Journal of Hazardous Materials 197 (2011) 361–368

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Simultaneous mobilization of trace elements and polycyclic aromatic hydrocarbon (PAH) compounds from soil with a nonionic surfactant and [S,S]-EDDS in admixture: Metals

Yuexiang Wen, William D. Marshall*

Department of Food Science and Agricultural Chemistry, Macdonald Campus of McGill University, 21,111 Lakeshore Road, Ste-Anne-de-Bellevue, Québec, Canada H9X 3V9

ARTICLE INFO

Article history:
Received 4 November 2010
Received in revised form
27 September 2011
Accepted 28 September 2011
Available online 4 October 2011

Keywords:
Soil remediation
Trace elements
Soil washing
Surfactant
Complexometric extraction

ABSTRACT

This study evaluated the efficacy of soil washing with a nonionic surfactant (Brij98) in combination with a complexing reagent (ethylenediaminedisuccinic acid, [S,S]-EDDS) for the simultaneous mobilization of macro- and trace elements (MTEs) and PAH compounds from a field-contaminated soil. Soil fractionation studies indicated that an appreciable fraction of the Al, Ca, Cu, Fe and Mn was associated with the residual fraction but that much of the other trace elements (As, Cd, Cr, Ni, Pb and Zn) might be susceptible to soil washing. Ultrasonically aided mixing of the field contaminated soil with Brij98 and a sparing quantity (2 mmol) of [S,S]-EDDS, simultaneously mobilized virtually all of the benzo[α]pyrene {B(a)P} and chrysene (CRY) and appreciable quantities of the trace elements (Cd, Cr, Mn, Ni, Pb, Zn) burdens. The recovery of both PAHs and trace elements were increased from the soil organic matter (SOM)-rich soil. This report concerns the fate of MTEs during soil washing. Multiple ultra-sonically aided washes (five or nine) with the same dosage of reagents mobilized virtually all of PAHs and decreased the levels of Cd, Cr, Ni, Pb and Zn to comply with recommended maxima. By contrast, the levels of As and Cu remained excessive after the treatments.

1. Introduction

Among the currently more popular strategies for remediating soil, washing [1–3] can be used for both metals and organic compound if a suitable washing reagent or combination of reagents can be identified.

Ethylenediaminetetraacetic acid (EDTA) continues to be explored extensively for soil treatment [4,5] because of its ability to mobilize trace elements 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 [6,7] and a high level of metal coordinating capacity [8]. Conversely, the low selectivity of EDTA causes increased consumption of this reagent due to complexation with macro-elements present in soil [9]. When present in excess, EDTA remains a powerful extractant of trace metals; recoveries in excess of 60% have been observed frequently [10,11].

EDDS, like its structural isomer EDTA, forms strong hexadentate chelates with transition metals. Unlike EDTA, the [S,S]-stereoisomer of EDDS, is readily degraded in activated sludge systems [12–14] and cell-free extracts [15]. The fate of metal–EDDS complexes are of concern because [S,S]-EDDS used in consumer products or soil washing formulations may end up in surface waters. Relative to EDTA, the increased biodegradability of [S,S]-EDDS and an overall favorable profile [16] has prompted its expanded use in industrial processes (pulp and paper, textile, metal, photographic, and leather industries) as well as consumer products (cosmetics and washing powders). Reviews on chelant extraction of heavy metals from contaminated soils [17,18] have indicated that soil washing with solutions of chelating agents is an attractive technology but there remains a lack of consensus concerning the choice of the most appropriate chelating agent(s).

Surfactants are attractive for the extraction of contaminants from soil [19,20] because of their decreased acute toxicity (relative to organic solvents) and their favorable rates for environmental degradation to innocuous products [21–23]. The success of soil washing with surfactants [24–26] can be attributed to the capacity of these compounds, at concentrations above the critical micelle concentration (CMC), to appreciably enhance the aqueous solubility of hydrophobic organic compounds (HOCs). Surfactant washing can be ineffective for soils that contain more than 20–30% silt and clay [22,27] or appreciable quantities of organic matter. It has been suggested [28,29] that nonionic surfactants are better choices than anionic surfactants in washing performance.

Remediation of metal-contaminated soils by chelation – extraction with the recovery and reuse of the complexing reagent

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* Corresponding author. Tel.: +1 514 398 7921; fax: +1 514 398 7898.
E-mail address: william.marshall@mcgill.ca (W.D. Marshall).

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doi:10.1016/j.jhazmat.2011.09.097

represents an attractive objective. The removal of metals from the EDTA solution by hydroxide precipitation can be inefficient due to the high stability of the EDTA complexes. By contrast, precipitation as sulfides was more efficient [30]. Copper, Zn, and Pb were recovered efficiently with a 1:1 chelator/precipitant ratio. Improved extraction performance was achieved with a higher EDTA concentration (50 mM) and with more washing cycles [31]. The EDTA was reclaimed using a slight excess of Na_2S precipitant (5 mM) at moderately alkaline conditions (pH 10), so that the chelant could be reused for several cycles. Yet hydroxide precipitation remains the more widely practiced approach on the basis of performance, ease of operation, and cost. Although sulfide precipitation has advantages that include increased efficiency and less pH dependency, it has found limited application because of the hazardous nature of the sludge produced, the cost, and operational difficulties. Other strategies to liberate EDTA from metal complexes have involved the use of ion exchange materials [32] or zero-valent bimetallic mixtures (Mg^0–Pd^0, Mg^0–Ag^0) [33,34].

The objectives of this study were to evaluate the efficiency of a nonionic surfactant in combination with a sparing quantity of [S,S]-EDDS for the simultaneous extraction of selected PAH compounds and toxic trace elements from soil and to optimize reaction conditions that permit the recycling of mobilization reagents while generating toxicologically innocuous extraction products.

2. Materials and methods

2.1. Chemicals

Brij98 (polyoxyethylene(20) oleyl ether, CAS Number: 9004-98-2), was purchased from Sigma–Aldrich (Oakville, ON). Ammonium acetate, disodium EDTA, H_2O_2, hydroxylamine hydrochloride, $MgCl_2$, and Na acetate were obtained from Fisher Chemical Co., Napean, ON. [S,S]-EDDS, 30% (w/w), Octaquest E30, was purchased from Innospec Limited, Cheshire, UK.

For trace element analyses, distilled, deionized water (18.3 MΩ cm, Milli-Q purification system, Millipore, Bedford, MA) was used throughout. Aqueous MTE standard solutions of Al, As, Ca, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn (1000 mg L^{-1}, traceable to the National Institute of Standards and Technology primary standard) were purchased from SCP Chemical Co. (St-Laurent, QC). Sulfuric acid (17 M), glacial acetic acid and HNO_3 (700 g L^{-1}, trace-metal grade) were purchased from Fisher Chemical (Napean, ON). All chemicals, solvents, and reagents were of ACS reagent grade or better and were used as received.

2.2. Soil pretreatment, texture, and MTE characterization

The soil for this study was obtained from the Sydney Tar Ponds Agency, Sydney, NS. The soil was classified as sandy loam [35] and had been field contaminated with PAH compounds and selected trace elements. The soil was air dried at room temperature in a conventional fume hood, mixed thoroughly, passed through a 500-μm sieve and then stored in a sealed plastic bag to await further testing. The soil was characterized with respect to particle size [36], pH (determined using a glass electrode in a soil/water ratio of 1:2.5), cation exchange capacity [37] and organic matter [38].

The content of Al, As, Ca, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in soil digests, prepared by conventional HNO_3–H_2O_2 block digestion [39] was determined by inductively coupled plasma optical emission spectrometry (ICP-OES, VISTA-MPX, Varian Australia Pty Ltd., Melbourne, 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 macro-elements, Al, Ca, and Fe were included among the target elements to evaluate the selectivity of the extraction process. The metal content in a standard reference material (Montana soil, SRM 2711) as determined with ICP-OES agreed with stated values.

2.3. Soil fractionation

The Community Bureau of Reference (BCR) cation-based three-step sequential extraction procedure [40] was followed with minor modification. The soil was characterized with respect to element burdens in the exchangeable, reducible and oxidizable fractions. The residual fraction was determined as the difference between the total and sum of the other three fractions. Extraction solutions were modified with Brij98 (3 mL, 3%, v/v), which served as wetting agent for the soil that contained a high content of organic matter. Dry sieved soil or soil residue, 0.10 g, was extracted sequentially with HAc (11 mL, 0.1 M) for 24 h in a mechanical, end-over-end rotary shaker at 30 rpm. The soil residue was then equilibrated with 11 mL, 0.5 M $NH_2OH{\cdot}HCl$ during 24 h again with shaking. The final step involved low temperature digestions with 2 mL 30% (v/v) H_2O_2 (acid-stabilized to pH 2–3) initially at room temperature overnight. Subsequently, the temperature was slowly raised to 85 °C to decrease the volume to ~0.5 mL. Then, 2 mL 30% (v/v) H_2O_2 was added and the digestion was repeated. After cooling, 13 mL NH_4Ac (1.0 M) was added into the digestion tube and the contents were sonicated then centrifuged. The supernatant fraction was analyzed for MTE content by ICP-OES.

2.4. Mixed contaminant extraction

Dry sieved soil (3 g) was combined with 20 mL [S,S]-EDDS (2 mmol), in aqueous Brij98 (30 or 60 g L^{-1}), or with surfactant alone, in a 50-mL centrifuge tube. The pH of the resulting suspension was adjusted to 9.0 with 0.1 M NaOH. Equilibration of the suspension was achieved by sonication of the soil suspension for 30 min with an ultrasonic homogenizer (XL 2020 Sonic Dismembrator, Misonix, Farmingdale, NY). An extended horn of 25-cm length by 1.2-cm diameter, tuned at 20 kHz frequency, delivered ultrasonic energy (240 W) in a pulsed mode with a fixed vibration amplitude setting of 6. The extraction consisted of pulsed surges of power delivered for 3-s followed by a 2-s resting phase, to the soil suspension contained in a 50 mL plastic tube. Subsequently, samples were centrifuged at 4000 rpm (1 min) to recover the supernatant fraction. For timed trials, the soil suspension was sonicated for 5, 10, 15, 20 or 30 min with pulsed surges of power. The treated suspension was centrifuged then back-extracted with hexane–MIBK (9:1, v/v) to recover PAH compounds from the aqueous supernatant fraction.

After PAH removal with three washes of 5 mL hexane–MIBK (9:1, v/v), the aqueous soil extracts (20 mL) were acidified to pH 4 then treated for metal removal. In a 50-mL test tube, 0.00 g, 0.053 g, 0.073 g, or 0.144 g Mg^0 granules were combined with the acidified soil extract. The resulting suspension was reacted for 1 h with stirring. The sample was centrifuged at 4000 rpm followed by filtration to remove precipitated metal oxyhydroxides and the supernatant fraction was assayed for MTEs by ICP-OES.

After PAH and MTE removal, the pH of the cleaned mobilizing solution was readjusted to 9.0, then recombined with the soil particulate fraction to mobilize more PAHs and MTEs. After equilibration with recycled reagents, the aqueous fraction was treated to remove PAHs and MTEs as described above. After five (or nine) washing cycles, the soil particulate fraction was oven dried and analyzed for residual PAH and MTE contents.

Table 1
Toxicant burdens in the soil and permitted maxima.

Toxicant	Total content ($\mu g\, g^{-1} \pm 1RSD^{b}/\mu mol\, g^{-1} \pm 1RSD$)	CCME[a] Guideline ($\mu g\, g^{-1}$)			
		Agr[c]	Residential/Parkland	Ind[d]	Comm[e]
B(a)P	234 ± 12/	0.7	0.7	0.7	0.7
CRY	215 ± 10/				
Al	14250 ± 6/528 ± 6				
As	355 ± 8/5.2 ± 8	12	12	12	12
Ca	7880 ± 5/197 ± 5				
Cd	39 ± 8/0.35 ± 8	1.4	10	22	22
Cr	135 ± 9/2.6 ± 9	64	64	87	87
Cu	560 ± 6/8.9 ± 6	63	63	91	91
Fe	170000 ± 6/3044 ± 0.6				
Mn	2000 ± 8/36 ± 8				
Ni	55 ± 3/0.94 ± 5	50	50	50	50
Pb	630 ± 7/3.0 ± 5	70	140	600	260
Zn	390 ± 6/6.0 ± 6	200	200	360	360

$\Sigma_{MTEs} \cong 3.8\, mmol\, g^{-1}$

[a] Canadian Council of Ministers of the Environment (CCME) [40].

[b] RSD = relative standard deviation.

[c] Agricultural.

[d] Industrial.

[e] Commercial.

3. Results and discussion

3.1. Soil characterization

The soil from the site had been field contaminated with both MTEs and PAH compounds. Initial experiments characterized the sieved soil with respect to particle size (sand, 47%; silt, 8%; clay, 45%), cation exchange capacity (CEC, 23 cmol kg^{-1}), pH (3.5), and organic matter (59%). The relatively higher proportions of silt and clay, high organic matter content, and intermediate CEC suggested that remediation by soil washing might be challenging. The soil's textural properties were supplemented by determinations of the MTE content of the soil and by a fractionation study to assess the ease of extraction of the investigated elements. As summarized in Table 1, the levels of B(a)P, As, Cd, Cr, Cu, Ni, Pb and Zn exceeded the maxima for Canadian quality guidelines (as recommended by the Canada Council of Ministers of the Environment, CCME) [41] for soils destined for commercial or industrial use. Remediation of the soil was warranted.

The remediation procedure to be evaluated consisted of a series of four sequential steps. Initially, the dried soil was to be equilibrated with a combination of a complexing reagent ([S,S]-EDDS) and a non-ionic surfactant (Brij98) in the presence of high energy (ultrasound). After the supernatant fraction had been separated from the soil particulates (stage 2), the aqueous phase was to be back-extracted with a non-polar solvent to recover PAHs (stage 3). The MTE fraction was to be removed from the aqueous phase by precipitation (stage 4). The precipitating agent was to be generated *in situ* by the controlled release of hydroxide induced by the spontaneous corrosion of added zero-valent magnesium granules [33]. Concurrently, MTE–EDDS complexes were anticipated to be transformed to the corresponding Mg–EDDS complex. The aqueous solution, once freed of HOCs and MTEs, was to be recycled by recombination with the soil particulates to extract more toxicants. The Mg^0-induced corrosion was anticipated to release hydroxide at a controlled rate that would benefit to the purity and size of particles of MTE-oxide/hydroxide precipitate. After filtration, the cleaned aqueous phase (now containing Mg–EDDS complex and surfactant) was to be returned to the soil particulates to mobilize more contaminants. This recycle of reagents could be repeated as many times as necessary to decrease contaminant loads to conform to recommended maxima. A companion report [42] focused on the fate of two PAH compounds. Nine successive washes with a combination of Brij98 and [S,S]-EDDS decreased the residual levels of B(a)P in soil to meet CCME guidelines for levels acceptable for residential/parkland use (Table 1).

The choice of the quantity of [S,S]-EDDS in the washing solution was arbitrary. It represented a sparing quantity (0.67 mmol g^{-1} soil, less than the stoichiometric equivalent) with respect to the total MTE burden (Σ_{MTEs} = 3.8 mmol g^{-1} soil, Table 1) but an excess relative to the sum of the trace elements (0.063 mmol g^{-1} soil). Equilibration of the soil with the washing solution was presumed to have occurred after 30 min of contact in the presence of ultrasound. In the current study, the quantities of analyte released after 20 min of contact were not significantly different from the 30 min treatment for either Al or Fe or B(a)P ([43], Fig. 1).

The soil was fractionated to determine the portions of each target element (As, Cd, Cr, Cu, Mn, Ni, Pb, or Zn) that could be dislodged from the soil (Table 2) with specific reagent protocols (BCR procedure) [44]. When performed successively on a soil sample, these protocols were considered to estimate the metal content associated with the exchangeable, reducible, oxidizable and residual fractions. As a means of characterizing the distribution within a soil, this

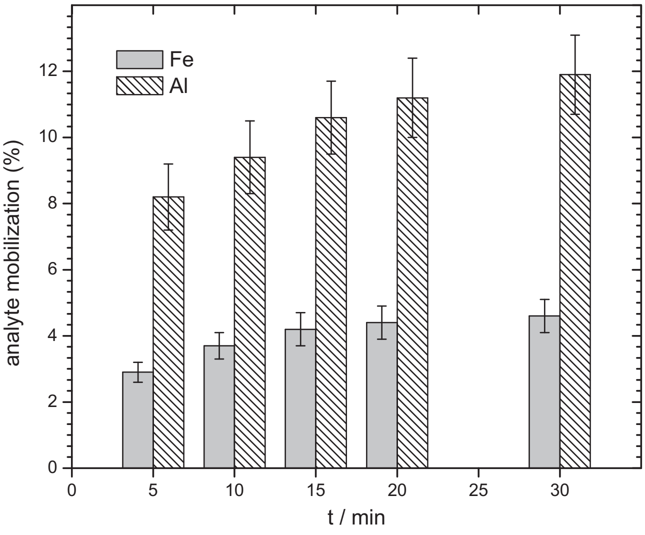

Fig. 1. Increaed mobilization of iron or aluminum with time.

Table 2
Percent of MTEs ($\mu g\,g^{-1}$ soil) that remained with each fraction of the soil particulates post five soil washing cycles with 0.1M EDDS in 6% (v/v) Brij98.

Target Element	Soil fraction	Original Soil	Residues post 5 surfactant washes	Residues post 5 surfactant + EDDS washes	% of original removed by 5 surfactant + EDDS washes
Al	Exchangeable	5.5	3.3	2.8	2.7
	Reducible	11	11	3.1	8.7
	Oxidizable	45	44	35	9.9
	Residual	36			
As	Exchangeable	4.8	2.2	3.1	1.7
	Reducible	24	9.0	12	12
	Oxidizable	70	70	54	16
	Residual	0.5			
Ca	Exchangeable	60	16	16	46
	Reducible	5.8	3.2	0.9	4.9
	Oxidizable	19	17	11	8.0
	Residual	17			
Cd	Exchangeable	26	26	20	6.0
	Reducible	28	26	15	13
	Oxidizable	44	44	10	34
	Residual	2.5			
Cu	Exchangeable	5.3	2.5	1.7	3.6
	Reducible	11	10	4.5	6.5
	Oxidizable	62	59	44	18
	Residual	21			
Fe	Exchangeable	1	0.1	1.0	0
	Reducible	11	10	4.5	6.5
	Oxidizable	68	68	63	5.0
	Residual	20			
Mn	Exchangeable	5.7	0.4	0.8	4.9
	Reducible	1.9	1.6	1.5	0.4
	Oxidizable	60	57.5	58	2.0
	Residual	33			
Ni	Exchangeable	7.1	1.8	0.2	6.9
	Reducible	8.9	0	3.6	5.3
	Oxidizable	84	83.6	71	13
	Residual	−1 (0)			
Pb	Exchangeable	12	15	0.9	11
	Reducible	30	29	29	1.0
	Oxidizable	57	39	22	35
	Residual	0.6			
	Exchangeable	38	4.4	0.5	38
Zn	Reducible	11	6.7	6.7	4.3
	Oxidizable	43	40	29	14
	Residual	8.5			

Mean mobilization: exchangeable 57%; reducible, 49%; oxidizable, 31%.

approach is subject to limitations [4,45] that have been recognized widely.

It has been considered [46] that it is the sum of exchangeable, carbonate and reducible fractions that approximates the portions of metal that can be dislodged by complexometric washing procedures. These fractionation studies indicated that a small proportion of most macro-elements Al (16%), Ca (66%), Fe (12%), Mn (8%) and an appreciable portion of the trace element content of As (29%), Cd (54%), Ni (16%), Pb (42%) and Zn (49%) were susceptible to washing by complexometric extraction. Among the trace elements, only Cu (21%) possessed an appreciable residual fraction.

The fraction of trace elements associated with organic matter forms a component of the oxidizable fraction within the BCR soil fractionation scheme. It was not possible with the BCR protocol to differentiate the portion of metal associated with Fe-oxides from the portion associated with organic matter. An appreciable portion of Cu is considered to be associated with organic matter whereas a large proportion of the Al, Fe and Mn were associated with the residual (36, 20, 33%) and the oxidizable (45, 58, 50%) fractions respectively. Similarly for Ni, Pb and Zn, an appreciable portion of the total burden (88, 57, 43%) was associated with the oxidizable fraction probably in large part with Fe-oxides. In contrast, Ca and Cd were associated in large part with the exchangeable (60, 26%) and the reducible (6.8, 28%) fractions respectively. Arsenic was anticipated to exist principally as oxyanions, $AsO(OH)_2^-$, $H_2AsO_4^-$. An appreciable portion of the soil As was associated with the oxidizable fraction (70%) presumably bound with the Fe-oxide fraction.

In subsequent experiments, metal extraction efficiencies were determined in the presence of nonionic (Brij98) surfactant alone or in combination with 2 mmol [S,S]-EDDS. Five sequential washes of soil, 3 g, resulted in appreciable mobilizations but incomplete recoveries of target PAH compounds [42]. The mobilization efficiencies for individual elements, expressed as a percentage of the burdens in separate soil fractions have been added to Table 2. The results of the sequential extraction demonstrated that [S,S]-EDDS was able to extract metals from Mn-oxides and organic complexes, together with the more labile exchangeable fraction. On the other hand, it was not possible to extract appreciable amounts of metals from the Fe-oxides or the silicates.

3.2. Extraction pH

It was of interest to evaluate the influence of slurry pH on metal recovery. PAH compounds seemed to be associated with the organic

Table 3
Variations in pH values after each of five soil equilibrations.

Mobilizing solution[a]	Original pH	Post 1st washing	Post 2nd washing	Post 3rd washing	Post 4th washing	Post 5th washing
6% Brij98 alone	9.15 ± 0.00	3.76 ± 0.01	3.81 ± 0.02	3.85 ± 0.01	3.88 ± 0.02	3.95 ± 0.03
6% Brij98 + 0.1 M EDDS	9.15 ± 0.00	8.54 ± 0.01	8.56 ± 0.01	8.59 ± 0.02	8.62 ± 0.03	8.67 ± 0.03

[a] The pH of 0.1M Na_3–EDDS has been reported to be 9.15 [51].

matter fraction of the soil. It was observed that the slurry pH was decreased appreciably by adding the acidic soil to the surfactant solution but the change was less severe when added to a mixed EDDS–surfactant solution. The final pHs of various soil slurries are recorded in Table 3. The pH of both the aqueous surfactant and the EDDS–surfactant mixture, both initially adjusted to pH 9.15, was decreased by the addition of the acidic soil to the aqueous solution. The terminal pHs of the equilibrated slurries was 3. 6 and 8.5 for the surfactant slurry and the [S,S]-EDDS-surfactant slurry, respectively. Clearly, the EDDS component buffered the soil slurry appreciably. During subsequent equilibrations, the pH of the slurry was little changed. In subsequent studies, the pH was adjusted to 9.0 after mixing the soil with the aqueous extracting solution but before the ultra-sonication step.

The influence of pH on the quantities of metals mobilized is summarized in Tables 4 and 5. As anticipated, the recoveries of most metals from the soil (Table 4) were greater at pH 5 than at pH 9 reflecting the general trend of the influence of pH on metal solubility [46]. Only the quantities of Ca and Cu were increased modestly (∼10%, pH 9 vs. pH 5, Table 4). However, when changes to the metal content of the oxidizable fraction of the soil were considered, the trend was reversed. Increased metal mobilization from the oxidizable fraction with increased pH (Table 5) was evident for all investigated elements.

3.3. Chelating reagents/ultra-sonication

Chelating agents can alter the association between SOM and the inorganic matrix or affect the structure of SOM itself [47]. Polyvalent metal ions can act as cross-linking agents of the SOM ‘polymer’ phase by coordinating to carboxylate or phenolate groups on different strands, increasing the rigidity of the matrix and hence the diffusive resistance of partitioned molecules. By extracting metal ions either bridged between SOM and minerals or serving as cross-linking agents within the organic phase of humic macromolecules, chelating agents cause SOM release from the solid phase via two pathways. First, macromolecules bound to the mineral surfaces via metal linkages can be released into the aqueous phase and second, removal of metals functioning as cross-linking agents within SOM can lead to a change in the phase properties of SOM from a more constrained, compact state to a more flexible, open state, resulting in an increased mass transfer of organic compounds into the aqueous phase. It was anticipated that a portion of the B(a)P and CRY might be associated with the SOM and it was decided to perform extractions with alkaline conditions that favor SOM solubility.

Ultra-sonication is a relatively inexpensive source of high energy that can be exploited to enhance the performance of soil washing [49]. Ultrasonic energy can break apart soil aggregates and disrupt the electrostatic interactions between soil surfaces and PAHs. Sonication has been demonstrated to be especially useful in soil washing if the soil texture is fine-sized, if the SOM content is elevated and/or if PAHs are trapped within the three-dimensional structure of SOM [48]. Fine-textured soils contain higher proportions of silt and clay that are prone to form larger soil aggregates mediated by organic matter [49]. As a result, a considerable proportion of SOM can be trapped within the soil macro-aggregates. Without disrupting these aggregates, both PAHs and SOM, located beneath the outer surfaces of aggregates, do not contact the surfactant micelle solution. In consequence, sonication is effective during soil washing processes for fine-texture soils and elevated SOM contents.

The influence of the duration of ultra-sonication step on metal mobilization was studied. It had been observed that the recovery of B(a)P from the soil was increased moderately with longer ultra-sonication times [41]. The percentage increase of element mobilized from the soil increased between 5 min and 30 min of ultra-sonication for all investigated elements. The increased sonication time, from 20 to 30 min, did not increase the metal recovery significantly (Fig. 1). However the fraction of MTEs that could be dislodged from the oxidizable fraction was not known; a sonication time of 30 min was chosen for subsequent experiments.

3.4. Recycle of [S,S]-EDDS complexing reagent

Equilibrations of the soil (with 0.1 M [S,S]-EDDS in 6% Brij98) were performed to evaluate the influence of zero-valent magnesium (Mg^0) on reagent reactivation. Four separate washing trials were completed. One trial served as the control in which no Mg^0

Table 4
Percentage of element (±RSD[a]) extracted from the soil with a single wash consisting of 0.05 M [S,S]-EDDS in 3% (v/v) Brij98 at various pHs.

pH	Al	As	Ca	Cu	Fe	Pb	Zn
5	9.1 ± 0.3	11 ± 0.8	20 ± 0.4	15 ± 0.4	6.6 ± 0.2	13 ± 0.5	38 ± 1.8
6	8.8 ± 1.8	9.6 ± 0.2	20 ± 0.6	15 ± 0.4	6.1 ± 0.3	13 ± 0.3	37 ± 0.8
7	7.9 ± 0.4	6.5 ± 0.6	23 ± 0.2	16 ± 0.2	4.7 ± 0.3	13 ± 0.2	35 ± 0.5
8	8.0 ± 2.1	4.8 ± 0.8	23 ± 0.2	16 ± 0.4	4.0 ± 0.2	13 ± 0.5	36 ± 0.5
9	7.8 ± 0.1	6.2 ± 0.8	22 ± 0.1	16 ± 0.2	3.8 ± 0.07	13 ± 0.1	34 ± 0.8

[a] Relative standard deviation.

Table 5
Percentage of element extracted from the oxidizable fraction within the soil (±RSD[a]) with a single wash consisting of 0.05 M [S,S]-EDDS in 3% (v/v) Brij98 at various pHs.

pH	Al	As	Ca	Cu	Fe	Pb	Zn
5	2.5 ± 0.2	1.7 ± 0.3	2.0 ± 0.1	2.9 ± 0.2	1.0 ± 0.09	5.2 ± 0.5	5.4 ± 0.5
6	3.1 ± 0.2	2.5 ± 0.3	2.0 ± 0.2	8.2 ± 0.4	1.3 ± 0.1	6.7 ± 0.3	6.7 ± 0.8
7	3.5 ± 0.4	3.1 ± 0.3	2.2 ± 0.2	9.5 ± 0.2	1.4 ± 0.1	7.5 ± 0.2	7.4 ± 0.3
8	3.9 ± 0.2	3.9 ± 0.3	2.5 ± 0.2	10 ± 0.4	1.6 ± 0.1	8.7 ± 0.5	8.2 ± 0.5
9	4.0 ± 0.4	4.5 ± 0.3	2.5 ± 0.1	11 ± 0.4	1.6 ± 0.1	9.7 ± 0.3	8.5 ± 0.5

[a] Relative standard deviation.

Table 6
Trace element removal efficiencies (expressed as % removed from the soil).

	As	Cd	Cr	Cu	Ni	Pb	Zn
Control	30	54	32	27	27	56	55
0.053 g Mg^0	66	77	52	74	30	13	64
0.073 g Mg^0	78	56	48	70	31	ND [a]	55
0.144 g Mg^0	83	105	57	73	34	3	54

[a] ND = none detected above background.

flakes were added to the aqueous extract whereas the other three trials involved the addition of Mg^0 granules (0.053, 0.077 or 1.44 g) to the aqueous solution followed by reaction, filtration and pH re-adjustment to 9.0 prior to re-combination with the soil particulates.

The MTEs that remained in the soil following treatment with Mg^0 were considerably decreased relative to control extractions for most elements. Treatment with Mg^0 acted as a source for the controlled release of hydroxide ion to precipitate the target metals as insoluble oxides/hydroxides. From theoretical principles [50], a pH corresponding to a minimum solubility for each of the metal hydroxides can be predicted. These values ranged from 6.5 for Pb to 10.6 for Mn [43]. In addition, the solubilities of individual metal hydroxides varied greatly (from 2.3×10^{-5} for Cd to 2.1 mg L^{-1} for Pb, [44]). Increased solubility for pH values in excess of the minimum, has been attributed to the formation of anionic hydroxide complexes. Frequently, metal precipitations with hydroxide solutions have been reported to result in sols/gels that are very difficult to filter. In contrast, the subsequent removal of the solids from the Mg^0 treated extract was readily filtered.

The removal efficiencies (expressed relative to the original soil concentrations) for treatment with three quantities of Mg^0 are summarized in Table 6. The quantity of added Mg^0 (0.00, 0.053, 0.073 or 0.144 g) corresponded to 0.0, 0.7, 1.0 or 2.0 equivalents of the EDDS dosage. After hydrolysis, the pH of the slurry was ≥10 as determined with universal indicating paper. For most trace elements (As, Cd, Cr, and Cu), recoveries were increased appreciably with increased Mg^0 treatment. The increase was modest for Ni and remained relatively unchanged for Zn. However the recovery of Pb was decreased appreciably and appeared to be related to the quantity of hydroxide ion released when the Mg^0 was corroded. Both Pb and Zn are known to form anionic hydroxide complexes ($Pb(OH)_3^-$, $Zn(OH)_3^-$) if the concentration of precipitating agent is sufficiently high. Both analytes seemed to display a similar behaviour, however the Pb seemed to be more sensitive to the effects of excess hydroxide. The pH corresponding to minimum hydroxide solubility for Pb is 6.5 vs. 8.5 for Zn. Somewhat arbitrarily, it was decided to add the smaller quantity of Mg^0 (0.053 g) to effect the precipitation of trace element and transpose the trace metal complexes to the corresponding Mg-complexes.

3.5. Procedure evaluation

Stability constants for metal–EDDS complexes [51] reveal that [S,S]-EDDS is a potent chelating agent for many heavy metals. However, most metal–EDDS complexes are weaker than corresponding metal–EDTA complexes. An exception is Cu, which forms almost equally stable complexes with both [S,S]-EDDS and EDTA (log K_{stab} = 18.50 and 18.78 respectively, [52]). EDDS complexes with Zn and Pb are somewhat weaker compared to the corresponding EDTA complexes.

When modified for the degree of protonation of the ligand and for the influence of hydroxide that competes with the EDDS for the metal ion, an effective stability constant K_{eff} that is pH dependant has been calculated [52]. The predicted order of metal complexation by EDTA at pH 4, Fe > Cu > Pb > Zn > Mn > Ca; suggests that extractions at this pH would be inefficient for the extraction of trace elements given the quantities of Fe in the soil. Extractions at pH 7 are considered [52] to represent an optimal compromise between trace metal complexation and macro-element complexation (Fe or Ca). For EDTA, the order at pH 7 is Cu > Pb > Fe > Zn > Mn > Ca whereas the order for EDDS at pH 7 is Cu > Fe > Zn > Pb > Mn > Ca. The predicted order for EDDS at pH 9 is Cu > Zn > Pb > Fe > Mn > Ca. However, the increased selectivity for trace elements relative to macro-elements comes at the expense of the magnitude of K_{eff} that were decreased for all elements. At pH 9, EDTA forms stronger complexes than does EDDS with both macro- and trace elements. However the differences are very large for macro-elements (differences of ∼6 orders of magnitude for Ca, ∼5 orders of magnitude for Mn and 3 orders of magnitude for Fe). By contrast, the decrease was 2 orders of magnitude for Pb, 1 order of magnitude for Zn and 0.3 orders of magnitude for Cu. Extraction at pH 9 represents an interesting compromise between increased metal selectivity and decreased avidity of metal binding. Losses of EDDS by adsorption to soil particles at pH > 5 have been reported to be minimal [52] corroborating the manufacturer's claim that [S,S]-EDDS is nonsorbtive.

Table 7
MTEs mobilized from or remaining with the soil (μg g^{-1} soil ± RSD[a]) after nine sequential equilibrations of the soil with the same initial dosage 0.1 M [S,S]-EDDS formulated in 6% (v/v) Brij98.

	Element mobilized from the soil (μmol g^{-1} soil ± 1RSD)			Element residues remaining with the soil particulates (μg g^{-1} soil ± 1RSD)			CCME [b]. suggested maximum (commercial/industrial)
	EDDS	EDTA	Brij98	EDDS	EDTA	Brij98	
Al	143 ± 2.8	22 ± 4.6	27 ± 3.7				
As	1.7 ± 5.9	0.5 ± 0.0	1.1 ± 11	226 ± 6.6	318 ± 6.3	269 ± 8.2	12/12
Ca	131 ± 3.1	164 ± 3.0	111 ± 2.7				
Cd	0.2 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	13 ± 7.7	26 ± 12	27 ± 18	22/22
Cr	1.0 ± 0.0	0.1 ± 0.0	0.0 ± 0.0	82 ± 6.1	128 ± 7.0	132 ± 8.3	87/87
Cu	3.0 ± 6.6	2 ± 5.0	1 ± 0.0	374 ± 5.9	434 ± 8.1	482 ± 7.7	91/91
Fe	410 ± 2.0	219 ± 2.7	90 ± 4.4				
Mg	10 ± 10	10 ± 10	12 ± 8.3				
Mn	3 ± 6.7	3 ± 6.7	3 ± 6.7				
Ni	0.3 ± 0.0	0.3 ± 0.0	0.2 ± 0.0	37 ± 8.1	39 ± 7.7	41 ± 7.3	50/50
Pb	2 ± 5.0	2 ± 5.0	1 ± 10	205 ± 5.4	216 ± 9.3	354 ± 9.0	260/600
Zn	4 ± 7.5	4 ± 7.5	3 ± 10	136 ± 7.4	141 ± 7.8	181 ± 8.3	360/360
Σ_{MTEs}	709	427	249				

[a] Relative standard deviation.

[b] Canadian Council of Ministers of the Environment (CCME) guideline for soil destined for commercial/industrial use [40].

Based on the preliminary trials above, the optimized extraction conditions were considered to be 20 mL of 0.1 M [S,S]-EDDS formulated in 6% (v/v) Brij98/3 g soil, pH 9. The resulting suspension was subjected to ultra-sonication during 30 min. Subsequently, the aqueous supernatant was back-extracted with non-polar solvent then treated with Mg^0 (53 mg). Post reaction, the filtrate was recombined with the soil particulates to extract more toxicants.

Soil trace element residues after five washing cycles indicated an incomplete removal of the target elements/compounds. When expressed as residue in the soil, the level of Cd ($18\,\mu g\,g^{-1} \pm 11\%$), Cr ($90\,\mu g\,g^{-1} \pm 8.9\%$), Ni ($40\,\mu g\,g^{-1} \pm 10\%$) and Zn ($173\,\mu g\,g^{-1} \pm 9.2\%$) equalled or were less than the CCME recommended maxima. The content of Pb ($274\,\mu g\,g^{-1} \pm 8.0\%$) met the criterion for soil destined for industrial use but exceeded the criterion for commercial use. However, the soil residual content of As ($244\,\mu g\,g^{-1} \pm 9.0\%$) or Cu ($401\,\mu g\,g^{-1} \pm 6.5\%$) or B(a)P soil residues ($12.4\,\mu g\,g^{-1} \pm 11\%\,g^{-1}$) failed to meet the recommended criteria.

A second trial involved nine successive washes. The collective metal mobilization, after nine sequential equilibrations with optimized operating conditions and various mobilization reagents is presented in Table 7. The total, mobilization of twelve elements by [S,S]-EDDS was ($709\,\mu mol\,g^{-1}$ soil), which was 1.7-fold greater than the total metal extracted ($427\,\mu mol\,g^{-1}$ soil) by an equivalent quantity of EDTA and 2.8-fold of total extraction ($249\,\mu mol\,g^{-1}$ soil) by surfactant in the absence of complexing reagent. The differences in element extraction efficiencies among the three mobilizing solutions were mainly the result of differences in Fe and Al mobilization. In terms of the residual contents of trace metals in the washed soil, the levels of Ni, Pb and Zn met the CCME criteria for commercial and industrial use after treatment by either complexant, the levels of Cd and Cr also met the criteria post EDDS treatment but remained excessive after EDTA treatment and the levels of As and Cu remained excessive after all three washing treatments. In soil, the predominant forms of As are anionic and are not anticipated to react with anionic complexing reagents. The observed efficiencies of extraction must have resulted, in large part, from the pH of the extracting medium.

4. Conclusions

Soil washing with a mixture of surfactant and EDDS can be an efficient remediation treatment for soil containing mixed contaminants. The optimum condition for trace element extraction from the contaminated soil depended on the geochemistry and metal fractionation, whereas the optimum condition for EDDS regeneration was influenced by the identities of the target analytes. Lead and Zn were removed from solution less efficiently at higher pHs presumably the result of formation of anionic hydroxide complexes. The integration of MTE extraction with EDDS, subsequent MTE precipitation and reagent regeneration improved the economic viability of soil washing of contaminated sites. The overall process resulted in a soil particulate fraction that has been cleaned and a limited volume of aqueous extract that had been detoxified. Expressed on a per kg soil basis, the procedure consumed 6.6 L of water whereas if fresh water had been used for each recycle, 53.3 L of water would have been required.

Despite nine successive washes with the same dosage of mobilization reagents, the levels of As and Cu in the soil remained excessive. It should be noted that the residual fraction of Cu in the soil ($21\% \times 560\,\mu g\,g^{-1} = 118\,\mu g\,g^{-1}$) exceeded the CCME maximum permissible limit of $91\,\mu g\,g^{-1}$ and 70% of the soil As burden was associated with the oxidizable fraction possibly bound to Fe-oxides and not readily displaced by the complexing reagent. It remains to determine the optimum concentration of the EDDS complexing reagent.

Acknowledgements

The financial support of the Natural Science and Engineering Research Council of Canada (NSERC) is gratefully acknowledged. The authors also thank Dr. M. Rivero-Huguet for help and advice with ICP-OES determinations.

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