

# Simultaneous mobilization of heavy metals and polychlorinated biphenyl (PCB) compounds from soil with cyclodextrin and EDTA in admixture

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## Abstract

This study evaluated the efficacy of a washing process with cyclodextrin in combination with ethylenediaminetetraacetate (EDTA) for the simultaneous mobilization of heavy metals and PCBs from a field contaminated soil. Ultrasonically aided mixing of the field contaminated soil with a combination of cyclodextrin solution (10%, w/v) and a sparing quantity (2 mmol) of EDTA, simultaneously mobilized appreciable quantities of PCBs and much of the analyte metal (Cd, Cr, Cu, Mn, Ni, Pb, Zn) burdens. Relative to the action of individual reagents, a combination of randomly methylated (RAMEB) or hydroxypropyl  $\beta$ -cyclodextrin (HPCD) with EDTA did not alter the PCB extraction efficiency nor did the presence of cyclodextrin change the efficiency of mobilization of most heavy metals (Al, Cd, Cr, Fe, Mn, Ni, and Zn) but did increase the recovery of Cu and Pb modestly. Three sonication-washes with the same charge of reagents mobilized appreciable quantities of PCBs (40–76%) and quantitatively extracted the labile fraction of Cd, Cu, Mn, and Pb. RAMEB proved to be more efficient than HPCD for PCB extractions. Three successive extractions with a single charge of cyclodextrin mobilized almost as much PCB (RAMEB, 76%; HPCD, 40%) as did the companion extractions that used fresh reagents each time (RAMEB, 78%; HPCD, 42%). Collectively, these studies demonstrated that PCB compounds and selected heavy metals can be co-extracted efficiently from soil with three successive washes with the same washing suspension containing EDTA and cyclodextrin.

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## 1. Introduction

The cleanup of soil contaminated with both heavy metals and organic compounds is a contemporary issue of remediation efforts considering the fact that most of the current techniques are directed to the removal of a specific group of contaminants; either hydrophobic organic com-

pounds (HOCs) or metals. Among organic contaminants, polychlorinated biphenyl (PCB) compounds are frequently found at many hazardous waste sites, as are combinations of PCBs and metals. From a remediation perspective, the removal of PCBs and metals concurrently is difficult due to differences in their physical–chemical properties. PCBs are bound to soil by nonspecific hydrophobic interactions, whereas metal ions are bound to surface sites via specific chemical interactions and by weaker electrostatic forces. Consequently, it is frequently difficult to identify a remediation process that can overcome both of these types of binding mechanisms.

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Removal of contaminated soils was once a preferred procedure that could also be applied to mixed contaminants. However, the elevated costs associated with excavation, transport and storage in a secure landfill site have made this strategy less attractive. In addition to a paucity of suitable sites, the continued risk of fugitive releases of contaminants from the site have rendered this remediation strategy less acceptable to the public. Among the currently more popular remediation procedures, soil washing can be used for both metals and organic compound if a suitable washing aid or combination of reagents can be identified. Ethylenediaminetetraacetic acid (EDTA) continues to be explored extensively for soil treatment (Doong et al., 1998; Wasay et al., 1998, 2001) because of its ability to mobilise metal cations efficiently coupled with only a minor impact on the physical and chemical properties of the soil matrix. This reagent is considered to possess a low degree of biodegradability in soil (Hong et al., 1999; Peters, 1999) and a high level of complexing capacity with respect to heavy metals (Tejowulan and Hendershot, 1998; Martínez and Motto, 2000). Conversely, the low selectivity of EDTA causes increased consumption of this reagent due to the potential chelation of all the exchangeable cations present in soil, such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Fe}^{3+}$  (Kedziorek and Bourg, 2000). Remediation of soils by chelation – extraction with a focus on the recovery and reuse of the complexing reagent represents an attractive objective that might increase the complexing selectivity if the washing is conducted with a sparing quantity of reagent.

Soil washing with surfactants remains an efficient technology for enhancing the mobilization of hydrophobic organic contaminants (HOCs) from soil (Abdul et al., 1992; Mulligan et al., 2001). More recently, cyclodextrins (Jozef and Eva, 1994; Khan et al., 1998; Szejtli, 1998) have also been evaluated as alternative solubilization reagents for soil cleanup. Cyclodextrins or cycloamyloses are cyclic glucose oligosaccharides (formed from the enzymatic degradation of starch by bacteria) that are classified as  $\alpha$ ,  $\beta$ , or  $\gamma$ , corresponding to 6, 7 or 8 glucose units, respectively. The unique property of these lampshade-shaped molecules is that they have hydrophilic exterior and substantially more hydrophobic cavity. Low-polarity organic compounds with a size and shape complementary to the cavity predominantly form water-soluble, 1:1 inclusion complexes. Because of the inclusion complex forming ability of cyclodextrins or their derivatives, many of the hydrophobic organic pollutants in soil [polyaromatic hydrocarbons (PAHs), PCBs, chlorinated phenols, dioxins and furans] are suitable guests for complex formation with cyclodextrins. The ability of cyclodextrins to increase the apparent solubility (and bio-availability to degrading microorganisms) of organic compounds is the basis for exploitation in soil remediation.

While natural cyclodextrins are themselves of interest as molecular hosts, much of their utility in supermolecular chemistry derives from their modification. Cyclodextrin

can be tailored to match particular guests and meet the specific requirements of their host–guest interaction. Thus far,  $\beta$ -cyclodextrins have been used more frequently than other CDs because of the appropriate cavity size for a range of organic compounds.

The solubilization power of cyclodextrin derivatives is less than that of typical surfactants. However, cyclodextrins may have some advantages in comparison to surfactants in that: (a) certain cyclodextrin derivatives are very water-soluble relative to many surfactants (Brusseau et al., 1994). Hence, sorption, retention or pore volume exclusion of these derivatives by soils is anticipated to be much less than that of many surfactants. (b) Neither cyclodextrins nor their inclusion complexes are subject to precipitation, phase separation or foaming. This is beneficial for situations when emulsion formation is undesirable. (c) Cyclodextrins are nontoxic and biodegradable (Brusseau et al., 1994), thus posing no apparent hazard to the ecosystem. (d) Cyclodextrins have been reported to enhance the biodegradation of low-polarity compounds. By promoting desorption, cyclodextrins also serve to enhance the microbially mediated catabolism of organic contaminants within soil. Hence, CDs can be useful for both chemical and biological remediation-enhancement techniques.

Various alkyl substituted  $\beta$ -cyclodextrin derivatives [hydroxypropyl (HPCD) methyl (MeCD) and randomly methylated  $\beta$ -cyclodextrin (RAMEB)] have been evaluated as aids for the mobilization of hydrophobic organic contaminants from soil. The target contaminants have included selected polyaromatic hydrocarbons (Cuypers et al., 2002; Stokes et al., 2005), pentachlorophenol (Fenyvesi et al., 1996; Hanna et al., 2004), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and transformation products (Sheremata and Hawari, 2000), polychlorinated biphenyl compounds (PCBs, Fava et al., 1998, 2003). Other trials have been directed to the desorption of trichloroethylene (TCE) and perchloroethylene (PCE) (Shirin et al., 2003, 2005) or to diesel, transformer oil and mazout (Molnár et al., 2002, 2005).

Even though, the possibility of enhancing the simultaneous mobilization of organic compounds and metals using cyclodextrin(s) was suggested more than two decades ago (Brusseau et al., 1994), fewer reports (Wang and Brusseau, 1995; Brusseau et al., 1997; Vulava and Seaman, 2000) have evaluated cyclodextrins for their capacity to mobilize HOCs and metals simultaneously from soil. Collectively, these reports seem to suggest that cyclodextrins are less efficient at mobilizing metals from soil.

The objective of the current study was to evaluate the combination of a cyclodextrin with a chelating reagent for the simultaneous mobilization of heavy metals and PCBs from a field contaminated soil. To date, the applications of cyclodextrins to soil washing have remained limited because of the costs of processing. These costs might be reduced substantially if the reagents could be regenerated and recycled.

## 2. Materials and methods

### 2.1. Chemicals

Beta-cyclodextrin and hydroxypropyl- $\beta$ -cyclodextrin (HPCD) were purchased from Sigma–Aldrich, Oakville, ON, Ca. Additionally, an analytical sample of hydroxypropyl- $\beta$ -cyclodextrin (HP $\beta$ CD) was also kindly provided by Dr. Jalal Hawari, Biotechnology Research Institute, Montréal, Que., CA. Randomly methylated  $\beta$ -cyclodextrin (RAMEB), degree of substitution (DS):12.6 (CAVASOL W7M) was generously provided by Dr. Mark Harrison, Wacker Specialties, Adrian, MI, USA. Disodium ethylenediminetetraacetate (EDTA), Na<sub>2</sub>HPO<sub>4</sub>, NaH<sub>2</sub>PO<sub>4</sub> and Cr (NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O were purchased from Fisher Chemical (Fair Lawn, NJ, USA). HPLC grade ethanol, and hexane were obtained from Fisher Scientific, Napean, Ont., CA.

For metal measurements, distilled de-ionized water (18.3 M $\Omega$ ) from a Milli-Q-purification system (Millipore Bedford, MA, USA) was used throughout. Aqueous metal standard solutions of Al, Cr, Cu, Cd, Fe, Ni, Mn, Pb, and Zn [1000 mg l<sup>-1</sup>, traceable to the National Institute of Standards and Technology (NIST) primary standard] were purchased from SCP Chemical Co., St-Laurent, Que., CA. Nitric acid (700 g l<sup>-1</sup>, trace metal grade) was purchased from Fisher Chemical (Fair Lawn, NJ, USA). Standard reference material SRM 2711 was purchased from the National Institute of Standard and Technology (NIST, Gaithersburg, MD). All chemicals, solvents and reagents were of ACS Reagent grade or better and were used as received.

### 2.2. Soil characteristics

The soil was classified as loamy sand (Agriculture and Agrifoods Canada, 1976) and was obtained from a secure soil storage site. The soil had been contaminated historically with Aroclors 1242, 1248, 1254, and 1260 along with Cd, Cr, Cu, Pb, Ni, Mn, and Zn. The soil was air dried, mixed thoroughly, passed through 500  $\mu$ m sieve (35-mesh),

and was stored in a sealed plastic bag for further testing. The initial soil PCB concentration (92.4  $\mu$ g g<sup>-1</sup>, Table 1) was estimated by gas chromatography–mass spectrometry (GC–MS) following hydrodehalogenation with Pd<sup>0</sup>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Ehsan et al., 2003).

The soil was characterized with respect to particle size (sand, 52%; silt, 33%; clay, 16%, Bouyoucos, 1962) cation exchange capacity (CEC, 9.5 cmol kg<sup>-1</sup>, Rhoades, 1982), pH (7.5, determined using a glass electrode in a soil to water ratio of 1:2.5), organic matter (12.5%, ASTM, 1993). Poorly crystalline Al and Fe (hydr)oxides were estimated by extraction with oxalate buffer (1.31  $\pm$  0.23 g Al kg<sup>-1</sup>; 5.70  $\pm$  0.23 g Fe kg<sup>-1</sup>, McKeague and Day, 1993) or with pyrophosphate solution (0.57  $\pm$  0.03 g Al kg<sup>-1</sup>; 0.20  $\pm$  0.04 g Fe kg<sup>-1</sup>, McKeague, 1967).

The heavy metal burden of Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in clear solution that resulted from soil digests, prepared by conventional nitric/perchloric acid block digestion (Sommers and Nelson, 1972), was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, VISTA-MPX; Varian Australia Pty Ltd., Australia). Multiple emission lines for each element were selected to assess the spectral interferences and a FACT (Fast automated correction technique) model was used to correct the possible interferences. The heavy metal content in a standard reference material (Montana soil, SRM 2711), as determined with ICP-AES and by flame atomic absorption spectroscopy (FAAS) (AAS903; GBC Scientific Equipment Pty Ltd., Australia) agreed with their certified values.

### 2.3. Mixed contaminant extraction/mobilization

Based on the sum of the metal burdens (other than Fe) in the soil (~4.2 mmol/3 g), a sparing quantity of EDTA (2 mmol/3 g soil) was chosen to perform the equilibration trials. In a typical trial, soil (3 g) was equilibrated with 20 ml EDTA solution (0.1 M) or EDTA solution containing 100 g l<sup>-1</sup> cyclodextrin in a 50 ml centrifuge tube immersed

Table 1  
Concentrations ( $\mu$ g g<sup>-1</sup>  $\pm$  1 RSD<sup>a</sup>) of PCB compounds and heavy metals within the test soil relative to the maximum concentration that is permitted for soil destined for various activities within the province of Québec

Analyte	Soil burden ( $\mu$ g g <sup>-1</sup> $\pm$ 1 RSD)	A <sup>b</sup> ( $\mu$ g g <sup>-1</sup> )	B <sup>c</sup> ( $\mu$ g g <sup>-1</sup> )	C <sup>d</sup> ( $\mu$ g g <sup>-1</sup> )
PCBs <sup>e</sup>	92.4 $\pm$ 12	0.05	1	10
Al	(1.1 $\pm$ 0.003) $\times$ 10 <sup>3</sup>			
Cd	66 $\pm$ 2	4	5	20
Cr	436 $\pm$ 2	85	250	800
Cu	2732 $\pm$ 6	40	100	500
Fe	(3.5 $\pm$ 0.2) $\times$ 10 <sup>3</sup>			
Mn	1455 $\pm$ 5	770	1000	2200
Ni	364 $\pm$ 3	50	100	500
Pb	17943 $\pm$ 3	50	500	1000
Zn	8939 $\pm$ 2	110	500	1000

<sup>a</sup> One relative standard deviation based on three replicate trials.

<sup>b</sup> Soil designation that approximates natural background levels.

<sup>c</sup> Maximum permissible level in soil destined for residential, recreational or institutional use.

<sup>d</sup> Maximum permissible level in soil destined for commercial or industrial use.

<sup>e</sup> PCBs were determined by conversion to a common product, dicyclohexyl, by hydrogenation over Pd<sup>0</sup>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Ehsan et al., 2003).

in an ice bath. Equilibrations were achieved by sonicating the soil suspension for 10 min with an ultrasonic homogenizer (XL 2020 Sonic dismembrator, Misonix Inc., NY). An extended horn of 25 cm l × 1.2 cm W, tuned at 20 kHz frequency, delivered ultrasonic energy (240 W) in a pulsed mode with a fixed vibration amplitude setting of 6. The equilibration consisted of pulsed surges of power delivered for 3 s followed by a 2 s cooling phase. Post-sonication, the suspension was centrifuged at 4000 rpm. A portion of the supernatant fraction was retained for determination of the total PCB or heavy metal content and the remainder was treated to remove solubilized contaminants.

#### 2.4. PCB removal from soil extracts and analysis

PCBs in the supernatant fraction were back-extracted three times with hexane (3 ml) to partition PCBs from the aqueous soil extract. The cumulative hexane fraction was centrifuged (4000 rpm, to remove aqueous cyclodextrin). PCBs that had been extracted with hexane were determined by GC–MS following hydrodechlorination in the presence of H<sub>2</sub>, Pd<sup>0</sup>/γ-Al<sub>2</sub>O<sub>3</sub> (Ehsan et al., 2003).

GC–MS was performed on a Varian model 3400 gas chromatograph fitted with a model 8200 autosampler and a model 2000D ion trap mass analyzer. The DB5-MS capillary column (30 m × 0.25 mm i.d.; 0.25 μm film thickness) was eluted with helium at 1.0 ml min<sup>-1</sup>. After an initial hold for 2 min at 70 °C, the temperature was ramped, at 10 °C min<sup>-1</sup>, to 270 °C, and held for a further 3 min prior to cool down. An on column injection technique was performed and the injector, transfer line and detector were maintained at 250 °C, 250 °C and 150 °C respectively. Eluting components were identified tentatively by comparison of experimental mass spectra with spectra catalogued in the National Institute of Standards and Technology (NIST) or the Saturn mass spectral libraries.

#### 2.5. Heavy metal removal from soil extract and measurement

Post PCB removal with hexane, the soil extracts were treated for metal removal. In a 50 ml test tube, magnesium flakes (Mg<sup>0</sup>, 0.5 g) were combined with K<sub>2</sub>PdCl<sub>6</sub> (50 mg) followed by the addition of the soil extract. The resulting suspension was stirred, heated to 70 °C, and permitted to react for 2 h. Post reaction, solid Ca(OH)<sub>2</sub> (50 mg) was added and pH was further raised to 12.5–13 with NaOH. The sample was centrifuged at 4000 rpm followed by filtration to remove precipitated metal oxy-hydroxides. Aliquots of extraction solution [before and after treatment with Mg<sup>0</sup> and Ca(OH)<sub>2</sub>] were set aside for metal analyses.

#### 2.6. Recycle of mobilizing reagents

Post PCB and heavy metal removal, the pH of the cleaned mobilizing reagent solution was adjusted to 6.0 and then re-equilibrated with the soil particulate fraction

to mobilize more PCBs and metals. Soil particulates were equilibrated again by sonication with 20 ml of cleaned mobilizing reagent. The resulting aqueous supernatant fraction was treated for PCB and heavy metal removal as described above. After three washing cycles, the soil particulate fraction was oven dried and analyzed for residual PCB and heavy metal contents. A portion of the soil particulate fraction (0.2 g) was further equilibrated with deionised water (0.5 ml) for 1 h and the supernatant fraction was assayed for cyclodextrin and EDTA contents as described below.

#### 2.7. Cyclodextrin analysis

Cyclodextrin determinations were carried out using an ABB Bomem (Quebec City, Que., CA) MB-150 dual range (NIR/mid-IR) FTIR spectrometer equipped with a deuterated triglycine sulfate (DTGC) detector and purged with dry air from Balston dryer (Balston, Lexington, MA, USA). Single bounce attenuated total reflectance (SB-ATR) spectra were recorded with the use of ZnSe accessory (Harrick, Ossining, NY, USA). Spectral collection parameters for SB-ATR analysis were 32 co-added scans at resolution of 8 cm<sup>-1</sup> and gain of 1.0. In all cases, a background single beam spectrum was recorded prior to loading the sample and followed by a series of aqueous standards of cyclodextrin.

#### 2.8. EDTA analysis

The combined concentration of free and complexed EDTA was determined spectrophotometrically (Flaska, 1964). Aqueous soil extract (1 ml) was added to a glass tube (1 mm i.d. × 10 cm) containing 0.1 M Cr (NO<sub>3</sub>)<sub>3</sub> · 9 H<sub>2</sub>O solution (1 ml). The pH of the solution was adjusted to 2–3 with HNO<sub>3</sub> (200 g l<sup>-1</sup>) followed by digestion at 100 °C for 15 min. On cooling, the absorbance at 555 nm was recorded vs. a blank sample containing DDW that was treated analogously.

### 3. Results and discussion

The loamy sand from a secure soil storage site had been historically contaminated with both heavy metals and persistent organic pollutants. The soil, sieved to pass a 35-mesh screen, was used for all experiments. Initial experiments characterized the sieved soil with respect to particle size, cation exchange capacity, pH, organic matter and reactive Al and Fe oxides. The relatively low levels of silt/clay, low organic matter content, low content of amorphous/micro-crystalline aluminum and iron oxy-hydroxides and intermediate CEC suggested that the soil might be amenable to remediation by soil washing. The soil's textural properties were supplemented by determinations of the heavy metal content of the soil and by a fractionation study (Tessier et al., 1979) to assess the ease of extraction of the analyte metals. Estimates of the heavy metal burden



Table 4

Buffered extraction conditions: (A) Mean mobilization of PCBs ( $\mu\text{g g}^{-1} \pm 1\text{RSD}^{\text{a}}$ ) or (B) Mean extraction of organic matter ( $\% \pm 1\text{SD}^{\text{b}}$ ) with EDTA (0.1 M) + RAMEB (100 g l<sup>-1</sup>) in phosphate or carbonate buffer (0.1 M)

Treatment	RAMEB concentration ( $\mu\text{g g}^{-1} \pm 1\text{RSD}$ )	
	5%	10%
<b>A</b>		
RAMEB + EDTA in water	19 ± 8 (21 %)	36 ± 6 (40 %)
RAMEB + EDTA in phosphate buffer	28 ± 5 (31 %)	47 ± 10 (51 %)
RAMEB + EDTA in carbonate buffer		35 ± 9 (38 %)
	Organic matter ( $\% \pm 1\text{SD}$ )	
	5% RAMEB	10% RAMEB
<b>B</b>		
Untreated soil		12.2 ± 1.4%
RAMEB + EDTA in water	16.9 ± 0.2	17.7 ± 0.6
RAMEB + EDTA in phosphate buffer	15.4 ± 0.9	16.8 ± 0.4

<sup>a</sup> RSD: one relative standard deviation.

<sup>b</sup> SD: one standard deviation.

Since hydrophobic organic contaminants tend to interact strongly with the soil's organic matter, further cyclodextrin extractions were conducted in phosphate buffer in an attempt to dislodge PCBs bound to the this fraction. A combination of RAMEB (5% or 10%) and EDTA (0.1 M) in phosphate buffer (0.1 M, pH 8) further increased the extraction efficiency appreciably (Table 4A). A single equilibration in phosphate buffer (but not in carbonate buffer) increased the recovery from 40% to 51% of the initial soil PCB burden. By contrast, an equilibration in carbonate buffer did not affect PCB recovery appreciably. Alkaline solutions of EDTA (EDTA 0.25 M, NaOH 0.05 M; Bowman et al., 1991) have long been used to estimate the soil's organic matter (SOM) content so that there was concern that this washing treatment would remove a portion of the organic matter and potentially decrease soil productivity. The SOM content before and after treatments are summarized in Table 4B. Soil washing with RAMEB-EDTA in water increased the SOM content for both the 5 and 10% solutions appreciably. When the washing solutions were formulated in phosphate buffer the increase in SOM was slightly less. Relative to the untreated soil (12.2%) organic matter was increased to 17.7% by washing with the RAMEB (10% w/v) in water or to 16.8% when washed in phosphate buffer. None the less, if this type of treatment is to be pursued, its influence on soil productivity will have to be investigated in detail.

### 3.2. Heavy metals mobilization

The concentrations of heavy metals within the soil are summarized in Table 1. Currently, the Province of Québec uses a generic classification system to characterize and assess soil pollutant burdens. The generic criteria serve to assess the scope of contamination and as decontamination objectives for a given use. Soils are classified with respect to the levels of a variety of organic and metal contaminants. The A designation approximates the background level so

that the use of soils with less than this designation is unrestricted. The B classification represents the maximum permissible levels for residential, recreational and institutional sites (as well as commercial sites within a residential sector). The C designation is reserved for industrial or commercial activities. For burdens in excess of the C designation, soil use is prohibited without treatment; if not treated successfully, the contaminated soil must be confined to a recognized storage site.

Metal extraction efficiency was determined with either a sparing quantity of EDTA or RAMEB or HPCD, either separately or in combination. A single equilibration with EDTA-cyclodextrin mobilized 29–31% of the Cd, 46–49% of the Cu, 27–29% of the Mn, 67–68% of the Pb and 38–41% of Zn (data not shown). In comparison to metal extraction with only EDTA, the presence of RAMEB or HPCD in the mixture did not influence the mobilization of metals. By contrast, soil washing with RAMEB or HPCD alone proved to be inefficient (in all cases, appreciably less than 4% of the burden of available metals, data not shown).

Subsequent experiments involved the metal stripping from metal·EDTA complexes for the release of EDTA for further mobilization of heavy metals. The release of metals from their M·EDTA complex are summarized in Fig. 1. Most of the metals were stripped efficiently from their M·EDTA complexes and precipitated as insoluble oxy-hydroxides when Ca(OH)<sub>2</sub> had been added after 2 h reaction with Pd<sup>0</sup>/Mg<sup>0</sup>. Again, for EDTA alone or in combination with RAMEB or HPCD, no appreciable difference was found for the precipitation of Al, Cu, Fe, Mn, Pb and Zn. Metal precipitation was virtually complete for Al, Cu, Fe and Zn and efficient for Mn and Pb (>90%). Relative to EDTA alone, the presence of cyclodextrin depressed the stripping of Cd and Ni from their EDTA complexes but slightly increased the precipitation of Cr (58%). Metal stripping followed the same trend for metal precipitation post the second and third equilibrations with reclaimed

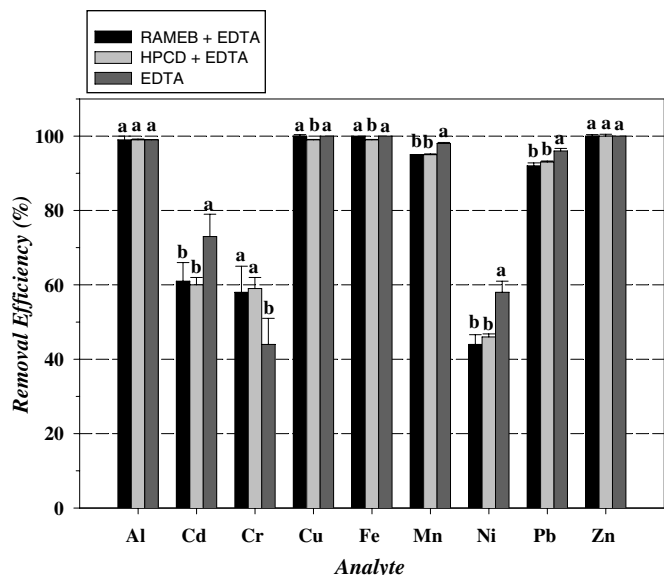


Fig. 1. Metal removal efficiency (%  $\pm$  1 SD) from soil extracts after reaction with Pd<sup>0</sup>/Mg<sup>0</sup> for 2 h followed by addition of Ca(OH)<sub>2</sub>.

EDTA (data not shown). The fluid properties (Table 2) of 10% (w/v) RAMEB or HP-CD solution were very favorable for Mg treatment and filtration when compared with to more viscosity surfactant suspensions (3% w/v).

Post metal removal, the pH of the aqueous phase was adjusted to 6.0 then recombined with the soil particulate fraction to mobilize more toxicants. The recycle procedure was repeated a second time. The cumulative quantity of metals extracted from the soil is summarized in Table 5. Three successive equilibrations with EDTA alone or in combination with RAMEB or HPCD mobilized appreciable quantities of the burdens of Cd, Cu, Mn, Pb and Zn, but lesser quantities of Cr and Ni or the macro elements Al and Fe. It has been considered that it is the sum of exchangeable, carbonate, organic and reducible fractions

that approximates the portions of heavy metal that can be dislodged by complexometric washing procedures. Extraction with recycled EDTA alone mobilized virtually all of the available fraction of Cu, Mn and Pb and if fresh EDTA was used for each cycle the recovery of Cd, Cr and Fe became very efficient. However, the mobilization of Al, Ni and Zn remained incomplete. The presence of RAMEB (either recycled or fresh) did not change metal mobilization efficiencies appreciably although Al, Cu and Pb mobilization was increased somewhat. In comparison to recycled EDTA, three successive equilibrations with fresh reagent increased the mobilization of all metals (Table 5, column 4 vs. column 3). The combination of either RAMEB or HPCD with EDTA did not contribute to these differences (column 6 vs. column 4; column 7 vs. column 5). The decrease in metal mobilization efficiency when using recycled reagents might be explained by differences in the tendency of various EDTA complexes to exchange metal ions. Whereas the identity of the EDTA reagent was Na<sub>2</sub>EDTA for all three cycles with fresh reagents, the second and third equilibrations with recycled reagents were performed with Ca · EDTA, an appreciably stronger complex than Na<sub>2</sub> · EDTA. ( $pK_F$  Ca · EDTA, 10.69 vs.  $pK_F$  Na<sub>2</sub> · EDTA, = 1.66). Thus, a sparing quantity of recycled EDTA cyclodextrin mixture was able to mobilize virtually all of the available Cu, Mn and Pb and fresh reagents were also able to mobilize virtually all of the Cd and Cr but the removal of Ni and Zn remained incomplete.

### 3.3. EDTA fate post soil washing and Mg<sup>0</sup> treatment

The recovery of EDTA, at each stage of the study, was determined spectrophotometrically; results are summarized in Fig. 2. The initial equilibration with soil resulted in a 9% loss presumably the result of adsorption to the soil particulate fraction. As expected, back extraction with hexane did not cause any measurable EDTA loss and only a fur-

Table 5

Mean cumulative metal recoveries (%  $\pm$  1 SD<sup>a</sup>) in the supernatant fraction after equilibration of soil (3 g) with the same charge (recycle mode) of EDTA (2 mmol) or with fresh reagent each time

Analyte	$\sum$ exch <sup>b</sup> + carb <sup>c</sup> + oxy-hyd <sup>d</sup> + organic <sup>e</sup>	Cumulative % ( $\pm$ 1 SD) mobilized					
		Recycled EDTA	Fresh EDTA	Recycled RAMEB + EDTA	Fresh RAMEB + EDTA	Recycled HPCD-EDTA	Fresh HPCD-EDTA
Al	31 $\pm$ 3	7 $\pm$ 0.3 B	16 $\pm$ 0.9 A	9 $\pm$ 0.8 B	17 $\pm$ 2 A	9 $\pm$ 0.3 B	18 $\pm$ 3 A
Cd	52 $\pm$ 2	42 $\pm$ 4 A,B	49 $\pm$ 7 A	39 $\pm$ 0.8 B	48 $\pm$ 3 A	40 $\pm$ 5 B	46 $\pm$ 1 A,B
Cr	13 $\pm$ 0.9	4 $\pm$ 0.3 C	10 $\pm$ 0.4 B	4 $\pm$ 0.2 C	12 $\pm$ 0.3 A	4 $\pm$ 0.01 C	12 $\pm$ 0.6 A
Cu	58 $\pm$ 4	57 $\pm$ 4 D	71 $\pm$ 4 B,C	67 $\pm$ 5 C	80 $\pm$ 7 A	64 $\pm$ 2 C,D	79 $\pm$ 5 A,B
Fe	7 $\pm$ 0.5	2 $\pm$ 0.1 C	10 $\pm$ 0.6 A	3 $\pm$ 0.3 C	8 $\pm$ 0.4 B	2 $\pm$ 0.1 C	9 $\pm$ 0.7 B
Mn	34 $\pm$ 2	33 $\pm$ 3 B	38 $\pm$ 0.4 A	33 $\pm$ 0.9 B	39 $\pm$ 2 A	31 $\pm$ 1 B	37 $\pm$ 0.8 A
Ni	41 $\pm$ 3	20 $\pm$ 2 B	33 $\pm$ 0.1 A	20 $\pm$ 1 B	35 $\pm$ 2 A	19 $\pm$ 2 B	35 $\pm$ 2 A
Pb	82 $\pm$ 1	78 $\pm$ 5 C	85 $\pm$ 4 B	82 $\pm$ 0.8 B,C	94 $\pm$ 1 A	83 $\pm$ 1 B,C	92 $\pm$ 2 A
Zn	91 $\pm$ 2	51 $\pm$ 4 B	62 $\pm$ 4 A	50 $\pm$ 2 B	67 $\pm$ 5 A	49 $\pm$ 3 B	67 $\pm$ 4 A

<sup>a</sup> One standard deviation based on three replicate trials.

<sup>b</sup> Exchangeable fraction as determined by the procedures of Tessier et al. (1979).

<sup>c</sup> Carbonate fraction as determined by the procedures of Tessier et al. (1979).

<sup>d</sup> Reducible fraction as determined by the procedures of Tessier et al. (1979).

<sup>e</sup> Organics fraction as determined by the procedures of Tessier et al. (1979).

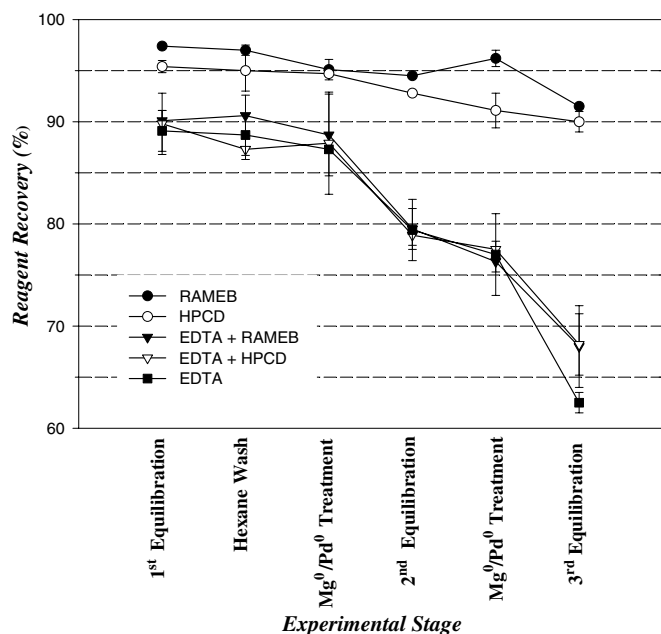


Fig. 2. Reagent (EDTA or CD) recovery (%  $\pm$  1 SD) post each experimental stage for three successive washes of soil (3 g) with same charge of EDTA (2 mmol) or EDTA + cyclodextrin (100 g l<sup>-1</sup>).

ther small portion (1–2%) was lost during the Mg<sup>0</sup> treatment and subsequent filtration. The recovery of EDTA post second and third equilibration resulted in a further 9% and 8% loss to the particulates fraction. A cumulative loss of 32% of the initial EDTA concentration was observed during three washing cycles, of which a total of 6% was lost during the two Mg<sup>0</sup> treatments and two hexane back-extractions. EDTA recovery (68%) from soil, hexane, or Mg<sup>0</sup> treatment post three wash cycles was independent of the presence of cyclodextrin.

### 3.4. Cyclodextrin fate post soil washing and Mg<sup>0</sup> treatment

The concentrations of RAMEB and HPCD were monitored after each experimental stage to estimate the cyclodextrins adsorption to soil or losses during Mg<sup>0</sup> treatment. Reagent recovery post treatment was calculated on the basis of starting concentration of cyclodextrins (10%, w/v). As illustrated in Fig. 2, 3% of the RAMEB had been lost to the soil particulates fraction after the first equilibration, a 5% decrease was observed for HPCD. The decrease in the cyclodextrin content was not the result of biodegradation but was due to adsorption process in soil as evidenced by re-analysis of samples after a further 4 weeks. The quantities of RAMEB (97%) and HPCD (95%) did not change perceptibly when the suspension was back-extracted with hexane and a further 1–2% loss was observed when suspension were treated with Mg<sup>0</sup>. Similar losses were observed for each recycle stage. In total, 4% of RAMEB and 5% HPCD were sorbed to the particulate fraction during 3 soil washings and further 5% and 4%

were lost during two Mg<sup>0</sup> treatments. Relative to fresh reagents, recycled reagents were equally efficient at PCB mobilization. The quantity of cyclodextrin remaining in the suspension (90–91%) after the third soil equilibration indicated that cyclodextrin recycle can be cost effective for soil remediation.

## 4. Conclusions

The combination of low reactivity with soil, relative insensitivity to pH and ionic strength effects and their non-toxic nature, provide advantages for the use of cyclodextrins as a reagent to enhance the mobilization of PCB compounds from soil. When combined with a sparing quantity of EDTA, much of the available fraction of metals can be co-extracted from soil and recovered by precipitation so that the EDTA-cyclodextrin reagent combination can be recycled efficiently. This approach is anticipated to be cost efficient relative conventional soil washing techniques with the same reagents.

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