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Amendments to enhance phytoremediation: Single or repetitive applications in time?

Madejón, P.*, Pérez de Mora, A., Burgos, P., Cabrera, F., Madejón, E.
Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS), CSIC. Av. Reina Mercedes 10, Po Box 1052 41080 Sevilla, Spain.
Tel. +34954624711 FAX 0034 954624002
*Corresponding author: pmadejon@irnase.csic.es

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Abstract
We tested the effectiveness of single and repetitive additions of three amendments on trace element stabilisation and volunteer vegetation development in a contaminated soil. The results showed the need of repeated addition depending on the amendment. In the case of inorganic amendments (sugar lime) a single addition was enough to accelerate natural attenuation in soil. However, when organic materials were used solubility of these compounds increased trace element availability with time and new addition were necessary for trace element stabilization.

Introduction

Natural remediation of trace element-contaminated soils can be improved by *in situ* inactivation of contaminants through the use of soil amendments (Adriano et al, 2004). The use of amendments has been proposed as a low input alternative for remediation of metal polluted soils. However, little information is available on the stability and duration of the remediation treatments.

Total concentrations in soil do not decrease and long-term use of amendments that contain trace elements may lead to trace element accumulation in soil (Pérez de Mora et al, 2006). Therefore more research is needed to evaluate the potential of this technique for reclamation of trace element contaminated soils. The prediction of phytoavailability of trace elements is of crucial importance for the assessment of environmental quality and their possible risk through the food chain (Madejón et al, 2006). The utilization of chemical extractants has become the most common approach to estimate the available fraction of trace elements in soil, because they represent the most labile fractions subject to leaching and to being uptaken by plants and microorganisms.

The aim of this work was to evaluate the efficiency and duration of three amendments in regulating trace element bioavailability and in helping plant development in a mine-spill contaminated soil under field conditions. We also show the importance of repeated amendment applications.

Materials and methods

The study site was affected by the Aznalcóllar mine sludge spill, located on the margin of the Guadiamar river (37º 26’ N, 06º 13’ W) (Madejón et al, 2006). The only remediation work carried out in this field was the removal of the sludge from the surface of the soil together with a layer of soil (10-15 cm). An experimental field trial with a plot (20 x 50 m) divided into 12 subplots (each subplot was divided equally into four parts (4 x 3.5 m), establishing 48 different sampling sites) was established. Three amendments from different sources and a control without amendment addition (NA) were tested. The amendments were a biosolid compost (BC), a leonardite (LE), and sugar beet lime (SL). The experiment was carried out in a completely randomised block design with three replicates per treatment. More information about the amendments and experiment design are in Madejón et al (2006). The amendments were applied twice (October 2002 and October 2003), SA soils (single amendment). In September 2005 each subplot was split in two parts: in one part new additions of the amendments were done in October 2005 and October 2006 at the same doses as in 2002 and 2003, RA soils (repetitive amendment).

Soil samples (0 to 15 cm depth) were collected from 48 sites (four sites per subplot) in September 2006 and 2007, therefore 1 and 2 years after the second application of amendments, 24 sites RA, and 4 years after the first amendment application, 24 sites SA.

Soil samples were air-dried, crushed and sieved (<2 mm) prior to preparation for chemical analysis. Soil pH values were determined (1:2.5 w:v in KCl) by a pH meter. Total organic C (TOC) was analysed by dichromate oxidation and titration with ferrous ammonium sulphate. Available trace elements were determined by 0.01 M $CaCl_2$. Pseudo-total trace element concentrations in soil and amendments (<60 µm) were determined by ICP-OES following *aqua regia* digestion in a microwave oven.

For plant survey, a 30 x 30 cm quadrant was used (three quadrants within each sampling site). Plant species were listed and vegetation cover estimated. The most frequent grass species, *Lamarckia aurea* L. Moench, was collected for shoot chemical analysis. Plant samples were washed with a 0.1N HCl solution and then with distilled water. Plant material was then dried at 70ºC, ground and passed through a 500-µm stainless-steel sieve and then was digested by wet oxidation with concentrated HNO_3 under pressure in a microwave digester. Analysis of trace elements the extracts was performed by ICP-OES.

Results and discussion

The repetitive addition of amendments neutralized the soil pH values and the repetitive addition of the organic amendments (BC and LEO) increased TOC (Table 1). The pH neutralization is a frequent remediation practice for trace element polluted soils, as the majority of the elements are less soluble in alkaline conditions. The increase of organic matter content was crucial to improve soil quality (Pérez de Mora et al, 2006).

Table 1. pH, total organic Carbon (%) and total trace element contents (mg kg^{-1}) in soil of 2006 and 2007 in SA (last amended in 2003) and RA (amended again in 2005 and 2006) soils.

Treatment	Sampling	Addition	pH	TOC	Cd	Cu	Zn
NA	2006	-	3.82	0.82	2.88	112	212
	2007	-	3.45	0.99	2.57	112	205
SL	2006	SA	7.10	1.34	3.26	114	412
		RA	7.14	1.20	2.92	113	284
	2007	SA	7.28	1.38	2.95	106	358
		RA	7.47	1.17	2.94	120	284
BC	2006	SA	5.47	1.43	3.33	133	372
		RA	6.00	1.84	3.48	134	448
	2007	SA	5.58	1.72	2.93	129	332
		RA	6.25	2.03	3.38	131	457
LEO	2006	SA	4.90	1.83	3.32	135	305
		RA	6.26	2.43	3.12	117	301
	2007	SA	5.27	1.65	2.93	121	265
		RA	6.14	3.00	2.87	117	300

When amendments that contain elevated trace element concentrations are added to soils (even if soils themselves contain high concentrations) it is necessary to study their impact on total soil metal concentrations. Repeated application of amendments (especially BC and LEO) slightly increased total Zn concentration (Table 1). Total analysis trace element concentration provides information on soil contamination, but trace element mobility is more relevant for environmental protection and ecological risk assessment. The $CaCl_2$-extractable concentrations of Cd and Zn in RA soils amended with BC and especially with LEO were lower than in SA soils (Figure 1). Six years after the beginning of the experiment maximum values were always found in NA soils. Extractability of trace element is closely related to the pH behaviour (Pérez de Mora et al, 2006).

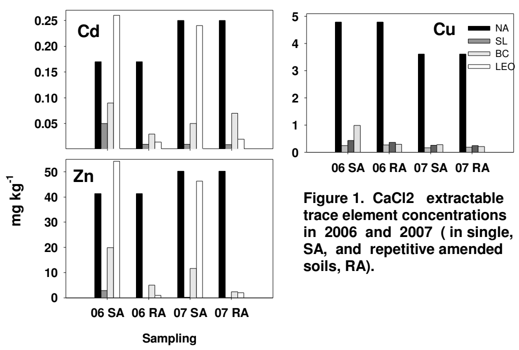

Figure 1. CaCl2 extractable trace element concentrations in 2006 and 2007 (in single, SA, and repetitive amended soils, RA).

Vegetation development was higher in amended plots than in NA from the beginning of the experiment. In any case, plant cover and species richness was slightly higher in RA soils compared to SA soils, however the differences were not significant for any treatment during the two years of study.

Table 2. Mean values of number of species and vegetation cover in soils treated with different amendments in soils of 2006 and 2007 in SA (last amended in 2003) and RA (amended again in 2005 and 2006) soils.

		Treatment			
	Sampling	NA	SL	BC	LEO
No of species	2006 SA	4	16	15	10
	2006 RA	4	15	17	12
	2007 SA	4	12	12	9
	2007 RA	4	14	15	12
Plant cover (%)	2006 SA	0.92	47.8	36.8	21.2
	2006 RA	0.92	47.5	32.5	22.5
	2007 SA	37.0	75.0	77.0	55.0
	2007 RA	37.0	80.0	85.0	57.0

As it occurred with trace element extractability, the largest trace element decrease due to repeated amendment addition was found in plants growing on LEO soils. Values of Cd, Cu and Zn in plants of the RA soils were, in general, significantly lower than those found in SA soils. For BC and SL treatments no differences due for the new additions were found.

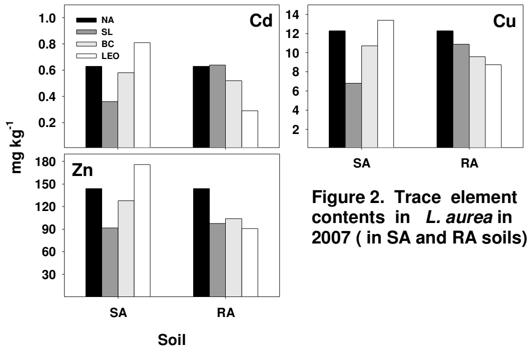

Figure 2. Trace element contents in *L. aurea* in 2007 (in SA and RA soils)

Conclusions

The need of repeated soil treatment depended on the used amendment. In the case of inorganic amendments, sugar lime, a single addition could be enough for acceptable natural attenuation in soil. However, when organic materials are used, solubility of these compounds could increase trace element availability with time and new addition may be necessary for permanent stabilization purposes.

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