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Science of the Total Environment 363 (2006) 28 – 37

Science of the Total Environment
An International Journal for Scientific Research into the Environment and its Relationship with Humankind

www.elsevier.com/locate/scitotenv

Trace element availability and plant growth in a mine-spill contaminated soil under assisted natural remediation I. Soils

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Received 23 June 2005; received in revised form 10 October 2005; accepted 21 October 2005
Available online 3 April 2006

Abstract

We evaluated the effects of different amendments and/or a plant cover on reclamation of a trace element contaminated soil. Seven treatments were established: four organic (leonardite (LEO), litter (LIT), municipal waste compost (MWC), biosolid compost (BC)), one inorganic (sugar beet lime (SL)) and two controls (control without amendment but with *Agrostis* (CTRP) and control without amendment and without *Agrostis* (CTR)). Results showed that total organic C was significantly higher in organic treatments in all samplings. Water-soluble C was lower in CTR compared to other treatments, but no significant differences were observed between organic treatments and SL and CTR. SL, BC and MWC treatments increased soil pH and reduced 0.01 M $CaCl_2$-extractable Cd, Cu and Zn concentrations more efficiently, especially in the first 2 years. At the end of the experiment 0.01 M $CaCl_2$-extractable trace element concentrations were similar in all treatments. 0.01 M $CaCl_2$-extractable As and Pb were below the detection limit. Addition of amendments showed no clear reduction in 0.05 M EDTA-extractable trace element concentrations and some amendments even increased 0.05 M EDTA-extractable As and Cu with time. Pseudo-total trace element concentrations were higher for As in controls. On the other hand, mean values of Cu and Zn were higher in MWC treatment. BC and SL treatments also showed higher Zn mean concentration than controls. No amendment effect was observed for Cd and Pb.
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Keywords: Agrostis; Amendments; Assisted natural remediation; Bioavailability; Trace elements

1. Introduction

Remediation of trace element contaminated soils is still a challenge, since trace elements cannot be decomposed in the environment unlike degradable organic contaminants or short-lived radionuclides (Knox et al., 2001). Remediation options for trace-element contaminated soils are based on physical, chemical or biological techniques (Vangronsveld and Cunningham, 1998) and can be classified as "ex situ", if the soil is excavated and treated at the affected site or transported and treated somewhere else, or "in situ" if the soil is not excavated and is treated at the affected site. Excavation of trace-element contaminated soils ("ex situ" techniques) may be impractical due to the excessive cost involved, the magnitude (area, depth, volume) of the soil contamination, and the degree of disruption incurred at the affected site. Within the "in situ" techniques (isolation, removal/extraction and stabilization) few of them are cost-effective and reliable for land treating of extensive contaminated areas.

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0048-9697/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.scitotenv.2005.10.015

Assisted natural remediation is based on the use of amendments and/or plants to accelerate processes (sorption, precipitation and complexation reactions) that occur naturally in soils to reduce the mobility and bioavailability of toxic elements (Bolan and Duraisamy, 2003). Natural attenuation processes on their own may not be sufficient to mitigate risks from trace elements. This process may also enhance microbial activity, plant colonisation and development and nutrient cycling in the affected soils. Plant cover also prevents re-movement of contaminant particles and may reduce migration to groundwater.

Numerous amendments have been used to immobilize trace elements in contaminated soils (Knox et al., 2001). These include lime, zeolites, apatite, Fe and Mn oxides, alkaline composted biosolids, clay minerals and industrial by-products such as beringite. Although many studies have shown positive effects of amendment application in reducing trace element solubility and availability (Vangronsveld et al., 2000), there is still concern regarding the longevity of remediation. Those amendments that promote sequestration of trace elements in non-labile pools, such as the inorganic fraction of biosolids or surface complexation by covalent bonding have greater potential longevity (Li et al., 2001). Reacidification of soil may reverse the action of amendments that make soils alkaline. Mineralization of organic matter present in biosolids may also release trace elements in potentially bioavailable forms. Traditionally, repeated applications of amendments have been recommended to maintain trace element immobilization, but more work is required to refine these procedures.

Plant growth experiments in field lysimeters offer several advantages over other field- and laboratory-based studies conditions for evaluating certain aspects. This semifield-based method can be standardised, replicated and metal inputs and outputs may be measured under field conditions.

Our aim was to evaluate the effects of various amendments with and without a plant cover under semi-field conditions on trace element bioavalability in a mine-spill contaminated soil. We hypothesized that utilization of different amendments and plant growth might change soil pH and organic C content affecting trace element bioavailability. To prove this we studied several soil chemical properties (pH, TOC and WSC), and trace element bioavailability (0.01 M $CaCl_2$-extractable and 0.05 M EDTA-extractable As, Cd, Cu, Pb and Zn concentrations). Total trace element concentrations at the end of the experiment were also investigated.

2. Materials and methods

2.1. Soil characteristics

Soil was collected from "El Vicario" (N 37°26′21″; W 06°12′59″) affected by the Aznalcóllar mine accident (Southern Spain, 1998), where the sludge layer from the mine spill had been removed together with the upper 15 cm of top soil. The soil is a Typic Xerofluvent (USDA, 1996). Its most relevant characteristics are presented in Table 1. Wide information about the mine-spill accident can be found in The Science of the Total Environment 242 (1999).

2.2. Experimental design

The experiment was carried out in 28 containers (70 cm long × 60 cm wide × 40 cm deep) that were placed outdoors in the experimental farm "La Hampa" (IRNAS-CSIC) in Coria del Río (Southern Spain). The containers were filled with the upper 20 cm of the soil (1.32 g cm^{-3} bulk density). Containers were arranged according to a complete randomised block design with seven treatments (four organic, one inorganic and two controls) and four replicates per treatment. The organic treatments were: leonardite (LEO), a low rank coal between peat and sub-bituminous rich in humic acids from a coal mine in Teruel (Northern Spain) (DAYMSA), litter (LIT) collected from a deciduous forest (*Castanea sativa* Miller.) in the Sierra of Aracena (Huelva, Southern Spain), municipal waste compost (MWC) from a city refuse treatment plant (Villarrasa, Southern Spain), and biosolid compost (BC) constituted from wastewater sludge from a water treatment plant and green waste from parks and gardens (EGMASA, Sevilla, Southern Spain). The inorganic treatment was sugar beet lime (SL), a residual material from the sugar manufacturing process with 70–80% of $CaCO_3$ (dry basis) (AZUCARERA EBRO, San José de la Rinconada, Southern Spain). Two control treatments without amendments were also

Table 1
Characterization of the soil

	Average	S.D.	Pseudo-total concentration	Average	S.D.
pH	3.32	0.76	As (mg kg^{-1})	120	2.65
TOC (g kg^{-1})	5.40	0.07	Cd (mg kg^{-1})	2.43	0.04
N (g kg^{-1})	0.90	0.10	Cu (mg kg^{-1})	78.3	1.41
P (g kg^{-1})	0.42	0.08	Mn (mg kg^{-1})	645	24.6
K (g kg^{-1})	2.30	0.40	Pb (mg kg^{-1})	201	5.51
Ca (g kg^{-1})	4.70	0.40	Zn (mg kg^{-1})	226	1.53

S.D. = standard deviation; TOC = total organic C. n = 3.

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