In-Situ Stabilization of Arsenic-Contaminated Soil Using Industrial By-Products

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Abstract

Contamination of terrestrial ecosystems by arsenic (As) and heavy metals is a very sensitive environmental issue due to its adverse impact on human health. Tests were conducted on the effects of amendments (limestone, red mud, and furnace slag) on the extractability of As and heavy metal contaminants, on microbial activities, and on phytoavailability of trace elements (assessed using lettuce, *Lactuca sativa* L.). The application of soil amendments significantly decreased the amount of extractable As and other heavy metals in the soil ($p < 0.05$) and were accompanied by increased microbial activity (microbial biomass, urease and dehydrogenase activity), and a decreased uptake of contaminants by lettuce. The effects of Fe-rich amendment on extractability and phytoavailability were also confirmed by field lysimeter experiment. As and metal concentrations in soil solution and uptake of As and heavy metals by Chinese cabbage was significantly reduced by Fe-rich amendment additions. From these results, it can be said that stabilization of As and heavy metals in a contaminated soil could be achieved through incorporation of Fe-rich industrial by products.

Keywords: Amendments, Arsenic, heavy metals, phyto-availability, in-situ stabilization

Introduction

Concentrations of As and heavy metals in soil exceeding permissible limits according to current standards have been identified in many regions of the world. With greater public awareness of As and heavy metals poisoning in animal and human nutrition, there has been growing interest in developing guidelines and remediation technologies for mitigating As-contaminated ecosystems.

In Korea there has been a marked increase in reports of soil contaminated by heavy metals and metalloids at abandoned mines. This has led to members of the environmental community undertaking detailed site investigations and identifying appropriate remediation technologies. In Korea there are some 2500mines, including 900 metals mines, 380 coal mines, and 1200 nonmetallic mines. More than 80% of these mines are now closed, and may have become long term sources of environmental pollution. In particular, mining and refining facilities at abandoned metal mines have been left ruin, with mine tailing and ore wastes were scattered haphazardly. Tailings and rock waste are major sources of contamination of agricultural soils and water systems around the abandoned mines. They are directly responsible for adverse crop production and impaired human health. The national monitoring system of the Ministry of the Environment cites As as the second most common inorganic contaminant after Zn, being present at

30% of the contaminated sites [1]. Because As is usually associated with Au, Cu, Pb ores, mining and smelting of these ores can lead to complicated situations where mixed pollution with anionic As and cationic metals.

Current practice for contaminated soil remediation is by excavation to landfill followed by replacement with clean soil. This technique is, however, environmentally disruptive and is becoming progressively more expensive [2]. Alternative potential remediation strategy for metal/metalloid contaminated soils is in-situ stabilization. In-situ stabilization of contaminants is based on the reduction of As and metals mobility and availability, either by precipitation or increased sorption. The application of certain soil amendments may decrease the solubility of contaminants and thus reduce the detrimental effects of heavy metals on environmental receptors, such as microorganisms, plants, animals, water bodies, and humans [3]. Numerous amendments have been proposed and tested for in-situ stabilization of heavy metals and metalloids in soils. Oxy-hydroxides of Fe and Al have been identified as primary sinks for As in soils. Since Fe oxides are also able to bind heavy metals, the use of Fe-rich materials provides an appropriate treatment of soils contaminated with both As and cationic metals.

Although, the efficient in-situ stabilization of contaminants may benefit soil functionality by reducing labile element pools of trace elements, the dynamics and restoration of soil-based ecosystem processes have received little systematic attention. The microbiological and biochemical status of a soil has often been proposed as a sensitive early indicator of soil ecological stress in restoration processes [4]. It can provide a measure of the potential a soil holds to sustain microbiological activity and hence a means of evaluating the effectiveness of a soil remediation process [5].

Here we assessed the ability of Fe-rich industrial byproducts (red mud and furnace slag) to reduce the availability of As and other metals in soil, and determined the subsequent response of biological indicators to the soil amendments. The indicators chosen were soil microbial activity and uptake of As and other metals by plants. The soil used in this investigation also contained elevated levels of heavy metals; limestone was added to the list of amendments to determine its effects in situations of multi-element contamination.

Materials and Methods

Pot experiment

Soil was collected from agricultural land adjacent to the abandoned Munbaek gold mine in Chungbuk province, Korea. Amendments (limestone, red mud, and furnace slag) were applied to soils at 2 and 5 % w/w ratios, both individually and combined two amendments (limestone + red mud, limestone + furnace slag). The amendments were thoroughly mixed with the soil to obtain homogeneity and then equilibrated for 40 d. The effect of each amendment on contaminant extractability was evaluated using 0.1 M $Ca(NO_3)_2$, following the procedure of Conder et al. [6]. Soil urease activity was measured using the method of Kandeler [7], and phosphatase activity was determined using *p*-nitrophenyl phosphate disodium as a substrate [8]. Dehydrogenase activity was determined by the reduction of 2,3,5-triphenyltetrazolium chloride to triphenyl formazan [9]. The effect of amendments on the phytoavailability of contaminants, lettuce (*Lactuca sativa*. L) was grown in plastic pots (1 kg capacity, 15-cm diameter, 25-cm height) filled with contaminated soils. The lettuce seeds were germinated in peat-based horticultural compost and the seedlings were transplanted after 2 weeks into contaminated soils: 5 seedlings/pot, 3 pots per treatment. The trials were conducted under controlled greenhouse conditions (temperature 15–25 °C, relative humidity 60–70 %) with daily watering. After 45 d the lettuce was harvested, rinsed with distilled water, and dried at

80°C for 48h. The lettuce leaves were digested in hot nitric acid, and the resultant solutions were filtered. Heavy-metals and As contents were determined by inductively coupled plasma optical emission spectrometry.

Field experiment

The results of the pot experiment were confirmed by a field trial conducted adjacent to abandoned Dukgog gold mine, contaminated with As. Lysimeters (4 × 4m) were constructed and three levels of furnace slag (2, 4, 6% w/w) and red mud (1, 2, 4% w/w) were applied. After 3 months of aging, a crop of Chinese cabbage was grown and, after a further 2 months, the cabbage was harvested analyzed As and metals contents. To assess the effect of the remediation in terms of potential for water contamination, As and metals concentrations in soil pore water were measured during the experiment.

Results and Discussion

Pot experiment

Following the application of amendments, both pH and EC increased significantly ($p < 0.05$). Soil pH increased from 5.22 to approximately 8.09, 9.35, and 5.78 with the addition of 5% limestone, 5% red-mud, and 5% furnace-slag, respectively. Soil EC increased from 151 to 326, 638, and 170 μScm^{-1} following treatments with the 5 % limestone, red-mud, and furnace-slag, respectively.

The $Ca(NO_3)_2$ were non-aggressive and developed to measure readily labile As and metals in the soil. The application of amendments also significantly decreased $Ca(NO_3)_2$-extractable As and metal concentrations, with limestone + red mud proving the most effective. Compared to the control soil, the addition of limestone + red mud reduced $Ca(NO_3)_2$-extractable As, Cd, Pb, and Zn by 58, 98, 98, and 99 %, respectively.

The significant decrease of $Ca(NO_3)_2$-extractable As and metal concentrations represents the extent of sorption of As and heavy metals onto the soil solid phase. Clearly As and metals can be desorbed into solution to replenish the soluble As and metals pool [10]. The decreased concentrations of soluble and extractable As and metals in the amended soils can be attributed in part to an increase in and available Ca content and soil pH. The high Ca content in limestone and red mud led to As immobilization by sorption and/or inclusion in pozzolanic reaction products and/or the formation of Ca-As precipitates. A concurrent increase in pH caused by the alkaline amendments, leads to an increase of metals associated with carbonated fractions. Moreover, red mud and furnace slag, which are rich in Fe oxides with reactive surface sites able to bind metals, leading to a greater proportion of As and metals associated with the Fe-Mn oxide fraction.

Compared to non-amended soil, soil enzyme activities were significantly higher in amendments amended soils ($p<0.05$). There was strong negative correlation between $Ca(NO_3)_2$-extractable As and heavy metal contents and soil enzyme activity, as has been recognized elsewhere [11]. Soil enzymes are highly sensitive to trace elements and have been recommended as standard biochemical indicators to assess the quality of contaminated soils [12]. Consequently, soil enzyme activity provides useful indicators of the re-establishment of biotic connections and restoration of healthy functions in formerly degraded systems.

Compared to non-amended soil, the concentrations of As and heavy metals in lettuce grown in amendments amended soils showed significant ($p<0.05$) decreases. Most notable was the grown in soil amended with limestone + red mud, which had 13, 25, 47, and 12 % of the As, Cd, Pb, and Zn detected in lettuce shoots grown on the control, respectively. This decreased uptake of As and metals is clearly related to the decrease of the phyto-available fraction of As and metals. Even if single chemical extractions may not reflect the labile pool of trace elements in natural situations the $Ca(NO_3)_2$-extractable pool can be used as a rapid test for evaluating changes in labile elements after amendment incorporation into soil, their advantage being a limited effect on both the operative pH at the exchange sites and complexation [13]. The foliar As, Cd, Pb, and Zn concentrations correlate closely with concentrations in soil extracts (i.e. As $r^2 = 0.65$; Cd $r^2 = 0.96$; Pb $r^2 = 0.43$; Zn $r^2 = 0.98$)

Field experiment

As in the pot experiment, the As and heavy metal concentrations in Chinese cabbage were significantly reduced by amendment addition ($p < 0.05$) with 12 % As, 60% Cd, 24% Pb, and 73 % of Zn translocated to cabbage shoots in 1% of red mud amended soil when compared to cabbage grown on non-amended soil.

The exposure of plants and microorganisms to As and other metals in soil occurs primarily via the aqueous phase. As contaminants in soil pore water may leach into ground water; thus, a major effect of remediation is to reduce the potential for such water contamination. A comparison of As and metal concentrations in soil pore waters throughout the field trial showed that trace element concentrations in soil water were significantly lowered with amendment additions. In general the amendment additions led to a decrease in the potential for the water to become contaminated by As and other heavy metals, consistent with the well established ability of Fe-rich materials to sorb these contaminants [14].

Conclusions

The application of amendments that can immobilize As and heavy metals in situ may provide a cost-effective and sustainable solution for the remediation of contaminated soils. Industrial by-products such as red mud proved highly effective in stabilizing As and heavy metals and hence decreased the levels of extractable As and metals. As a result there was a corresponding reduction in the foliar concentrations of these contaminants in both lettuce and Chinese cabbage. In addition, the reduction in extractable As and metals, along with changes in soil pH, led to increase in microbial activity. These results suggested that Fe-rich industrial by-products could be used for remediation of soils, co-contaminated with heavy metals and anionic metalloids. However, any evaluation of the remediation efficiencies of different materials needs to involve a comparative risk assessment of the treatments and to take into account the relevant pathways of exposure, different environmental endpoints, and different sensitivities of such endpoints. More research is needed to understand the main mechanisms leading to successful stabilization of contaminated soils and to understand the fundamental ecological interactions.

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Table 1. pH, electrical conductivity (EC), total and extractable heavy metals (mgkg^{-1}) of the soils with different amendment addition

Treatment	pH	EC (μScm^{-1})	$Ca(NO_3)_2$-extractable			
			As	Cd	Pb	Zn
Control	5.22	151	0.11a	0.96a	1.64a	27.29a
LS 2 %	7.96	345	0.08b	0.03c	0.04d	0.15d
LS 5 %	8.09	326	0.05cd	0.03c	0.03d	0.11d
RM 2 %	8.10	457	0.04d	0.09c	0.06d	0.63d
RM 5 %	9.35	638	0.08b	0.02c	0.04d	0.20d
FS 2 %	5.63	166	0.09ab	0.75b	0.39b	19.34b
FS 5 %	5.78	170	0.07bc	0.65b	0.26c	16.61c
LR	8.90	488	0.05cd	0.02c	0.03d	0.10d
LF	8.05	310	0.09ab	0.03c	0.04d	0.16d

LS, Limestone; RM, Red mud, FS, Furnace slag; LR, Limestone + Red mud; LF, Limestone + furnace slag

Table 2. Correlation coefficients between heavy metal concentrations in soil and microbial activities and lettuce shoot concentrations (n = 27)

$Ca(NO_3)_2$ -extractable	Soil respiration	Soil enzyme			Trace element in lettuce
		URE	PME	DHA	
As	-0.097	-0.443^{*}	-0.143	-0.447^{*}	0.649^{**}
Cd	-0.503^{**}	-0.715^{**}	-0.503^{**}	-0.147	0.957^{**}
Pb	-0.605^{**}	-0.584^{**}	-0.447^{*}	-0.189	0.431^{*}
Zn	-0.514^{**}	-0.710^{**}	-0.470^{*}	-0.195	0.985^{**}

Significant at $^{*}p < 0.05$, $^{**}p < 0.01$

URE, urease; PME, phosphatase; DHA, dehydrogenase

Table 3. As and heavy metal concentrations in soil solution and Chinese cabbage at field lysimeter experiment

Treatment	Soil solution(mgL^{-1})				Chinese cabbage($mgkg^{-1}$ F.W)			
	As	Cd	Pb	Zn	As	Cd	Pb	Zn
Control	0.036	0.002	0.542	0.052	0.168a	0.018a	0.104a	6.15a
RM 1%	0.007	0.002	N.D.	0.041	0.012b	0.011b	0.026b	4.55b
RM 2%	0.016	0.001	N.D.	0.041	0.021b	0.011b	0.032b	5.39ab
RM 4%	0.010	0.002	0.005	0.122	0.027b	0.010b	0.043b	4.99ab
FS 2%	0.042	0.002	0.006	0.052	0.019b	0.016a	0.036b	5.38ab
FS 4%	0.025	0.001	N.D.	0.070	0.015b	0.013ab	0.022b	4.41b
FS 6%	0.017	0.003	0.003	0.136	0.018b	0.014ab	0.021b	4.78b

RM, Red mud, FS, Furnace slag