Leachability, bioaccessibility and plant availability of trace elements in contaminated soils treated with industrial by-products and subjected to oxidative/reductive conditions

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ABSTRACT

Two industrial by products, red mud (RM) and aluminum-rich water treatment residue (Al-WTR) were used (2% w/w) for the immobilization of As, Cu and Pb in two polluted soils. Soil-1 was a mine contaminated soil (2428 As, 234 Cu and 559 Pb mg kg^{-1}); Soil-2 was a chromated copper arsenate contaminated soil (860 and 1500 mg kg^{-1} of As and Cu respectively). Two different redox conditions (aerobic and 3 repeated reduction/oxidation cycles) were also applied. The immobilization of trace elements and their bioaccessibility were evaluated through a leaching test and simplified bioaccessibility extraction test (SBRC) respectively, whereas phytoavailability was assessed in pot trials with *Lolium perenne*.

The RM addition increased the solubility of As and Pb, under both redox conditions, in Soil-1 with respect to untreated soil (i.e., +40 and 38% respectively in RM$_{sw}$-Soil-1 in aerobic condition). In Soil-2 Al-WTR was the amendment most efficient at decreasing As mobility (<50% with respect to untreated soil). The high correlations detected between trace element mobility and dissolved organic carbon (DOC) suggests that As, Cu and Pb formed soluble organic complexes. The SBRC results suggested that this test was mainly affected by physical and chemical characteristics of soils, whereas trial pot showed that the treatments with RMsw and Al-WTR in aerobic condition were able to decrease the plant uptake of As by 34 and 57% in Soil-1, and by 88 and 87% in Soil-2. These treatments also reduced uptake of Cu from Soil-2 (by 68 and 86%) and of Pb from Soil-1 (by 52 and 34%).

The results of this study show that the efficacy of the soil amendments is a complex function of soil conditions, source of contamination, and perhaps most importantly the environmental endpoint considered.

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1. Introduction

Trace elements are ubiquitous, generally in small concentrations, in natural components of the environment. They are also emitted into the environment from different sources, i.e., transportations, industrial and mining activities, fossil fuels, pesticides manufacturing and their applications, and other human activities (Boruvka et al., 2005; Wong et al., 2002). Toxic trace elements of concern include metalloids such as arsenic and metals, e.g., cadmium, lead, and mercury.

In many areas of the world, soils are contaminated with toxic trace elements; however human and environmental risks posed by these potential toxic substances are related not only to their total concentrations but also to their leachability and bioavailability (Schmidt, 1997). Particularly, trace metal mobility depends on soil characteristics: soil pH and texture, the type and quantity of the oxy-hydroxides present, the content of organic matter, carbonates, phosphates and clays, which

are the main soil constituents, responsible for toxic metals and metalloids sorption (e.g., Holm et al., 2003; Marcussen et al., 2009).

Many technologies have been proposed for the remediation of soils polluted by trace elements, including physical, chemical and biological treatments. Among these approaches, in situ stabilization with soil amendments has attracted attention for its low cost and eases of implementation (e.g., Sakar et al., 2007). These remediation methods are based on the reduction of trace element mobility and bioavailability by using amendments, which promote adsorption and/or precipitation reactions (e.g., Lombi et al., 2002a,b, 2010). Many amendments used for in situ remediation techniques are rich in Fe/Al/Mn amorphous and/or crystalline oxy-hydroxides that can reduce the trace element bioavailability through sorption reactions (Violante et al., 2008). The retention mechanisms of these sorbents consist of adsorption of metals on external surface, metal binding, fixation inside mineral particles and promotion of surface precipitation reactions (Castaldi et al., 2008).

Some in situ technologies proposed to remediate As and toxic metal polluted soils include the use of industrial by-products such as bauxite residues (Red Mud, RM) or drinking-water treatment residues (WTR)

(Castaldi et al., 2008, 2011; Garau et al., 2007; Lombi et al., 2002a,b, 2004; Makris et al., 2006; Sakar et al., 2007; Santona et al., 2006).

Red mud (RM) is a waste material derived from the treatment of bauxite during the Bayer process, but it might also be considered as a secondary raw material for the fixation of (cationic) contaminants, due to its alkaline pH (10.0–12.5) and sorptive capacity. The combined presence in RM of ferric, aluminum, and tectosilicate-like compounds is expected to be particularly effective in relation to the removal and immobilization of toxic metals from waste waters and polluted soils (Castaldi et al., 2010a,b; Garau et al., 2011; Santona et al., 2006) or in the reduction of leaching of soil nutrients (Phillips, 1998).

WTRs are by-products resulting from the industrial process of drinking-water treatment, where suspended solids, organic matter, contaminants, etc., are removed from the raw water supply by addition of aluminum, iron or calcium salts as coagulants (Nagar et al., 2010). WTRs contain Fe or Al oxides and hydroxides generally amorphous in nature (Lombi et al., 2004; Makris et al., 2006; Sakar et al., 2007). Recent literature has shown that WTRs are cost-effective amendments that reduce both excesses of soluble P concentration (Agyin-Birikorang and O'Connor, 2009) and As concentration in soil and water (Cederkvist et al., 2010; Lombi et al., 2004; Makris et al., 2006; Sakar et al., 2007).

The success of a remediation treatment is also affected by chemical, physical and biological soil properties, such as pH and redox potential (Charlatchka and Cambier, 2000), CEC, salt content, soil constituents and microbiological activity. In nature, soil constituents are subject to variation in oxidation–reduction state which can affect the speciation of elements such as Fe, Mn, S but also as As, Cu and Cr. High Eh and pH values can favor the co-precipitation of Fe oxy-hydroxides with metals, while reducing conditions can cause the dissolution of Mn and Fe oxy-hydroxides and their co-precipitated elements can be released into the soil solution (Charlatchka and Cambier, 2000). The possibility of fixing toxic elements in Fe-(hydro)oxides by inducing in situ cycles of reduction/oxidation has been suggested and studied by Contin et al. (2007). Their study is based on the partial reductive dissolution of Fe(III) oxy-hydroxides which cause an increase of their specific surface area and of their temporary sorption capacity. The re-precipitation of re-oxidized Fe can also occlude the sorbed elements within the mineral (Bartlett and James, 1993).

In literature some researches have shown the negative impact of reductive conditions on the mobility of toxic metals bounded to Fe and Mn oxy-hydroxides (Davranche and Bollinger, 2000) or to industrial wastes (Davranche et al., 2003). Nevertheless few studies have assessed both the mobility and bioavailability of trace elements in polluted soils, treated with sorbents and subjected to aerobic and anaerobic conditions. The latter represents a clear knowledge gap as those conditions are likely to occur at many sites and have the potential to modify the longevity of the treatments.

The aim of this research was therefore to test industrial residuals such as RMs and Al-WTR as amendments to decrease the mobility of toxic trace element such as As, Cu and Pb in soils. These industrial by-products were added to two contaminated soils and solubility and bioavailability of As, Cu and Pb were investigated by inducing repeated cycles of reduction and oxidation. We hypothesized that redox cycles would have a more marked effect on RM treated soils, due to Fe redox reactivity, rather than to the Al-based WTR one. The leachability of metal(oid)s was assessed by leaching test (European Method EN, 12457-2) while bioaccessibility of As and Pb was evaluated by SBRC (gastric phase) (Juhasz et al., 2009). Moreover the effect of these industrial by-products and of redox cycles on As, Cu and Pb bioavailability was tested through pot trials with ryegrass (*Lolium perenne*), which was selected for its resistance to toxic metals (i.e. Bidar et al., 2007).

2. Materials and methods

2.1. Soils and amendments

Two arsenic contaminated soils were used in this study. A soil sample from southeast Sardinia (Soil-1) was collected near the Baccu Locci mine, Villaputzu (CA), where the principal As-ore extracted was arsenopyrite. Particle size analysis of Soil-1 classified the soil as sandy clay loam (USDA classification) (Table 1). The second soil (Soil-2) was collected from a chromated copper arsenate (CCA) contaminated site named Collstrup, a 6 hectare site, situated in northern Zealand, Denmark. The soil is a glacio-fluvial deposit consisting of a mixture of clay, silt and sand and it was classified as sandy loam (USDA classification) (Table 1). From 1936 to 1976 the area was used for impregnation of wood. Soil samples were air-dried and passed through a 2 mm sieve and their chemical characteristics were determined following standard methods (Table 1) (Castaldi et al., 2010a; Garau et al., 2011).

The total concentrations of As, Pb, Cu, Fe and Al was determined in both soils after digestion with HNO_3 and HCl mixture (1:3 v/v ratio) using a Microwave Milestone MLS 1200. The element concentrations presented in Table 1 were determined using a Perkin Elmer AAnalyst 600 Atomic Absorption Spectrophotometer equipped with an HGA-600 graphite furnace. The detection limits were: Al, 0.25 µg L^{-1}; Fe, 0.07 µg L^{-1}; As, 0.40 µg L^{-1}; Cu, 0.08 µg L^{-1}; and Pb, 0.08 µg L^{-1}.

The industrial by-products used as sorbents in this study were red muds (RMs) and drinking-water treatment residuals (WTRs).

The RM, obtained from the Ex-Eurallumina plant in Portovesme, SW Sardinia, Italy, was dried overnight at 60 °C and finely grounded with a mortar. X-ray powder diffraction analysis of RM, carried out with a Rigaku D/MAX diffractometer (CuKα) equipped with a graphite monochromator in the diffracted beam, identified hematite (44 wt.%), sodalite (20 wt.%) and boehmite (12 wt.%) as the crystalline phases, as previously described by Castaldi et al. (2010a,b) (Table 2). RM samples were neutralized with seawater (RM$_{sw}$) or with acid treatment (RM$_a$). RM$_{sw}$ was prepared by suspending 200 g of RM in 100 mL of synthetic seawater solution (Ferreira et al., 2002) (solid to liquid ratio 2:1 w/w); the mixture was shaken for 1 h and after centrifugation the liquid was discarded; this treatment was repeated three times until an equilibrium pH of 9.1 was reached. RM$_a$ was prepared by washing RM with 0.05 M HCl (RM/HCl = 1:25 w/w) in a stirred batch system with an equilibrium pH of 9.3 (Santona et al., 2006). After equilibration both red muds were rinsed with deionized water and dried overnight at 60 °C. Untreated red mud is highly caustic (the pH was 11.5), due to the use of NaOH during bauxite digestion. This high alkalinity is environmentally hazardous and, therefore, red mud needs to be neutralized before being used for soil treatment; for these reasons, as suggested by some researchers (Ciccu et al., 2003; Genç-Fuhrman et al., 2004), we first treated the red mud with both seawater and HCl, to lower the

Table 1
Properties of Soil-1 and Soil-2.

Chemical parameters	Soil-1	Soil-2
pH	6.22	5.45
Electric conductivity (mS cm^{-1})	0.41	0.86
Texture composition:		
Coarse sand (%)	36.62	34.00
Fine sand (%)	22.33	46.00
Silt (%)	16.63	4.00
Clay (%)	24.41	16.00
Total organic C (g kg^{-1} d.m.)	34.9	18.9
Total Fe (mg kg^{-1} d.m.)	25,600	7238
Total Al (mg kg^{-1} d.m.)	15,340	11,744
Concentrations of total As Pb Cu		
As (mg kg^{-1} d.m.)	2428	860
Pb (mg kg^{-1} d.m.)	558.59	–
Cu (mg kg^{-1} d.m.)	234.46	1500.12