1st Spanish National Conference on Advances in Materials Recycling and Eco – Energy
Madrid, 12-13 November 2009
S02-11

STRATEGIES FOR REMEDIATING POLLUTED SOILS

J. Pastor[1], R. Millán[2], A. J. Hernández[3], M. J. Sierra[2] and M.C. Lobo[4]

[1] Centro de Ciencias Medioambientales (CMA). CSIC. Serrano, 115-bis. 28006 Madrid, Spain
[2] Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT). Avda. Complutense, 22. 28040 Madrid, Spain
[3] Departamento de Ecología. Universidad de Alcalá de Henares. Edificio de Ciencias. Campus Universitario. Ctra. de Barcelona Km. 33,63. 28871 Alcalá de Henares (Madrid), Spain
[4]Instituto Madrileño de Investigación y Desarrollo Rural, Agrario y Alimentario (IMIDRA). Ronda de Atocha, 17. 28012 Madrid, Spain

Introduction

For several years, a group of researchers from several institutions has been evaluating strategies for remediating soils polluted with heavy metals and inorganic compounds (such as salts that separate into their anions and metals). Both these substances may be taken up as mineral nutrients of the plants growing in these soils.

In our ongoing work on environmental restoration, we have considered phytotechnologies given their low landscape impacts and good social acceptance. The phytorecovery of soil is based on the use of plants, soil amendments and agronomy techniques to retain the pollutants and reduce or abolish their toxic effects. Notwithstanding, bioremediation techniques and the use of sewage treatment sludges as soil amendments are also providing good results in soils with more than one heavy metal in their top layers. In this report, we systematize all the techniques we have assessed so far, though some methods have already been separately discussed including their conceptual/methodological frameworks by their respective authors (Hernández & Pastor, 2008; Millán & Lobo, 2008). This is an overview of the main restoration measures evaluated.

Systematizing the results obtained using different methods

1) The IRN's Department of Systems Ecology of the Environmental Sciences Centre, CSIC in Madrid, in collaboration with the Department of Ecology of the Universidad de Alcalá, have been testing methods in the field and under controlled conditions for the remediation of urban solid waste landfills and abandoned mine sites in the central-western area of the peninsula. To restore these scenarios, we have tried to apply the main principles and processes of ecology.

Field trials. Five years after sealing three domestic waste landfills of the Comunidad de Madrid (Móstoles, Villaviciosa and Mejorada) and having addressed the main eco-chemical relationships of the herbaceous species that have started to revegetate some zones of their sealing soils, we conducted an in situ trial. Basically we used the same remediation model for each landfill: fertilizing amendments applied to their soil covers (N, P, K), sowing with seeds of native and commercial species and adding a mixture of autochthonous seeds to the soil's seed bank. All trials were performed in 50 cm^2 plots as three replicates per control and treatment.

The biomonitoring over two consecutive years of these field trials has rendered scarce results in terms of improving the revegetation of these landfills. The main reasons for this include many factors such as: the constant erosion of fines and point sources of heavy metals, excess salinity and scarce soil matter along with a series of unforeseeable additional uses given to the landfill covers. However, we have started to observe the possible benefits of multispecies soil covers over the use of a single species to fix the soil covers to the landfill slopes, and the tolerance of many species to Zn as the most abundant heavy metal present in these scenarios. Of course, species selection has to take into account the composition of the covering soils.

Bioassays conducted in microcosms. Rubble landfills of old mining sites in pasture communities show soils polluted with several heavy metals. Phytoremediation techniques (*phytoextraction* and *phytostabilizatio*n) are the most suitable for restoring these sites. However, their efficiency depends on a good ecotoxicologic diagnosis in relation to the paragenesis of their minerals, as well as on a good understanding of the response mechanisms of the different plant species, at both the population and community levels, to the joint actions of several heavy metals. This determines a need for system scaling through the use of microcosms.

Other bioassays conducted in microcosms and controlled greenhouse conditions have addressed the effects of chelating agents (*EDTA* and *DTPA*) that complex the soil organic matter and retain heavy metals. These assays have also served to assess the use of *heat-dried sludges* as an amendment for the remediation of mine soils polluted mainly with Pb, Zn and Cd containing little organic matter. Thus, the most toxic elements are retained through adsorption of the organic matter by the sludges (Zn), or through their accumulation in roots (Pb). These findings suggest that these sludges might be useful for the restoration of terrestrial ecosystems polluted in this way as well as this being a good option for their management.

2) The Soil Degradation Unit (Environmental Sciences) of the CIEMAT has been investigating the use of different technologies to recover soils polluted with mercury. Several projects undertaken over the last ten years have essentially focused on sites affected by mines in Almadén, which to date is the area with the highest Hg concentrations on the planet since it represents the largest source of Hg in the world. Closure of the mines prompted a need for actions that would preserve the region's economy including: a) different rehabilitation strategies and b) alternative soil uses. This has meant an initial characterization of the soil and its plants, a study addressing soil pollution and the identification of wild plant species resistant to mercury followed by trials performed in controlled conditions using crop species as a socio-economic option.

Phytoavailability is emerging as a good tool to assess the risks of this metal as has also been noted for the other metals examined in section a). It is in this framework that the work underway in Almadén is being conducted as four lines: laboratory assays, controlled systems, lysimeter experiments and studies in real conditions.

Experimental assays in the laboratory: Tests have been performed on the soil variables that affect the availability of Hg for the plant; selective and sequential extraction studies, subsequent chemical speciation of Hg in the soil and determining the concentrations of macro- and micronutrients in relation to Hg changes produced during plant growth. Hg contents are determined by specifically designed atomic absorption spectrometers (AMA-254 LECO). Studies on the mobility of Hg in soils are performed by the addition of water, chelating agents, fertilizers and amendments in 1L glass columns containing representative soil samples. Next, physico-chemical properties, Hg, macro and micronutrients are determined both in the leachates and in the useful water for the plant. In some cases, it has been observed that Hg, Ca and Fe become mobilized, thus impoverishing the soil. It has also been determined that the most easily available fraction represents a small proportion of the total amount and that it is more indicative of the real exposure of the plant to Hg. Finally, the soil has been microbiologically characterized by estimating microbial mass by substrate-induced respirometry, obtaining the metabolic coefficient and the specific respiration rate. These tests provide information on the possible effects on the soil's microfauna of the presence of Hg and allow for discriminating the cause of the perturbation in cases in which a value indicative of stress is detected.

Studies in controlled greenhouse conditions: This involves experiments set up in pots filled with soils of the study area. These tests have been conducted on agricultural crops and natural flora. In general, it seems that Hg mainly builds up in the roots although an increased available Hg fraction in the soil produces in some species an increase in the Hg contents of the plant's stem and leaves. These studies serve to find species that could be used to phytostabilize soils polluted with Hg; sensitive species or bioindicators, and accumulating species for possible phytoextraction in areas with high bioavailable Hg levels. So far, complete cultivation cycles have been conducted for chickpea, lentil, vetch, aubergine (eggplant), white lupin, rapeseed and lavender, which are either common in Almadén, or planted as an alternative. No signs of toxicity have been observed in these plants. The lowest Hg concentrations have been found in the seed/fruit. In every case, the transfer factor is lower to that of wild plants such that their use in phytotechnologies would be fairly limited.

Pilot-assays on crops in lysimeters: Each lysimeter is a soil block of approximately a cubic metre in a metal vessel containing probes at different depths (15, 20 and 50 cm), which are used to measure physico-chemical soil variables (pH, Eh, moisture, temperature) during the crop's growth cycle. Lysimeters are the most realistic approach to the experimental field because they do not modify the soil volume (or affect soil horizons). Data were stored using a *datalogger*. The lysimeters were transferred to the CIEMAT, and 4 were sown with typical crops and a further non-cultivated lysimeter used as control.

The results of these lysimeter studies indicate highest Hg concentrations in the roots, followed by the stem and leaves. Lowest contents were detected in the seed/fruit.

For the food products, both greenhouse and lysimeter data have been analyzed. Reference data corresponding to national and European directives were applied considering maximal Hg ingestion levels for a balanced diet. Aubergine is suitable for human consumption with or without the peduncle and calix.

Consumption of chickpea and lentil would be permitted by the legislation as would the white lupin (for human consumption or as forage) and lavender. According to the European directive for species consumed by animals, vetch can be consumed as both grain and feed though its consumption as fodder (whole plant) is not recommended. Results have sometimes exceeded the recommended limits.

In situ studies: Mercury pollution in the area of Almadén has been addressed in experimental plots selected according to two criteria: they should differ in terms of (1) the impacts of mining activities suffered and (2) their flora and soil compositions. Highest Hg concentrations have been detected in the soils of the areas of most human impacts including mining activities.

The Hg contents of the above-ground portions of the plants were quantified to assess soil-plant Hg transfer. Findings indicate considerable differences depending on the species with some of the native flora of Almadén behaving as Hg accumulating species.

3) Presently, at the IMIDRA we are working on electro-bioremediation. This is one of the most widely used decontamination techniques in non-saturated zones and an *ex situ* method in which the site is excavated so that the soil can be treated using chemical, physical or biological methods either on site or at a treatment plant. This type of procedure has several limitations (large volumes of soil need to be moved and treated) yet both social pressures and those of the polluting firms advocate the use of *in situ* methods since these are less costly in both economic and environmental terms and do not require the cessation of normal activity at the sites. Among these *in situ* treatments the most popular have been physicochemical methods (SVE, MPE, airsparging, bottom pumping, etc.) and biological methods (bioremediation, bioventing, phytorecovery, etc). The past few decades have seen the emergence of electrokinetic methods such as the *in situ* remediation of polluted site, mainly focused on the saturated zone of the subsoil.

The system basically consists of a set of electrodes installed in the soil via which a constant current circulates. This makes the ions of the soil migrate towards the electrodes of opposite charge by a phenomenon known as ***electromigration***; the charged particles of the soil's water migrate towards the electrodes of opposite charge by ***electrophoresis***; and the water in the soil's pores migrates towards the cathode by ***electroosmosis***. Moreover, at the electrodes, ***electrolysis*** reactions occur. The combined effect of these phenomena is that the pollutants move towards the electrodes. The direction and magnitude of movement of pollutants depends on their charge and polarity, the degree of adsorption to the soil particles and the velocity of water flow by electroosmosis. Apolar organic compounds are mobilized by electroosmosis, such that surfactants need to be added to increase their solubility and promote the formation of micelles.

This has led to the strategy of applying a combination of technologies to achieve the greatest efficiency and lowest environmental impact on the soil.

Experiments: Experiments using electrokinetic techniques have been conducted on natural soils artificially polluted with diesel fuel. Some surfactants, known as biosurfactants, are produced by yeasts or bacteria and have been assessed for their capacity to complex this type of compound and because of their environmental suitability. The goal of introducing these substances is to improve the efficacy of the process by forming complexes and/or increasing electro-osmotic flow. In our assay, we evaluated the removal of diesel fuel from the soil using the electrokinetics procedure in the presence of a biosurfactant, rahmnolipid, produced by the bacterium *Pseudomonas aeuroginosa.*

The experiments were performed in a soil polluted with 20,000 mg/kg of diesel using a methacrylate prototype filled with 5 Kg of soil. A continuous current of 1 to 2 volt/cm was then applied through graphite electrodes. The biosurfactant was added to the soil as two concentrations, 1g/Kg (Exp. 1) and 2g/Kg (Exp. 2). Citric acid 1N was used as the mobilizing solution.

Experiments were run for 15 days, and pH, EC and the potential difference monitored daily. Observations were compared to those of applying the electrical field in the absence of surfactant (Exp. 4).

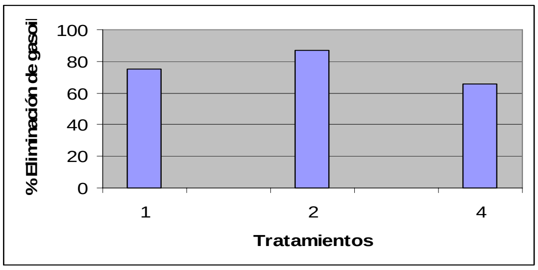

Figure 1. Percentage removal of diesel fuel by electrobioremediation (Exp. 1 and 2) versus only applying the electrical field (Exp. 4).

The results shown in Figure 1 indicate that an increased biosurfactant dose improves the efficiency of diesel fuel removal, achieving figures above 86%. Further, the lower concentration of fuel in liquid phase produced at the higher biosurfactant concentrations indicates that rhamnolipid could improve the degradation of the fuel.

The main effects of combining both remediation strategies are: removing the pollutant by electroosmosis, solubilization and biodegradation induced by the biosurfactant, low impact on soil, low cost and a high removal efficiency.

Concluding remarks

From a perspective of future soil use, combined technologies could represent a sustainable strategy with minimum impacts for recovering soils.

REFERENCES

- Hernández, A. J. & Pastor, J. 2008. Validated Approaches to Restoring the Health of Ecosystems Affected by Soil Pollution In: J. B. Dominguez & Frank Columbus (Eds.). *Chapter 2: Soil Contamination Research Trends*, pp. 51-72. Nova Science Publishers, Inc., Hauppauge, NY USA.

- Millán, R. y C. Lobo (eds.). 2008. *Contaminación de Suelos. Tecnologías para su Recuperación*.). Ed. CIEMAT.

ACKNOWLEDGEMENTS

This study was funded by the Programa IADES of the Comunidad de Madrid.