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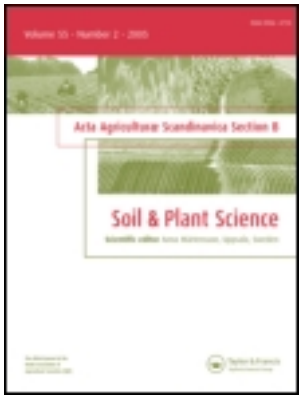

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SHORT COMMUNICATION

Cleaning heavy metal contaminated soil with soluble humic substances instead of synthetic polycarboxylic acids

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Abstract
Soils contaminated with heavy metals constitute a serious and widespread ecological problem but to clean such soils requires strong chemicals such as polycarboxylates; frequently ethylenediaminetetraacetic acid and nitrilotriacetic acid are used. However, these compounds are synthetic and toxic and their replacement by natural products such as soluble humic substances as washing agents for cleaning heavy metal polluted soils would be environmentally very attractive. In fact, such a replacement seems possible at least on cadmium and copper contaminated soil inasmuch as humic substances, depending on the concentration, were found to extract up to 45% and 54% of total cadmium and copper from a highly contaminated calcareous soil. Even though higher amounts of the two metals were extracted by ethylenediaminetetraacetic acid and nitrilotriacetic acid, the humic substances undoubtedly extracted the most reactive fractions. However, the humic substances extracted only 4% of total lead and 17% of total nickel, whereas the percentages for the synthetic polycarboxylates were about 30% for nickel and lead. Ethylenediaminetetraacetic acid and nitrilotriacetic acid may therefore be replaced by humic substances as washing agents for cadmium, copper and maybe nickel contaminated soils, whereas they seem unsuited for cleaning lead contaminated soils, at least if the soils are as calcareous as the soil tested.

Keywords: *Cadmium, calcareous soil, copper, lead, nickel, soil remediation, soil washing.*

Introduction

Soil washing (extraction) has been proposed for in-situ and ex-situ cleaning of heavy metal contaminated soils that pose a risk to human health and ecosystem functioning locally as well as globally (Adriano, 2001; European Environment Agency, 2007; Dermont et al., 2008; Leštan et al., 2008). Since heavy metals are generally strongly bonded to soil solids, removal of heavy metals requires harsh chemicals such as strong mineral acids or powerful complexants; often polycarboxylic acids are used, e.g. synthetic ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) (Adriano, 2001; Meers et al., 2005; Kirkham, 2006; Dermont et al., 2008). The use of such chemicals is not only problematic due to replacement of one pollutant by another pollutant but also because strong acids are soil destructive and complexants such as EDTA and NTA are toxic and rather persistent in the environment (Barona et al., 2001; Dermont et al., 2008; Bianchi et al., 2008; Leštan et al., 2008).

Therefore, it is environmentally attractive if these synthetic chemicals can be replaced by cheap naturally occurring compounds as soil washing agents (Leštan et al., 2008). Due to their natural ubiquity and their capacity to form complexes with heavy metals by means of the carboxylic acid and phenolic groups (Strobel et al., 2001; Weng et al., 2002; Zhao et al., 2007; Bianchi et al., 2008; Borggaard et al., 2009), it seems obvious to test soluble humic substances (HS) as cleaning agents. However, although HS has been investigated as a washing agent for soils contaminated by polyaromatic hydrocarbons (PAH) and other organic pollutants, testing

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on heavy metal polluted soils is limited (Conte et al., 2005; Zhao et al., 2007; Bianchi et al., 2008; Borggaard et al., 2009; Soleimani et al., 2010). Therefore the present investigation is focused on the suitability of using soluble HS instead of EDTA and NTA as a washing agent for cadmium (Cd), copper (Cu), lead (Pb) and nickel (Ni) contaminated soil.

Consequently, the aim of the present study was to compare the efficiency of soluble HS, EDTA and NTA to extract Cd, Cu, Ni and Pb from a strongly polluted calcareous urban soil. The comparison included three soluble HS samples comprising two natural HS solutions isolated from forest soils and a HS solution prepared from processed cow slurry.

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Materials and methods

Soil and HS samples

The long-term equilibrated (non-spiked) strongly polluted soil taken from a landfill deposit at Copenhagen Recycling Centre was air-dried and sieved (2 mm) before characterization. The pH was 7.5 as determined by potentiometry in a 1:2.5 suspension of soil in 0.01 M $CaCl_2$ and textural analysis showed the soil to consist of 10% clay, 16% silt and 74% sand. It contained 5.8% $CaCO_3$ and 1.4% organic C as determined by dry combustion (and corrected for C in $CaCO_3$). Total Cd, Cu, Ni and Pb were determined by inductive couple plasma-optical emission spectrometry (ICP-OES) in the extract obtained by boiling the soil with 7.3 M HNO_3 for 8 hours (Tjell & Hovmand, 1978) resulting in 15.6 ± 2.3 mg Cd kg^{-1}, 1000 ± 120 mg Cu kg^{-1}, 9.5 ± 1.1 mg Ni kg^{-1} and 500 ± 70 mg Pb kg^{-1}.

The natural HS samples were prepared from forest litter layers collected under beech (Beech-HS) and Norway spruce (Spruce-HS) and isolated by centrifugation followed by filtration and treatment with H^+-saturated cation-exchange resin as described by Strobel et al. (2001). Processed cow slurry (Bio-HS) donated by the firm BioCorrection A/S was prepared by oxidative hydrolytic destruction (BioCorrection, 2009). The concentration of dissolved organic carbon (DOC) in the HS samples was determined by a total carbon analyser (Shimadzu TOC-500) and the Cd, Cu, Ni and Pb concentrations were analysed by graphite furnace atomic absorption spectrometry (GFAAS). Before metal analyses, Bio-HS (originally 0.6 M DOC) was diluted to contain 100 mM DOC, while Beech-HS containing 89 mM DOC and Spruce-HS containing 64 mM DOC were analysed as prepared. Following potentiometric titration of the HS samples, the content of carboxylic acid groups was taken as titratable acidity between pH 3 and 7 and the content of phenolic groups was taken as titratable acidity between pH 7 and 11 (Strobel et al., 2001). Selected characteristics of the HS solutions are shown in Table I. To ease comparisons, the concentrations of EDTA and NTA with 10 and 6 C atoms per molecule, respectively were also expressed as mM DOC, e.g. 100 mM DOC as EDTA or NTA corresponds to 10 mM EDTA or 16.7 mM NTA, respectively.

Extraction

Multi-step extractions were carried in the batch-mode using 0.05 M KNO_3 as background electrolyte. In the extraction, 2.5 g of soil was shaken end-over-end (16 rpm) with 25 mL HS, EDTA or NTA solution adjusted to pH 6.0 in centrifuge tubes for 24 h; a preliminary test showed almost the same extraction after 24 h as after 7 d shaking. The tested extractant concentrations expressed as mmol L^{-1} dissolved organic carbon comprised 25, 50 and 100 mM DOC. After centrifugation, two 10 mL portions of the clear supernatant were withdrawn to test tubes, one containing 0.5 mL concentrated HNO_3 for metal determination and the other without HNO_3 for pH and DOC determination as described above. Then 20 mL fresh extractant solution was added to the centrifuge tube and the extraction procedure repeated 9 more times. Accumulated Cd and Cu extracted (Y_n) in mg kg^{-1} were calculated by the expression:

$$Y_n = 10 \times X_n - 2 \times X_{n-1} + Y_{n-1}$$

where X is the Cd, Cu, Ni or Pb concentration (mg L^{-1}) in the extract and n is number of extractions. The $2 \times X_{n-1}$ term accounts for the metal content in the 5 mL solution per 2.5 g soil left over from the previous extraction.

All extractions were carried out as triplicates and all chemicals were analytical grade or ultra pure. Triple-deionized water and acid-washed glassware were used throughout.

Results and discussion

The heavy metal concentrations of the HS solutions are negligible compared with the concentrations in the extracts and were therefore disregarded (Table I). The accumulated amounts of Cd, Cu, Ni and Pb after 10 extractions by the five extractants are shown in Table II. It may be seen that the amounts extracted are very different depending on extractant and metal. Thus, the three HS solutions extracted about 25% of total Cd, 38% of total Cu and 15% of total Ni but only 3% of total Pb (Table II). The capacity of HS to extract these cationic heavy metals may be ascribed to

Table I. Cadmium, copper, lead and nickel concentrations in the three HS samples together with contents of carboxylic acid (COOH) and phenolic groups Ar-OH) in the five extractants including humic substances (HS) from beech litter (Beech-HS), Norway spruce litter (Spruce-HS) and processed cow slurry (Bio-HS) together with ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA).

Extractant	Cadmium[a] μg L^{-1}	Copper[a] μg L^{-1}	Lead[a] μg L^{-1}	Nickel[a] μg L^{-1}	COOH mmol mol C^{-1}	Ar-OH mmol mol C^{-1}
Beech-HS	0.01	2.7	3.1	0.8	81	44
Spruce-HS	0.02	3.6	1.5	0.7	70	48
Bio-HS	0.03	2.9	4.1	1.2	100	70
EDTA	–	–	–	–	400	0
NTA	–	–	–	–	500	0

[a]Heavy metal concentrations in 89 mM Beech-HS, 64 mM Spruce-HS and 100 mM Bio-HS.

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formation of soluble metal-HS complexes (Strobel et al., 2001; Weng et al., 2002; Zhao et al., 2007; Borggaard et al., 2009; Soleimani et al., 2010). The similar efficiency of the three HS samples as heavy metal extractants is in fair agreement with the comparable contents of carboxylic acid groups and phenolic groups (Table I), which are the active groups forming soluble complexes with the heavy metals (Strobel et al., 2001; Weng et al., 2002; Zhao et al., 2007; Borggaard et al., 2009). The results in Table II clearly demonstrate the substantial capacity of HS to extract Cd, Cu and Ni but not Pb from contaminated soil. The extraction efficiency of HS for Cd, Cu and Ni is even more noticeable as the soil used was calcareous and long-term equilibrated (non-spiked), which generally reduces heavy metal extractability due to stronger bonding than in acidic and spiked soils (Kim et al., 2003; Meers et al., 2005; Dermont et al., 2008). The similarity between the amounts of Cd, Cu and Ni extracted by Bio-HS and by the natural HS (Beech-HS, Spruce-HS) is important from a practical soil washing point of view. Thus, provision of these natural HS samples is destructive and expensive as the litter is removed from one soil and transported to another place for treatment (Strobel et al., 2001; Borggaard et al., 2009), whereas HS based on processing of organic waste materials is environmentally friendly and is expected to be much cheaper, but that has to be shown by future investigations.

Compared with HS, EDTA and NTA are clearly more efficient heavy metal extractants (Table II). About 73% of total Cd, 53% of total Cu, 26% of total Ni and 24% of total Pb were extracted by EDTA and NTA. The difference between HS and EDTA/NTA efficiency may be explained by the considerably higher content of carboxylic acid groups in EDTA and NTA compared with HS (Table I) for the same DOC concentration. Thus, with a concentration of 25 mM DOC (Table II), EDTA and NTA contribute 10 and 12.5 mmol COOH, respectively, whereas the HS samples only contribute 1.8–2.5 mmol COOH. Furthermore, the structure of the complexes is possibly different with EDTA and NTA forming the well known stable 1:1 chelates (Sun et al., 2001; Martell et al., 2004; Leštan et al., 2008), whereas the metal-HS structure is unknown as HS is a mixture of many molecules (Weng et al., 2002; Soleimani et al., 2010).

The efficiency of especially EDTA to extract various heavy metals from soils has been demonstrated repeatedly (Barona et al., 2001; Sun et al., 2001; Tandy et al., 2004; Dermont et al., 2008; Leštan et al., 2008). Considering the stronger binding of metals by EDTA than by NTA as indicated by the complex formation constants (Martell et al., 2004), the similar efficiency of the two chelants as

Table II. Accumulated amounts of cadmium, copper, lead and nickel extracted after 10 extractions by 25 mM DOC of the five extractants from the soil in mg kg^{-1} (average ± SD, n = 3) and as percentage of total heavy metal contents (15.6 mg Cd kg^{-1}, 1000 mg Cu kg^{-1}, 500 mg Pb kg^{-1} and 9.5 mg Ni kg^{-1}). The five extractants include humic substances (HS) from beech litter (Beech-HS), Norway spruce litter (Spruce-HS) and processed cow slurry (Bio-HS) together with ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA).

	Cadmium		Copper		Lead		Nickel	
Extractant	mg kg^{-1}	%	mg kg^{-1}	%	mg kg^{-1}	%	mg kg^{-1}	%
Bio-HS	3.78 ± 0.10	24	412 ± 64	41	17 ± 3	3	1.33 ± 0.12	14
Beech-HS	3.90 ± 0.22	25	345 ± 17	35	–	–	1.56 ± 0.11	16
Spruce-HS	4.09 ± 0.23	26	368 ± 19	37	–	–	1.59 ± 0.11	17
EDTA	11.3 ± 0.3	72	531 ± 31	53	127 ± 7	25	2.37 ± 0.13	25
NTA	11.6 ± 0.6	74	533 ± 21	53	115 ± 11	23	2.67 ± 0.34	28

Cd, Cu, Ni and Pb extractants might seem surprising (Table II). However, previous efficiency comparisons of EDTA and NTA as heavy metal extractants are inconclusive inasmuch as EDTA has been shown to be more efficient and equally efficient as well as less efficient than NTA (Tandy et al., 2004; Dermont et al., 2008; Polettini et al., 2009). Reduced efficiency of EDTA has been attributed to co-extraction of calcium (Ca) forming rather strong complexes with EDTA (Sun et al., 2001; Tandy et al., 2004; Dermont et al., 2008; Polettini et al., 2009). However, in contrast to the stability constants in Martell et al. (2004), the conditional stability constants of EDTA and NTA at pH 7 are very similar (Soleimani et al., 2010). This may also explain the similar efficiency of EDTA and NTA found in the present investigation.

Even though HS extracted less Cd, Cu and Ni than EDTA and NTA, the HS-extracted Cd, Cu and Ni may comprise the most soluble, and hence most mobile, fractions as indicated by sequential extraction of Cu from the residues resulting from 10 extractions with Bio-HS and EDTA (Borggaard et al., 2009). Both extractants almost eliminated the most soluble fractions including exchangeable, carbonate- and oxide-bound Cu (Borggaard et al., 2009). Furthermore, the amounts of Cd, Cu and Ni extracted by HS increased with increasing HS concentration resulting in removal of up to 45% of total Cd, 54% of total Cu and 17% of total Ni by 10 extractions with 100 mM HS; and with Bio-HS, the concentration may be even higher, up to 600 mM. Consequently, HS can be considered a possible and environmentally friendly alternative to the environmentally problematic EDTA and NTA as washing agents for Cd, Cu and (maybe) Ni contaminated soils in accordance with previous studies (Bianchi et al., 2008; Borggaard et al., 2009; Soleimani et al., 2010). Although the present investigation did not directly test the suitability of HS as a washing agent for soils contaminated by a wider range of heavy metals, the results indicate a wider application inasmuch as Cd, Cu and Ni can be considered representative for groups of divalent cationic heavy metals. On the other hand, HS is unsuited for cleaning Pb contaminated soils at least if the soils are calcareous. In fact, difficulties with extraction of Pb from calcareous soils are not unexpected (Meers et al., 2005). Therefore, more powerful extractants such as EDTA and NTA are needed for remediation of Pb polluted calcareous soils.

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