ASSISTED NATURAL REMEDIATION OF TRACE ELEMENT POLLUTED SOILS

P. Burgos, A. Pérez De Mora, E. Madejón and F. Cabrera
Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS-CSIC), Spain. Apartado 1052. 41080. pburgos@irnase.csic.es

ABSTRACT

Organic and inorganic amendments are increasingly used to enhance natural attenuation in soils polluted with trace elements. Four organic materials: a litter from a deciduous forest (LIT), a municipal waste compost (MWC), a biosolid compost (BC), and a low rank coal, rich in humic acids, leonardite (LEO) and an inorganic material, sugar beet lime, (SL) were tested as amendments to assist natural remediation of a trace element polluted soil affected by the Aznalcollar mine accident. The efficiency of these amendments to immobilize trace elements in polluted soils was determined by $CaCl_2$ (labile) and EDTA (plant-available) extractions after two years of successive applications. Amendments reduced the concentration of labile trace elements in solution of polluted soils. The reduction of the trace elements mobility seemed to be caused to the increase of soil pH due to amendment application.
Keywords: *amendments, remediation, soil pollution, trace elements.*

INTRODUCTION

Reclamation of soils polluted with trace elements has led to a variety of techniques based either on the extraction or the stabilization of the contaminants. The first ones are generally carried out *"ex situ"*, and imply soil structure deterioration and high costs, which limits their use on vast contaminated areas. However, soils can naturally reduced mobility and bioavailability of trace elements as they are retained in soil by sorption, precipitation and complexation reactions. This natural attenuation process, (natural remediation), can be accelerated by the addition of amendments (Adriano et al., 2002) converting the soluble form to more geochemically stable solid phases and reducing biological availability and plant toxicity of trace elements (Vangronsveld and Cunninghan, 1998). On the other hand, plants can mechanically stabilize polluted soils to prevent bulk erosion and airborne transport (i.e. Phytostabilization) or/and prevent movement and transport of dissolved contaminants in soils (i.e. Phytoimmobilization) (Wenzel et al., 1999). The use of plants together with the application of amendments is a more natural approach to remediation when compared to some current remediation practices. This combined "*in situ"* inactivation technique can be classified as a "soft" or "low impact" rehabilitation technique (Vangronsveld and Cunninghan, 1998) and is within the so-called assisted natural remediation. Amendments commonly include phosphates, liming agents, metal (Fe/Mn) oxyhydroxides, and organic matter (Iskandar and Adriano, 1997; Vangronsveld et al., 1998), especially urban compost and biosolids are increasingly used for soil remediation (USEPA, 1997).

This study deals with the effect of five amendments and a vegetal cover on trace element solubility and availability in soils contaminated by the Aznalcollar mine accident occurred in 1998 (Cabrera et al., 1999).

The functional groups of the organic materials used as adsorbents were also studied to understand the mechanismstheir affinity for metal binding.

The knowledge of the mechanisms of binding onto organic matter and their long-term behaviour under the condition of impact of different and anthropogenic factors is thus crucial for understanding the processes affecting mobility and biovailability in soils.

MATERIALS AND METHODS

The experiment was carried out in 24 containers (70 cm long x 60 cm wide x 40 cm deep) placed outdoors. The containers were filled with the first 25 cm of a clay loam soil (1.2 g cm^{-3} bulk density) affected by the Aznalcóllar mine accident. The most relevant characteristics of the soil are in Table 1. Four different organic amendments were used in this experiment: two urban composts: a municipal waste compost (MWC) and a biosolid compost (BC) made by wastewater sludge mixed with green wastes, and two natural organic amendments: a litter (LIT) from a deciduous forest and a leonardite (LEO) a low rank coal between peat and sub-bituminous rich in humic acids. An inorganic amendment, sugar beet lime, a residual material from the sugar manufacturing process with 60-70% of $CaCO_3$ was also tested. Trace element content of all amendments was below the limits established by the European Union (Directive 86/278/EEC) for sewage sludge. The amendments were applied on a fresh basis (20-25 % moisture content) at doses of 100 Mg ha^{-1} at the beginning of the experiment and of 50 Mg ha^{-1} one year after. The amendments were mixed with the top soil (10 cm) in the containers.

The containers were sown with *Agrostis stolonifera L.* (167 kg ha^{-1}) twice. The first time one month after of the amendment addition in the beginning of the experiment and the second time about one year later, two weeks after the second addition. No-amended soil was used as control. Containers were arranged according to a complete randomised block design with six treatments (Control, MWC, LEO, BC, LIT, SL) and four replicates per treatment. Containers were also watered regularly to avoid drought during the warmest months.

***Table 1**. Characterization of the soil. SD = standard deviation; TOC = total organic carbon*

	Average	SD		Average	SD		Average	SD
pH	3.62	0.76	**Tot-As** (mg kg^{-1})	120	2.65	**EDTA-As** (mg kg^{-1})	3.25	0.38
TOC (g kg^{-1})	5.40	0.07	**Tot-Cd** (mg kg^{-1})	2.43	0.04	**EDTA-Cd** (mg kg^{-1})	0.43	0.15
N (%)	0.09	0.01	**Tot-Cu** (mg kg^{-1})	78.3	1.41	**EDTA-Cu** (mg kg^{-1})	32.7	4.48
P (mg kg^{-1})	415	8.14	**Tot-Mn** (mg kg^{-1})	645	24.6	**EDTA-Mn** (mg kg^{-1})	280	97
K (%)	0.23	0.04	**Tot-Pb** (mg kg^{-1})	201	5.51	**EDTA-Pb** (mg kg^{-1})	14.1	3.85
Ca (%)	0.47	0.04	**Tot-Zn** (mg kg^{-1})	226	1.53	**EDTA-Zn** (mg kg^{-1})	107	13.0

Samples were collected 18 months after the first amendment application. Ten soil cores (2 cm diameter, 10 cm depth) regularly distributed along the surface were taken in each container to make a composite sample. Soil samples were air-dried, crushed and sieved through a 2 mm sieve and then ground to <60 μm. The pH of the soil and the amendments was measured in a 1:2.5 sample/1M KCl extract after shaking for 1 hour. Total organic carbon (TOC) was analysed by dichromate oxidation and titration with ferrous ammonium sulphate (Walkley and Black, 1934). Total trace element concentrations in the soil (<60 μm) and in the amendments were determined by ICP-OES after *aqua regia* digestion in a microwave oven. Soil $CaCl_2$ soluble trace element concentrations were determined in 1:10 soil sample (2 mm)/0.01 M $CaCl_2$ extracts (Ure et al., 1993) using ICP-OES. EDTA-extractable metal contents in soil were determined in the solution after shaking for 1 h a mixture soil sample (2mm)/solution 0.05 M EDTA at pH 7.0 at a 1:10 (w/v) ratio (Quevauviller et al., 1998).

RESULTS AND DISCUSSION

Amendments may reduce trace elements solubility in two ways: they may raise soil pH or they may adsorb trace element ions. All amendments raised soil pH in comparison with the control soil with the exception of LEO and LIT. This was mainly due to the high $CaCO_3$ content of SL and the non acid cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) present in organic amendments such as BC, and MWC. It has been proved that each unit of increase in pH results in approximately a 2-fold decrease in heavy metal concentrations such as Zn, Ni and Cd in the soil solution (Christensen, 1984). Therefore the increase in soil pH seems to be the most important amendment effect in reducing trace element solubility in our soil.

EDTA extractable trace element concentrations were generally higher in the amended soils, and particularly within the MWC and BC treated soils. Statistical differences were found between these two treatments and Control (Table 3). Although, EDTA extractable concentrations are considered to represent the available fraction to plants, results may differ when compared with other soil extractants and with plant uptake (Kabata-Pendias and Pendias, 1992). In fact, we found lower trace element concentrations in plant biomass in the amended soils in comparison with plants of control soils (Perez de Mora et al., 2004).

Table 2*. pH and TOC values and soluble (0.01M $CaCl_2$) concentrations of heavy metals in soils treated with the different amendments after two years of experimentation.*

Treatment	pH		TOC (%)		$CaCl_2$ soluble metals (mgkg^{-1}) Cd		Cu		Zn	
Control	4.63	a	7.70	a	0.12	c	2.56	c	30.6	c
MWC	6.69	bc	16.8	b	0.00	a	1.01	ab	1.66	a
BC	6.73	b	17.4	b	0.00	a	0.79	ab	1.75	a
LEO	4.73	a	30.9	c	0.08	b	0.30	a	25.0	bc
LIT	5.40	a	21.7	b	0.08	b	0.65	ab	10.3	ab
SL	7.49	c	9.7	a	0.00	a	0.71	b	0.67	a

Values followed by the same letter in the same column do not differ significantly (P<0.05).

Table 3*. Available (EDTA) concentration of As and heavy metals in soils treated with the different amendments after two years of experimentation.*

Treatment	EDTA-extractable metals (mg kg^{-1}) As		Cd		Cu		Mn		Pb		Zn	
Control	2.37	a	0.18	a	31.3	ab	42.0	a	1.60	a	38.3	a
MWC	5.78	bc	0.61	b	49.3	c	219	bc	12.6	b	89.3	bc
BC	7.29	c	0.56	b	37.7	b	238	c	6.60	ab	110	c
LEO	1.71	a	0.44	ab	29.0	a	124	b	2.42	a	91.3	c
LIT	1.69	a	0.39	ab	32.8	ab	105	ab	3.05	a	63.1	b
SL	4.46	b	0.50	ab	25.1	a	39.7	a	1.47	a	48.4	ab

Values followed by the same letter in the same column do not differ significantly (P<0.05).

Moreover, organic amendments basically help to increase TOC levels in soils (Table 2). TOC increased by 2-4 fold in the organic amended soils with regard to SL and Control. This is especially interesting in this case: a highly degraded soil deprived of its superficial layer in which organic amendments contributed to enhance its fertility.

At the same time, increase of plant biomass production was observed in the amended soils whereby the influence of plant on soil restoration should not be discarded (Pérez de Mora et al., 2004).

The feasibility of assisted natural remediation lies therefore within the monitoring of the amendment application to ensure that their positive effects clearly surpass their possible risks.

REFERENCES

Adriano, D.C., Bolan, N.S., Koo, Boo-Jun, Naidu, R., Van der Lelie, D. Van der. Vansgronsveld, J., And Wenzel, W.W. 2002. Natural remediation processes: bioavailability interactions in contaminated soillis. *17th World Congress of Soil Science Thailand, Symposium no. 42*, paper no. 501, 1-12.

Cabrera, F., Clemente, L., Díaz Barrientos, E., López, R., Murillo, J.M. 1999. Heavy metal pollution of soils affected by the Guadiamar toxic flood. Sci. Total Envir. 242: 117-129.

CEC (Comission of the European Communities). 1986. Council Directive of 12 June on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. Off. J. Eur. Commun. No. L 151/6/(86/278/EEC).

Christensen, T.H. 1984. Cadmium soil sorption at low concentrations. I. Effects of time, cadmium load, pH and calcium. Water Air Soil Pollut., 21: 105-114.

Iskandar, I.K. and Adrianio, D.C. 1997. Remediation of soils contaminated with metals – a review of practices in the USA. .In: Iskandar, I.K., D.C. Adriano, D.C. (Eds.), Remediation of soils contaminated with metals. (Eds. I.K. Iskandar y D.C. Adriano). Science Reviews, Northwood,. pp 47-66.

Kabata-Pendias, A., Pendias, H. 1992. Trace elements in soil and plants. CRC Press LLC, Boca Raton, FL, pp 71-73.

Pérez de Mora, A., Madrid, F., Madejón, E., Cabrera, F. 2004. Solubilidad y disponibilidad de elementos traza en suelos contaminados tratados con distintas enmiendas. Edafología (*In press*).

Quevauviller, Ph., Lachica, M., Barahona, E., Gomez, A., Rauret, G., Ure, A., Muntau, H. 1998. Certified reference material for the quality control of EDTA- and DTPA- extractable trace metal contents in calcareous soil (CRM 600). Fresenius J. Anal. Chem., 360: 505-511.

Ure, A.M., Quevauviller, P.H., Muntau, H., Griepink, B. 1993. Speciation of heavy metals in soils and sediments. An account of the improvement and harmonisation of extraction techniques undertaken under the auspices of the BCR of the Comission of the European Communities. Int. J. Environ. Anal. Chem., 51: 135-151.

USEPA. 1997. Innovative uses of compost. Bioremediation and Pollution Prevention. Solid Waste and Emergency Response (5306W), EPA530-F-042. pp 1-15.

Vangronsveld, J.C.H.M. and Cunningham, S.D.,1998. Introduction to the concepts. In: Vangronsveld, J., Cunningham, S.D. (Eds.), Metal-contaminated soils: In situ Inactivation and phytorestoration. R.G. Landes Co., Georgetown, TX, pp 1-15.

Vangronsveld, J.C.H.M. and Cunningham, S.D., Lepp, N.W and Mench, M. 1998. Pohysico-chemical aspects and efficiency of trace elements immobilization by soil amendments. .In: Vangronsveld, J., Cunningham, S. D. (Eds), Metal-contaminated soils: In situ Inactivation and phytorestoration. R.G. Landes Co., Georgetown, TX, pp. 151-182.

Walkley, A. and Black, I.A. 1934. An examination of the Degtjareff method for determining soil organic matter and a proposed determination of the chromic acid tritaton method. Soil Sci., 37:29-38.

Wenzel, W.W., Adriano, D.C., Salt, D., Smith, R. 1999. Phytoremediation: a plant-microbe-based remediation system. In: *Bioremediation of contaminated soils. Agronomy Monograph* No. 37. American Society of Agronomy. SSSA, Madison.