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Heavy metal immobilization by cost-effective amendments in a contaminated soil: Effects on metal leaching and phytoavailability

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ABSTRACT

The combination of revegetation and application of stabilizing soil amendments on heavy metal-contaminated soils is generally considered to be a promising alternative to expensive classical remediation techniques. Here, we simultaneously investigated the effects of six cost-effective amendments ($CaCO_3$, iron grit, fly ash, manure, bentonite and bone meal) on Cd, Zn and Pb leaching and phytoavailability (assessed using white lupin, *Lupinus albus* L.). The Cd and Zn leaching was reduced by all amendments mainly due to alkalinity increase. The Pb leaching was strongly affected by the dissolved organic carbon (DOC) release. Therefore, bone meal and manure treatments, which highly increased DOC concentrations in leachates, increased the flow-weighted mean Pb concentrations by 2.3 and 16 times, respectively. Surprisingly, while iron grit induced strong Cd and Pb leaching reductions, this amendment doubled Cd and Pb concentrations in shoots of white lupin. Conversely, the addition of bone meal reduced Pb concentrations in shoots by 74%, probably because organo-Pb complexes (predicted using Visual MINTEQ) were largely dominant in solution. Overall, the addition of $CaCO_3$ offered the best compromise as it successfully reduced both the leaching and the phytoavailability of the three considered metals. Our results demonstrate the efficacy of several amendments while stressing the need to measure simultaneously the leaching and the phytoavailability of metals induced by each amendment.

1. Introduction

Since the onset of the Industrial Revolution, metal refining plants using pyrometallurgical processes have generated large emissions of heavy metals such as Cd, Zn and Pb. As the main target of such contaminants, a large number of soils are, nowadays, intensively contaminated by metals in widespread areas (Nriagu and Pacyna, 1988). As a result, degradation of the quality of the environment (Dudka and Adriano, 1997), human health (Cui et al., 2005; Pruvot et al., 2006) and surface and ground water (Rosner, 1998) is observed in the vicinity of such polluted soils. Although the restoration of these hazardous soils is essential, the use of most traditional remediation practices, including excavation and landfilling, is unfeasible on a large scale because these techniques are environmentally disruptive and cost-prohibitive. These concerns have prompted the emergence of cost-effective and less disruptive alternatives for soil remediation. Among these technologies, in situ immobilization of metals has received a growing amount of interest and is turning out to be a promising solution for soil remediation (Guo et al., 2006; Ruttens et al., 2006a). This technique aims at alleviating the risk of groundwater contamination, plant uptake and exposure of other living organisms by inactivating metals using metal immobilizing amendments (Boisson et al., 1999b). The main intent of the incorporation of amendments into contaminated soils is not to alter the total metal concentration but to impair the mobility and toxicity of metals by accelerating key immobilizing processes such as (ad)sorption, precipitation, complexation and redox reactions (Adriano et al., 2004). An additional advantage to this technique is that some amendments are inexpensive and readily available in large quantities because they derive from bio-products or industrial by-products (Guo et al., 2006; Kumpiene et al., 2008). In situ metal immobilization using such materials may therefore be an enticing option to reclaim contaminated soils while effectively diverting materials from the waste stream and reusing them (Gadepalle et al., 2007). In this context, significant efforts have been made to assess different potentially effective additives to remediate metal-contaminated soils (e.g. Basta and McGowen, 2004; Berti and Cunningham, 1997; Lombi et al., 2004; Vangronsveld et al., 1995). However, few studies have simultaneously compared the effectiveness of a large number of amendments with contrasting properties to immobilize metals. Such comparisons are almost only available in specific literature reviews (e.g. Knox et al., 2001; Kumpiene et al., 2008). These comparisons should therefore be interpreted with caution since the results of each separate study are dependent on several parameters such as the soil properties or the method used to assess the amendment's ability to immobilize metals.

Moreover, the immobilization of metals by amendments is frequently combined with the revegetation of the contaminated soil,

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the so-called phytostabilization technique. The rationale is that the establishment of a suitable plant cover on the soil is helpful in preventing the dispersion of contaminants through erosion, runoff and percolation while increasing biodiversity as well as being aesthetically pleasant (Alkorta et al., 2004; Mench et al., 2006; Tordoff et al., 2000; Vangronsveld et al., 1995). Among suitable plants for phytostabilization, white lupin (*Lupinus albus* L.) appears to be an excellent candidate (Castaldi et al., 2005; Vazquez et al., 2006). Indeed, its nitrogen-fixation capacity, adaptability to poor acidic soils, tolerance to lime excess, high salinity, elevated heavy metal content in soils and several other biotic and abiotic stresses (Huyghe, 1997; Kerley, 2000; Pastor et al., 2003; Ximenez-Embun et al., 2002), allow white lupin to thrive in poor and contaminated soils.

Although the revegetation of contaminated sites offers many environmental benefits, excessive metal uptake by plants may nevertheless jeopardize the food chain (Love and Babu, 2006). Thus, implementing a phytostabilization strategy on contaminated soils requires a serious evaluation of the effects of amendments on the metal phytoavailability (Madejon et al., 2006). Moreover, despite the fact that various metals in soils show contrasting leachability and phytoavailability (Marseille et al., 2000; Zhu et al., 1999), evaluation of the simultaneous effects of amendments on these two transfer pathways has surprisingly been the subject of only limited attention (e.g. Lambrechts et al., 2011; Ruttens et al., 2006a,b). To address this problem, our study aimed at investigating the influence of cost-effective amendments on both the leaching and the phytoavailability of Cd, Zn and Pb. Since it is a potentially promising candidate for phytostabilization for the above-mentioned reasons, white lupin was chosen as the study plant. As the speciation of heavy metals in solution can profoundly affect their biological and geochemical cycling (Krishnamurti and Naidu, 2008), the distribution of metals among their various physicochemical forms in leachates was also assessed. For this purpose, we simulated the metal speciation in leachates by means of a computer-based chemical equilibrium model (Visual MINTEQ 3.0). Cost-effective amendments were selected in order to cover a wide range of additives with different properties: $CaCO_3$, zerovalent iron (Fe^0) in the form of iron grit, fly ash, dehydrated cow manure, bentonite and bone meal.

2. Materials and method

2.1. Contaminated soil

The study site was located at Prayon (Liège province, eastern part of Belgium). From the 1930s to the 1970s, this area was intensively subjected to Cd-, Zn-, and Pb-bearing atmospheric fallouts originating from emissions from the local zinc industries. Soil samples were collected from the top 14 cm of the slightly acidic (pH = 5.8) loam contaminated soil. After sampling around 200 kg, the soil was dried at ambient temperature and sieved through a 2-mm plastic sieve. Sieved soil was then stored at 4 °C prior to use. The soil CEC was 13.25 $cmol_c\ kg^{-1}$ and the soil organic carbon and total nitrogen contents were 3.91% and 0.31%, respectively. Its elemental composition is listed in Table 1.

2.2. Amendments

Six amendments were tested: (i) calcium carbonate ($CaCO_3$), (ii) iron grit (zero-valent iron; Fe^0), (iii) fly ash, (iv) dehydrated cow manure, (v) bentonite and (vi) bone meal. Calcium carbonate was of pro analysi grade (Merck). Iron grit was a by-product from machining tools in a machine shop. Fly ash was a by-product from a thermoelectric power plant. Bone meal, bentonite and manure were obtained from a commercial supplier and are identical to those used for garden fertilization. The chemical compositions of iron grit, bone meal, fly ash, bentonite and manure were measured in our laboratory by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Jarrell Ash) after calcination at 450 °C followed by either (i) Li-metaborate/Li-tetraborate fusion for major elements (Chao and Sanzolone, 1992) or (ii) acid digestion (HNO_3, $HClO_4$ and HF) for trace metals. Data are presented in Table 1 and show that none of the amendments contained excessive metal concentrations compared to the soil metal content.

Table 1
Elemental composition of soil and some amendments. All concentrations are expressed in $mg\ kg^{-1}$.

	Soil	Iron grit	Fly ash	Manure	Bentonite	Bone meal
Al	70,200	ND[a]	124,000	3420	80,700	230
Ca	2070	1360	24,900	18,200	34,700	150,000
Fe	42,100	995,000	49,800	2620	36,200	405
K	29,000	ND	28,500	19,900	3630	10,700
Mg	7030	ND	8920	575	19,700	3900
Mn	640	4690	765	225	320	15
Na	4450	ND	4280	4290	5780	8250
P	435	ND	1360	8535	360	71,800
Si	285,000	ND	226,000	83,500	227,000	2500
Cd	33	ND	0.57	0.41	ND	ND
Zn	2090	ND	212	177	40	106
Pb	702	ND	97.60	5.88	3.26	0.02

[a] ND: not detected.

2.3. Experimental design

A leaching pot experiment, based on the design of Marseille et al. (2000), was carried out to investigate the effect of amendments on metal leaching and uptake by plants. A Whatman No. 41 filter followed by a quartz wool plug was inserted at the perforated bottom of each plastic pot in order to prevent coarse material from draining out of the pot and ensure free-drainage conditions. The base of each pot was connected to a funnel so that the leaching solution was channeled into a high-density polyethylene (HDPE) collector bottle. Each pot was filled with a mixture consisting of 500 g of contaminated soil, 250 g of washed sand to prevent soil compaction, and a constant 25 g mass of amendment. Each mixture was individually prepared by thoroughly mixing the soil, sand and amendment in plastic flask containers by rotation. A control treatment was also prepared following the same procedure but without adding amendment. All treatments were performed in 5 replicates. Before sowing, the pots were placed in a controlled dark room and the mixtures were equilibrated during 10 weeks at 20 °C and at 70% of the water holding capacity (WHC).

After the equilibration period, the pots were transferred to a controlled phytotron (temperature of 20 °C, relative humidity of 80%, 16-hour photoperiod and mean light intensity varying from 130 to 150 $\mu mol\ m^{-2}\ s^{-1}$) and were arranged according to a randomized design. Ten seeds of white lupin (*L. albus* L.) were sown in each pot and the surface of the mixture was then covered by a thin layer (2–3 mm) of polyethylene balls in order to limit the surface from drying-out, prevent soil destructuration by drop impact and ensure watering flow homogeneity. Pots were irrigated four times a week with deionized water and leachates were collected at 2, 6, 10 and 14 weeks after sowing. On irrigation days, each pot received the same irrigating amount of deionized water. However, according to the growth rate of the plants and related transpiration, the irrigating flow was modified during the course of the experiment so that the percolated volume from each pot was at least 25 $ml\ week^{-1}$. After 6 weeks, the less developed seedlings were pulled out so that each pot contained four plants. Shoots from the remaining plants were harvested 14 weeks after sowing.

2.4. Leachate analysis

At each date of leachate collection, the volume of solution was determined by weighing the HDPE collector bottles. A small aliquot