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Immobilisation of soil toxic metals by repeated additions of Fe(II) sulphate solution

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ABSTRACT

This study evaluates the possibility to immobilise toxic metals (Cd, Cu, Ni, Pb and Zn) in contaminated soils by applying a chemical treatment consisting in repeated cycles of soil saturation with 0.1 M $FeSO_4$, air drying and pH neutralisation with $Ca(OH)_2$. The treatment was tested on a contaminated arable soil analyzing exchangeable ($Mg(NO_3)_2$ extractable), phyto-available (DTPA/TEA extractable) and orally bio-accessible (PBET extractable) metals, after applying 1, 4 and 8 cycles.

After the 8th cycle, the treatment decreased the exchangeable fractions of Cd, Cu, Pb and Zn by 70%, 87.7%, 73.5% and 49.8% respectively, whereas those of Ni and Mn showed a marked increase. DTPA-extractable fractions followed the same trend with a decrease of 89%, 80%, 83% and 63% for Cd, Cu, Pb and Zn, respectively. Oral bio-accessibility of toxic elements showed a marked decrease for all metals ranging between 61% for Ni to 80% for Cu. The decrease in mobility, estimated by a leaching test performed on soil columns, was especially evident for Cu and Zn (65% and 61%, respectively) and highly significant for Cd and Ni (31% and 47%, respectively), whereas Pb mobility was unaffected.

The metals fixation obtained by this treatment seems compatible with a mechanism involving co-precipitation and metal adsorption onto freshly precipitated Fe (hydr)oxides, followed by occlusion of adsorbed metals at each subsequent cycle. Ageing of precipitates further increased immobilisation of all metals except Zn.

After 48 h since the end of the treatment, soil microbial biomass C and enzyme activities slightly decreased compared to the control, but recovered after 192 h of incubation. Soil treatment effectively reduced toxicity of metals to microrganisms as shown by increased microbial growth and enzyme activities in the treated soil after addition of glucose.

1. Introduction

It is well known and established that Fe (hydr)oxides can adsorb toxic metals (Jenne, 1968; McKenzie, 1980; McBride, 1994) and other trace elements such as As (Matis et al., 1997) on their surface or incorporate them into their structure (Schwertmann and Taylor, 1989). Molecular-scale X-ray spectroscopic studies showed that the strong bonding of Pb, Cu, Cr, Mn, Ni and Zn to the surface of Fe oxides is both due to the formation of inner-sphere metal surface complexes and of metal hydroxide precipitate phases (Brown and Sparks, 2001).

Technologies proposed to remediate soils polluted by heavy metals with Fe oxide rich waste materials (e.g. McKenzie, 1980; Mench et al., 1994; Chlopecka and Adriano, 1996; Lombi et al., 2002) would enable appreciable but variable reductions in metal bio-availability.

Recently, Contin et al. (2007) showed that it is possible to enhance metal fixation in Fe (hydr)oxides, either native or added as ameliorants, by inducing repeated redox cycles in soils. Reduction of Fe(III) was obtained biologically by water submersion of soils to generate anaerobic conditions. Remarkable results were obtained in soils treated with Fe waste together with the organic fraction of municipal solid waste. DTPA-extractable Cd, Cu and Zn decreased significantly after three redox cycles by 88%, 93%, 36% and 95%, 98%, 65% in the arable and grassland soil, respectively, whereas Ni and Pb showed a different behaviour. The mechanism of metal fixation was compatible with chemisorption and co-precipitation on Fe (hydr)oxides (Contin et al., 2007).

In heavily polluted soils this approach may not be feasible. Either the biological activity is too low and has no capacity for enhancement by substrate additions (caused by the inherent toxicity of soil containing high levels of heavy metals) or the soils are too permeable to foster reduction of Fe oxides *in-situ* by water submersion.

The present work was carried out to test whether comparable results can be achieved in *ex-situ* treatment at a laboratory scale. This consisted of a chemical treatment comprising the addition of Fe(II) solutions, which upon oxidation produce Fe (hydr)oxides with a high surface area and adsorption capacity which could efficiently entrap metals during precipitation.

Addition of Fe(II), as single step treatment, has already been proposed to remediate As and Cr contaminated soils (Moore et al., 2000; Warren and Alloway, 2003; Gemeinhardt et al., 2004) showing

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that $FeSO_4$ can greatly reduce mobility and plant availability of As and Cr.

Hartley et al. (2004), testing different forms of Fe treatments added to three As contaminated soils, found that Fe(II) and Fe(III) were the most effective at reducing the concentration of As in leachates. However these treatments produced a parallel increase in the level of other toxic metals (Cd, Cu, Pb and Zn). No explanation for this phenomenon was given. Also Warren and Alloway (2003) and Gemeinhardt et al. (2004) observed a significant increase in toxic metal solubility after Fe(II) additions, but attributed it to insufficient lime application and/or to a temporary drop in soil pH. To date, there have been no studies on the potential of multiple $FeSO_4$ additions to reduce the availability and mobility of metals in contaminated soils. We studied, at a laboratory scale, a treatment consisting of repeated cycles of soil saturation with a $FeSO_4$ solution to WHC (i.e. below the soil water content causing leaching) followed by air drying at room temperature. The basic difference between "single" and "multiple" Fe(II) additions is based on the possibility that the repeated precipitations of Fe can occlude previously adsorbed toxic metals, making them of lower biological concern.

The proposed approach is not based on removal of toxic metals from soils, but on their immobilisation: therefore the efficiency and limitations of the method have been tested in terms of biological availability of the contaminants to plants, animals and humans and their mobility in leaching water.

In addition, the effects of these treatments on soil microbiological activity were also investigated. The ultimate goal of soil remediation must, in fact, be the full restoration of the capability of the soil to fulfil its environmental role. The preservation or the amelioration of biological activity is therefore a fundamental prerequisite and microbiological tests are increasingly applied for toxicity assessment as microorganisms are far more sensitive to trace element stress than animals or plants growing in the same soil (Giller et al., 1998). Soil microbial biomass size and activity, both total (i.e. soil respiration) and specific (i.e. enzyme activities), have been proposed as a biochemical indicator of heavy metals toxicity (Nannipieri, 1994; Brookes, 1995). Combining microbial activity and population measurements has been demonstrated to provide a more sensitive indication of soil pollution by toxic metals than either activity or population alone (Brookes, 1995).

The aim of this study was the evaluation of the immobilisation efficiency of *ex situ* treatments based on multiple additions of Fe(II) solutions to reduce bio-availability and mobility of toxic metals. Immobilisation was also investigated during soil ageing.

2. Materials and methods

2.1. Soil

The soil utilised in this study was a sandy–loam Fluventic Eutrudept (Soil Taxonomy, 1999) with elevated levels of toxic metals collected from an arable site situated near Carpiano (Milan, Italy). Details of soil sampling, and sample preparation are given by Contin et al. (2007). Main soil characteristics are given in Table 1. Particle size analyses were determined by the pipette method (Gee and Dani, 2002). Soil pH was measured in water by a glass electrode (1:2.5 soil to water ratio), saturated paste extraction was used to determine electrical conductivity (EC), organic C and total N were determined by an automated flash combustion elemental analyser, and total metal concentration in the soil was determined by ICP-AES after microwave assisted digestion (USEPA 3051).

2.2. Immobilisation treatment

The treatment was performed by saturating the soil up to its water holding capacity (WHC) with 0.1 M $FeSO_4$ (analytical grade, 99%), then leaving it to dry at room temperature by spreading it on a polyethylene sheet; this process took about three to four days. The moisture content of the air-dried soil after each cycle was about 20–30% WHC. This treatments cycle was repeated 8 times to foster metals immobilisation. At the end of 8 treatments the total amount of Fe added to the soil was 26.8 g kg^{-1} soil (3.35 g Fe kg^{-1} soil for each treatment cycle). The precipitation of Fe upon exposure to air and oxidation of Fe(II) to Fe(III) caused an acidification of the soil which was neutralised after each cycle by addition of $Ca(OH)_2$ powder. The amount of $Ca(OH)_2$ added was calculated stoichiometrically on the basis of the theoretical acidity released by the precipitation of Fe(III).

Table 1
Main soil characteristics

Soil properties	Units	Value
Texture		
Sand (2–0.05 mm)	g kg^{-1}	773
Silt (50–2 μm)	g kg^{-1}	185
Clay (<2 μm)	g kg^{-1}	42
Organic C	g kg^{-1}	15.9
pH (1:2.5 H_2O)	–	7.87
Electrical conductivity (EC)	dS m^{-1}	1.35
Cation exchange capacity (CEC)	$cmol_+$ kg^{-1}	10.2
Water holding capacity (WHC)	%	40.2
Elements (total concentration)		
Cd	mg kg^{-1} dw	7.0±0.9[a]
Cu	mg kg^{-1} dw	75±7
Fe	mg kg^{-1} dw	24780±123
Mn	mg kg^{-1} dw	374±21
Ni	mg kg^{-1} dw	43±3
Pb	mg kg^{-1} dw	468±48
Zn	mg kg^{-1} dw	1117±65

[a] Standard error of the mean (n=3).

2.3. Extractability, ageing and bio-accessibility of metals

Exchangeable metals were estimated by shaking soil samples for 2 h with 0.1 M $Mg(NO_3)_2$ at a soil:solution ratio of 1:20 (Amacher, 1996). Suspensions were then filtered (0.2 μm), acidified with HNO_3 and stored at 4 °C before analysis. Exchangeable metals were determined in untreated control soil and after 4 and 8 treatment cycles.

Assessment of potential phyto-available metals was conducted by the DTPA/TEA method (Lindsay and Norvell, 1978). Briefly, 10 mL of diethylenetriaminopentaacetic acid (DTPA) 0.005 M and triethanolamine (TEA) 0.1 M solution (pH=7.3) was added to 5 g of soil and the soil mixture was shaken for 2 h. After centrifugation (4000 rpm for 10 min), the supernatant was removed, filtered (0.2 μm) and stored at −20 °C before analysis. Extractions were carried out after each treatment cycle.

Soils were stored dry after the end of the 8th cycle and DTPA extractions carried out at regular intervals up to 265 d to assess the effect of ageing on metal extractability.

Metal bio-accessibility to humans was assessed using the physiologically based extraction test (PBET) as described by Ruby et al. (1996) and Contin et al. (2007). Both gastric and intestinal PBET extractions were performed on control and treated soils after the 8th cycle treatment.

2.4. Leaching tests

A three step compliance batch leaching test was performed on both native and 8th cycle-treated soil. This incubation-leaching test assesses the potential release of soluble elements resulting from microbial activity and chemical equilibrium.

Plexiglas columns were incubated for 120 d at room temperature (20–25 °C) (Ø 120 mm, h 300 mm) after being filled with 2.5 kg of