk managements, phytostabilization and remediation of HM-contaminated sites.

A major step towards the development of phytoremediation of HM-impacted soils is the identification of HM hyperaccumulating and high tolerant plants. This study aimed at evaluating the potential of native plant species to extract and accumulate heavy metals from a soil of a battery recycling site (Marcianise, Campania Region, Italy) polluted by Pb and Cd.

All the screened plant species exhibited a good adaptability to Pb and Cd contaminated soil. In particular, *D. glomerata* with $BAF_{\text{roots}} > 1$ and $TF < 1$ was very suitable for phytostabilization of Cd in contaminated soil (Yoon et al., 2006) and could be used to avoid contaminated dust production by surface soil erosion.

Two plant species were suspected as metal hyperaccumulators: *Artemisia annua* for Cd and *Silene latifolia* for Tl. *A. annua* was most effective in taking up Cd (BAF_{shoots} and $TF > 1$) from a soil with low Cd content (4.9 mg kg^{-1}), that is a typical characteristic of hyperaccumulator plants (Reeves et al. 2001). *A. annua* was also suitable for phytostabilization of Cd ($BAF_{\text{roots}} = 1.73$), although Cd content in shoots was lower than 1000 mg kg^{-1} (Van der Ent et al., 2013). TF higher than 1 was already reported for the *Artemisia* genus by Baek et al. (2004).

Further experiments in controlled environment with soil highly polluted by Cd are needed to confirm this hypothesis. *S. latifolia* presented a Tl concentration in shoots higher than 100 mg kg^{-1} and TF higher than 1. So, according to Escarrè et al. (2011), *S. latifolia* might be an hyperaccumulator of Tl; however also in this case further experiments are needed to confirm the hyperaccumulator status of this plant species.

Atti del XLV Convegno della Società Italiana di Agronomia Sassari, 20-22 Settembre 2016 pg (42-43)

ACCUMULATION OF ZN AND CR IN NATIVE PLANTS GROWING ON A FARMLAND POLLUTED BY ILLEGAL TANNERY SLUDGES DISPOSAL: PRELIMINARY RESULTS

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Contamination of heavy metals deriving from illegal waste disposal and dumping represents one of the most pressing threats to water and soil resources as well as human health.

Phytoremediation can be potentially used for risk managements and remediation of these metal contaminated sites. This study aimed at evaluating the potential for phytoremediation of native plant species growing on a farmland contaminated by past disposal and dumping of tannery sludges.

None of the screened plant species had hyperaccumulator characteristics, while all exhibited high adaptability to Zn and Cr contaminated soil.

The highest accumulation of Zn and Cr was observed in *Cyperus rotundus* showing Zn and Cr content in shoots 3 and 23 times higher than value found in grasses from unpolluted soils.

High Cr accumulation was also observed in *C. dactylon* with shoot values 11 times higher than those measured in grasses from unpolluted soils.

The high accumulation of Zn and Cr by *C. rotundus* and *C. dactylonis* in accordance with observations by Suchkova et al. (2014).

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