



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

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ABSTRACT

A laboratory study was conducted to assess the feasibility of a washing process with nonionic surfactant in combination with EDDS for the simultaneous mobilization of MTEs and PAH compounds from a field-contaminated soil. Unit processes consisting of complexometric extraction and surfactant-assisted mobilization were combined with reagent regeneration and detoxification steps to generate innocuous products. Thirty minutes of ultrasonic mixing of the soil with a combination of 20 mL⁻¹ surfactant suspension and a sparing quantity (2 mmol) of EDDS mobilized virtually all of the benzo[α] pyrene (B(a)P) and chrysene (Cry) and an appreciable portion of the burdens of Cd, Cr, Mn, Ni, Pb and Zn, lesser amounts of the As and Cu, but only small quantities of Al and Fe. Relative to individual reagents, combinations of surfactant (Brij98), with EDDS increased the recovery of B(a)P but seemingly did not influence Cry extraction efficiencies perceptibly. Nine sequential washes with the same initial dosage of mobilization aids decreased the quantities of both PAHs to levels in the soil that conformed to recommended maxima. What resulted was a soil that had been cleaned and a limited quantity of innocuous wash water.

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1. Introduction

A number of Brownfield sites are burdened with mixed contaminants that can include volatile organic compounds, metals, or semivolatile organic compounds. In the United States of America, there are an estimated total of 294,000 contaminated sites [1] while in the United Kingdom, up to 100,000 sites have been listed as potentially dangerous [2] and in Canada some 30,000 contaminated Brownfield sites have been identified [3]. Whereas continued research has focused on the remediation of either organic contaminants or trace elements, there have been fewer published studies of the simultaneous removal of both organic and inorganic pollutants from soil. Soil washing is a treatment process that can be used for remediating both organic and inorganic chemicals from contaminated soils, sludges, and sediments [4–6]. Soil washing can be physical, chemical, or both, resulting in the separation, segregation, and volume reduction of hazardous materials or the chemical transformation of contaminants to nonhazardous, unregulated substances.

PAHs are found in higher concentrations at industrial sites associated with petroleum, coke and gas production and wood

preservative industries. Because certain members of this class have been demonstrated to be both carcinogenic and mutagenic, PAHs have long been considered as environmental priority pollutants [7] that require metabolic activation to electrophilic intermediates [8] and subsequent covalent adduct formation with cellular DNA to elicit their adverse biological activity [9]. Owing to their persistence and lipophilic character, PAH compounds can accumulate extensively in soils and sediments where they are recalcitrant [10].

The U.S. Environmental Protection Agency has classified seven PAHs, including B(a)P and Cry, as Group B2, probable human carcinogens [11]. It has been demonstrated that the mutagenic activity of selected PAH toxicants can be circumvented by catalytic hydrogenation [12]. Whereas B(a)P and Cry were potently mutagenic, their perhydrogenation products were without detectable activity in the reverse mutation assay with five strains of bacteria. Moreover, partial hydrogenation (that resulted in one aromatic ring of the substrate remaining intact) provided products that were non-mutagenic in these assays.

Proposals for the restoration of soils that have been polluted with PAH compounds have comprised a variety of treatment options including incineration, solidification–vitrification, phytoremediation, bioremediation, electrokinetic, washing with surfactants or cyclodextrins and chemical oxidation. These strategies, however, have been applied as treatments in the field only infrequently because of costs, environmental constraints, and

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efficacy. To remove PAH pollutants from the soil matrix, microbial degradation or thermal treatment have been the major processes employed [13]. However, it has been demonstrated that thermal processing can contribute to the formation of genotoxic PAHs that result from thermal isomerization and PAH formation [14,15].

Surfactants are particularly attractive for washing applications as they potentially have low toxicity and favorable biodegradability in the environment relative to organic-solvent-based systems. Yet, guidance in selecting surfactants for *ex situ* soil washing remains somewhat fragmentary [16,17].

Ethylenediaminetetraacetic acid (EDTA) continues to be explored extensively for soil treatment because it can mobilize metal cations efficiently coupled with only a minor impact on the physical and chemical properties of the soil matrix. EDTA is considered to possess a low degree of biodegradability in soil [18] and a high level of complexing capacity with respect to metal cations.

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 [19]. This increased biodegradability of EDDS and an overall favorable environmental profile [20] 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). Recent reports concerning EDDS have included the use of etyl lactate to facilitate Cu mobilization [21] or leaching [22] post size fractionation. Reviews [23,24] have indicated that although soil washing with solutions of chelating agents is an attractive technology, there remains a lack of consensus concerning the choice of the most appropriate chelating agent(s). EDDS seems to represent a promising alternative.

Soil remediation using surfactant–chelant washing aided by ultrasound [25] is a novel approach to increase contaminant extraction. A further processing stage that is able to decontaminate the soil extract can help to increase its remediation value [26] and often combinations of different techniques must be used during processing [27]. An attractive combination has involved surfactant recovery and reuse [28].

Soil organic matter (SOM) is widely accepted as being the most important soil component for the retention of hydrophobic organic compounds (HOCs) in soils and sediments [29,30]. The desorption of PAHs from the particulate organic matter fraction into surfactant solution can be facilitated with the use of mobilization additives that increase the solubility of the SOM. These chemicals have included strong acid, strong base, pyrophosphate, complexing reagents (citric acid or EDTA), formic acid and a variety of oxidizing protocols. It was hypothesized [31,32] that complexing agents might act by disrupting organic matter–metal–mineral linkages in the soil, resulting in the solubilization of SOM and facilitated dissolution of sorbed PAH molecules.

The sorption of HOCs is characterized by rapid adsorption to the external surfaces of soil particle and slow intra-particle diffusion to increasingly remote and sterically less accessible sites in the pores and voids of SOM and minerals. PAHs exhibit strong sorptive interaction with SOM and irreversible adsorption to SOM has been reported [33]. Whereas PAH fractions sorbed at or near external particle surfaces are mainly available, the fraction diffused into SOM and minerals exhibit strong steric or chemical hindrance of back-diffusion from solid phase into mobilizing solution. As a possible strategy to remove more PAHs, mobilizing reagents in combination with chelating agents have been used to disperse or release the SOM from soil consequently releasing more PAHs from soil particles.

The objective of the study was to evaluate the efficiency of a combination of unit operations to simultaneously mobilize hydrophobic organic contaminants and trace elements. Toxicant mobilization by soil washing with an aqueous mixture containing

surfactant and a sparing quantity of EDDS was to be followed by (i) non-polar solvent back-extraction (to remove PAH compounds and recover the surfactant), followed by (ii) treatment with zero-valent Mg (to precipitate heavy metals and liberate EDDS), and (iii) recycling of the cleaned extract. The precipitated heavy metal oxyhydroxides were to be recovered by filtration and the PAH-laden organic back-extract was to be detoxified by hydrogenation [12]. The recycling process was to be repeated at least twice. This report evaluates the mobilization of PAH compounds from a field-contaminated soil.

2. Materials and methods

2.1. Soil sample pretreatment and characterization

The soils for these studies was obtained from the Sydney Tar Ponds Agency, Sydney, NS. The soils, 0.5 or 10 kg grab samples from the 0–25 cm horizon of 2 sites adjacent to the brook that connects the coke ovens area with the tar ponds, within the 66 ha site were both classified as sandy loam [34] and had been field-contaminated with PAH compounds along with As, Cd, Cr, Cu, Mn, Ni, Pb, and Zn. The soils were air dried, mixed thoroughly, and passed through a 500- μm sieve, then stored in a sealed plastic bag for further testing. The soil was characterized with respect to particle size [35], (% sand, silt and clay); cation exchange capacity (CEC, cmol kg^{-1}) [36]; pH (determined using a glass electrode in a soil to water ratio of 1:2.5) and organic matter [37]. The element burden of Al, As, Ca, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in clear solution that resulted from soil digests, prepared by conventional nitric/ H_2O_2 block digestion [38], 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 element content in a standard reference material (Montana soil, SRM 2711), as determined with ICP-AES agreed with their certified values.

The initial soil PAH concentrations for soil B, B(a)P ($234 \pm 27 \mu\text{g g}^{-1}$) and Cry ($215 \pm 22 \mu\text{g g}^{-1}$) were estimated by exhaustive Soxhlet-extraction. Soil (1 g) was transferred to cellulose thimble and subjected to extraction with 150 mL of hexane-acetone mixture (3:1) for 16 h at a rate of 5–6 min per cycle. The extract was concentrated to dryness under a gentle stream of N_2 and the residues were re-dissolved in 3 mL hexane–methyl isobutyl ketone (MIBK) mixture (10:1) prior to analysis by gas chromatography–mass spectrometry (GC–MS, Saturn 2000, Varian, Walnut Creek, CA).

2.2. Chemicals

Nonionic surfactants, Brij98, Brij97, Triton DF-16 and Triton-770 were purchased from Sigma–Aldrich, Oakville, ON. Ivey-Sol 106, an industrial formulation, was kindly provided by Mr. G. Ivey, Ivey International Inc., Campbell River, BC. Sodium hexametaphosphate, sodium tripolyphosphate, dipotassium hydrogenphosphate, and disodium ethylenediaminetetraacetate were obtained from Fisher Chemical, Napean, ON. [S,S]-ethylenediaminedisuccinic acid (30% EDDS) as Octaquest E30 was obtained from Innospec Limited, Cheshire, UK. Trisodium salt of methylglycinediacetic acid (86% MGDA) with trade name Trilon M was purchased from BASF, Ludwigshafen, Germany. HPLC grade ethanol, chloroform, hexane and MIBK were obtained from Fisher Scientific, Napean, ON. All chemicals, solvents and reagents were of ACS Reagent grade or better and were used as received.

Table 1
Soil characteristics.

	Sand (%)	Clay (%)	Silt (%)	Organic C (%)	pH	CEC (cmol kg ⁻¹)
Soil A	71	3	26	30	6.9	21
Soil B	47	8	45	59	3.4	23

2.3. PAH mobilization

In a typical trial, soil (3 g) was equilibrated with 20 mL of chelating reagent (0.05–0.1 M) or chelating solution contained in 20 mL⁻¹ surfactant (3% v/v) in a 50 mL centrifuge tubes. Equilibrations were achieved by sonicating the soil suspension for 30 min with an ultrasonic homogenizer (XL 2020 Sonic dismembrator, Mis-onix 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. Sonication trials were performed with tubes at room temperature while the attendant heating increased the temperature to ~60 °C. 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 and aqueous fractions were collected to remove solubilized contaminants.

2.4. Removal of PAHs from soil extracts

PAHs in the supernatant fraction were back-extracted three to five times with 2–3 mL of a hexane–MIBK mixture (9:1) to partition PAHs from the aqueous surfactant solution. The hexane fractions were combined and centrifuged at 4000 rpm to remove aqueous surfactant then diluted with 1 mL ethanol to disrupt the hexane–surfactant emulsion induced by agitation. PAHs that had been extracted with hexane–MIBK mixture were determined by GC–MS.

2.5. Recycle of mobilizing reagents

Post PAH removal, the aqueous supernatant fraction was reacted with 0.053 g Mg⁰ granules then filtered, after 1 h, to remove the precipitated MTE-oxide/hydroxides. The pH of the cleaned mobilizing reagent solution was re-adjusted to 9.0 and then re-equilibrated with the soil particulate fraction to mobilize more contaminants. Once the requisite number of washing cycles had been completed, PAH residues in the particulates fraction were determined by exhaustive Soxhlet extraction.

2.6. Site description

A decommissioned steel plant and ancillary coke ovens in Sydney, Nova Scotia, Canada, operated from 1901 through 1988. The oven area contained 400 coke ovens, 4 blast furnaces, and 10 open-hearth furnaces [39]. The coking operations provided coke for the local steel manufacturing industry, while the by-products, such as coal tar and ammonia, were used to manufacture various other commercial products. The ~400 ha site is adjacent to the Muggah Creek estuary [40]. These tar ponds have acted as a settling basin for the steel-mill effluent and for coking-oven wastes trapping particles contaminated with PAHs, metals and other compounds.

3. Results and discussion

3.1. Sample characterization and rationale

The relevant characteristics of the dried, homogenized, soil samples are summarized in Table 1. The elevated levels of silt/clay, organic matter and intermediate CEC suggested that remediation of

the soil by soil washing might be difficult. The soil's textural properties were supplemented by determinations of the content of MTEs by ICP-OES and two PAH compounds B(a)P and Cry determined by exhaustive Soxhlet extraction and GC–MS. (Table 2). Included in Table 2 are the corresponding Interim Canadian Soil Quality Guidelines that recommend permissible maxima for toxicants in soil destined for various uses (agricultural, recreational/parkland, commercial or industrial) [41]. Remediation of both PAH compounds and trace metals were clearly warranted.

A companion report (with soil B) [42] focused on the fate of eight trace elements during soil washing. Nine successive washes with a combination of Brij98 and EDDS decreased the residual levels of Cd, Cr, Mn, Ni, Pb and Zn in soil to meet the Canadian Council of Ministers of the Environment (CCME) guidelines for levels acceptable for commercial/industrial use (Table 2). In contrast, levels of As and Cu remained excessive. The choice of the quantity of 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 ($\sum_{\text{MTEs}} \cong 3.8 \text{ mmol g}^{-1}$ soil, Table 2).

The trials described below were considered to be a proof of purpose study aimed at developing techniques for soil decontamination that would be *ex-situ* but *on-site*. Chelating reagents can disrupt the association between SOM and the inorganic matrix or modify the structure of SOM itself [43]. 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. To increase the solubility of SOM, it was decided to perform extractions with alkaline conditions in the presence of Na₃EDDS.

Ultra-sonication is a relatively inexpensive source of high energy that can be exploited to enhance the performance of soil washing [44]. Sonication has been demonstrated to be especially useful in soil washing if the soil texture is fine-grained, if the SOM content is elevated and/or if PAHs are trapped within the three-dimensional structure of SOM [43]. Fine-textured soils contain higher proportions of silt and clay that are prone to form larger soil aggregates mediated by organic matter [44]. Without disrupting the soil aggregates, both PAHs and SOM, located beneath the outer surfaces, do not contact the surfactant micelle solution.

3.2. PAHs mobilization

Initial trials involved surfactant screening for their ability to mobilize two mutagenic PAH compounds, Cry and B(a)P from soil A. The time for a single equilibration/sonication (10 min) and surfactant concentrations (3% v/v) used for these experiments was adopted from previous studies [45,46]. Among five surfactants, Brij98 and Ivey-106 were superior and mobilized 54–57% of the burden of the targeted compounds. Whereas, Brij97 mobilized lesser quantities of PAHs (36% and 37%), Triton DF-16 and Triton 770 extracted 17–28% of Cry and 19–30% B(a)P. In consequence, subsequent experiments were limited to equilibrations with Brij98 or Ivey-sol 106.

In further experiments with soil A, the relatively high organic carbon content in the soil was treated with various chelating agents and phosphate salts to release/disperse the target analytes. The results (Fig. 1) demonstrated that for a single equilibration of the soil with Brij98 in combination with EDTA, the percent Cry (44 ± 4%) and B(a)P (37 ± 5%) mobilized was somewhat more efficient than trials performed without EDTA (Cry, 37 ± 5%; B(a)P, 36 ± 6%). Even though, no appreciable increase was observed with EDDS (50 ± 2%)

Table 2
Toxicant burdens in the soil and permitted maxima.

Toxicant	Total content ($\mu\text{g g}^{-1} \pm 1\text{RSD}^b / \mu\text{mol g}^{-1} \pm 1\text{RSD}$)	CCME ^a guideline ($\mu\text{g g}^{-1}$)			
		Agr ^c	Residential/Parkland	Ind ^d	Comm ^e
B(a)P	234 ± 12	0.1	0.7	0.7	0.7
Cry	215 ± 10				
Al	14,250 ± 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	170,000 ± 0.6/3044 ± 0.6				
Mn	2000 ± 8/36 ± 8				
Ni	55 ± 5/0.94 ± 5	50	50	50	50
Pb	630 ± 5/3.0 ± 5	70	140	600	260
Zn	390 ± 7/6.0 ± 6	200	200	360	360
	$\sum \text{MTEs} \cong 3.8 \text{ mmol g}^{-1}$				

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

^b RSD = 1 relative standard deviation.

^c Agricultural.

^d Industrial.

^e Commercial.

or MGDA (53 ± 2%) for percent Cry removal, B(a)P mobilization was increased by EDDS (15%) or MGDA (13%) in comparison to EDTA. On the other hand, formulating the Brij98 in combination with EDDS in 0.1 M phosphate salt (hydrogen phosphate, polyphosphate or hexametaphosphate) at pH 8.0 did not change the recovery of PAHs perceptibly (56 ± 4, 56 ± 5 or 57 ± 5 for ortho-phosphate, HPO_4^{2-} or pyro-phosphate respectively, Fig. 1).

All subsequent experiments were performed using soil B because it was anticipated that this soil might provide a more demanding test of the washing strategy. The influence on pH of blending the soil with mobilization reagents was evaluated. It was observed that addition of the acidic soil (soil B) to the surfactant formulation had a profound influence on pH of the resulting slurry. For 20 mL of 3% (v/v) Brij98 solution that had been pre-adjusted to pH 9.15, the addition of 3 g of soil and subsequent sonication resulted in a dramatic decrease in pH to 3.76 of the resulting soil slurry. Subsequent equilibrations of the soil particulates fraction had only a minor influence on pH, so that after five successive equilibrations with fresh solution each time, the pH had increased slightly to 3.95. By contrast, formulating 0.1 M EDDS into the mobilizing solution (initial pH, 9.15) had less of an effect on pH. After one equilibration of 3 g soil with 20 mL of 0.1 M EDDS in 3% Brij98, the pH had decreased somewhat to 8.54 and after four more equilibrations of the soil particulates (with fresh reagent each time) the pH of the

resulting slurry had increased modestly to 8.67. Clearly, the EDDS had a strong buffering capacity. The addition of EDTA to the mobilizing solution provided an intermediate situation. For 0.1 M EDTA in 3% Brij98 mobilizing solution that had been adjusted to pH 6.0 or pH 9.0, the pH of the suspensions after sonication with 3 g soil had been decreased to 5.3 and 5.7, respectively. In subsequent studies, the pH of the soil slurry was adjusted to the desired value (9.0) after mixing but prior to sonication.

It was anticipated that the lipophilic PAH compounds would be associated with the organic matter fraction of the soil. The mobilization of organic matter from soil is generally effected with alkaline conditions. A preliminary comparison between EDDS and EDTA was performed at pH 6 and at pH 9. As summarized in Fig. 2, differences in mean analyte extraction efficiencies at pH 6 or at pH 9 for EDTA were not evident, 48 ± 5 vs. 50 ± 4 $\mu\text{g g}^{-1}$ soil for B(a)P and 40 ± 3 vs. 39 ± 3 $\mu\text{g g}^{-1}$ soil for Cry. In contrast, differences in mean mobilizations with EDDS were appreciable, 53 ± 4 (pH 6) vs. 67 ± 4 $\mu\text{g g}^{-1}$ soil at pH 9 for B(a)P and 48 ± 4 vs. 58 ± 7 $\mu\text{g g}^{-1}$ soil for Cry. In all cases, more analyte was extracted at the higher pH condition.

3.3. Ultra-sonication

Fig. 3 presents the influence of the ultra-sonication time on B(a)P recovery in 0.1 M EDDS–Brij98 (6%, v/v) solution. The application of

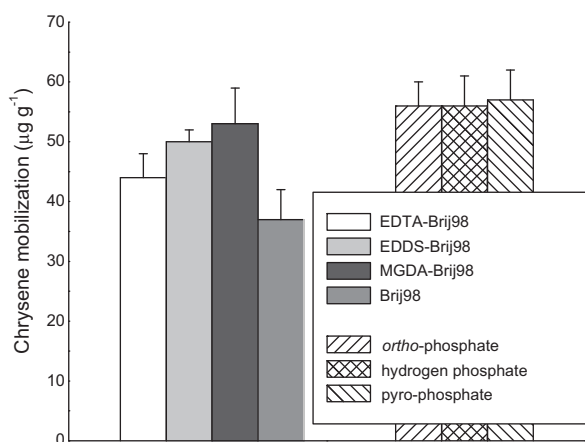


Fig. 1. PAHs extraction efficiencies ($\mu\text{g g}^{-1}$ soil) for Brij98 in the presence of various chelating reagents and phosphate salts.

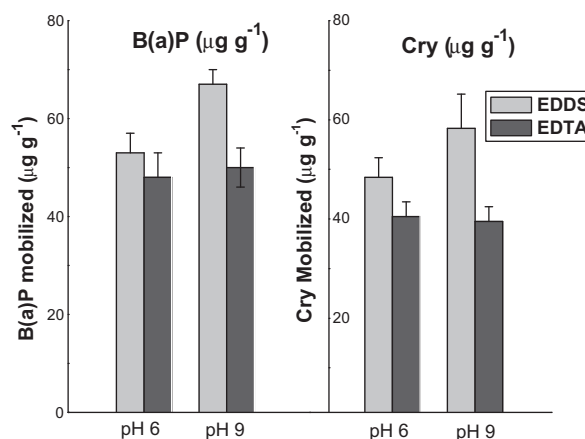


Fig. 2. Extraction efficiencies of PAH compounds ($\mu\text{g g}^{-1}$ soil) in the presence of 0.1 M EDDS or EDTA formulated in 3% (v/v) Brij98.

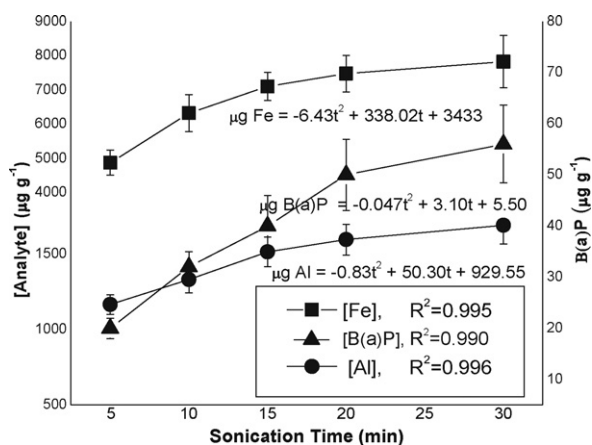


Fig. 3. The influence of the ultra-sonication time on the recovery of B(a)P, Fe or Al into 0.1M EDDS–Brij98 (6%, v/v) solution.

high intensity ultrasonic waves was aimed at disrupting aggregates within the soil as well as the relatively weaker interaction forces between contaminants and the soil particles. Fig. 3 suggests that the mobilization of B(a)P was adequately modeled as a quadratic function of the ultra-sonication time. The quantity of B(a)P mobilized after 30 min of agitation seemed to have reached the plateau within the curve that was 1.8-fold greater than after 5 min of sonication.

It was anticipated that metal ions might be responsible, in part, for maintaining the organic matter in the solid state. Two macro-elements, Fe and Al, which collectively comprised 90% of total metals extracted from the soil organic fraction [42], might have served as links between the macromolecules of organic matter and to maintain them in the solid phase. The quantities of Fe and Al extracted from the soil were also adequately modeled as quadratic functions of the ultra-sonication time (t) (Fig. 3). The process of equilibration by ultra-sonication, while rapid relative to Soxhlet extraction (16 h) or end over end wrist shaking (48 h) [47], still required time for the mobilization aids to penetrate the soil's micropores and for solubilized analytes to diffuse into the bulk medium. Both Fe and Al extraction efficiencies had reached maxima after 30 min. If the curves of Fig. 3 are compared, the trends for all curves are similar; the recoveries of the three analytes are all quadratic functions that increase with increasing ultra-sonication time and reveal that B(a)P mobilization from the soil is closely associated with the solubilization of Fe and Al.

3.4. Complexing reagent concentration, soil washwater ratio and CMC

The concentration of EDDS in the mobilizing solution and the soil/solution ratio were also evaluated. A comparison of three EDDS concentrations (0.05, 1.0 and 1.5 M) indicated that the mean quantities of B(a)P mobilized were not significantly different between the 1.0 and the 1.5 M EDDS extractant (51 ± 4 vs. $48 \pm 4 \mu\text{g g}^{-1}$ soil, Fig. 4A). A solution of 0.1 M EDDS was judged to be optimal.

Two solution/soil ratios were studied: 6.6 and 3.3 (v/w). The 6.6 ratio represented a convenient ratio that has been employed for several years for studies performed with 1–3 g soil. The 3.3 ratio was chosen based on the findings of Yin et al. [48]. According to Yin, with increased pH and decreased solution volume, the surfaces of soil particles became increasingly deprotonated and the repulsions between the negatively charged particles and SOM increase appreciably. The decreased spaces between the soil particles result in an increased colloid formation. The colloid was demonstrated to be dissolved organic matter-carrying metal ions. Correlation analysis indicated that the appreciable increase in Cu mobilization with

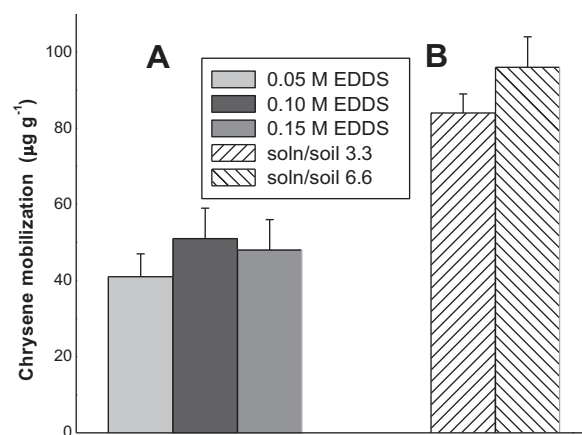


Fig. 4. The influence of (A) surfactant concentration on the efficiency of B(a)P mobilization or (B) solution/soil (v/w) ratio on the efficiency of chrysene mobilization.

decreased solution volume at high pH was strongly associated with the increased colloid formation of SOM. Yin also pointed out that the dispersion of particles (colloid formation) was very limited at lower pH values [48].

The results of solution/soil ratio study are illustrated in Fig. 4B. The results indicated that the solution/soil ratio 6.6 mobilized more B(a)P (5% higher per gram of soil) compared with the liquid to solid ratio of 3.3. Although the differences were not great, other problems with the lower solution soil ratio were evident. Both soil suspensions were observed to foam readily during ultra-sonication presumably the result of the elevated proportion of soil. The decreased recovery and more water made washing with the 3.3 ratio less attractive.

The critical micelle concentration (CMC) of the Brij98 surfactant has been reported to be at 3% (v/w) in soil suspension. By adding 0.05 M EDDS, the CMC of the surfactant solution was decreased somewhat (to between 1.5 and 3%). The decreased CMC of the surfactant solution might have resulted, in part, from the relatively higher pH during equilibrations with soil because of the presence of the EDDS additive. The presence of EDDS maintained the mobilizing solution pH between 8.5 to 9.0 through successive equilibrations. Studies have suggested that the sorption of surfactant decreased with increasing solution pH [49]. Although the slope above 3% became less steep, the 6% Brij98 solution displayed a considerably greater B(a)P mobilization capacity than the 3% solution (22% higher) and the 4.5% solution also increased the B(a)P mobilization (8% higher).

3.5. Procedure evaluation

During procedure evaluation studies, the optimized solution, 0.1 M EDDS–6%Brij98 (adjusted to pH 9.0, solution/soil ratio, 6.6) was compared with two other formulations, 0.1 M EDTA–6%Brij98 or 6%Brij98 alone for B(a)P or Cry mobilization. Two mobilization trials were completed; a preliminary trial was terminated after 5 successive soil washes and the second trial was terminated after 9 successive washes. The cumulative recovery of (a) B(a)P and Cry in the organic extracts after five cycles and (b) the analyte soil residues after 9 washes are recorded in Table 3. After 5 washes, the mobilization of PAH compounds was incomplete with either mobilization aid but the presence of EDDS additive increased recovery of both B(a)P and Cry. The cumulative mobilization after nine washes in the presence of EDDS was more efficient at solubilizing B(a)P in comparison with EDTA or with surfactant alone. The EDDS treatment had extracted virtually all (~101%, cumulative analyte sum

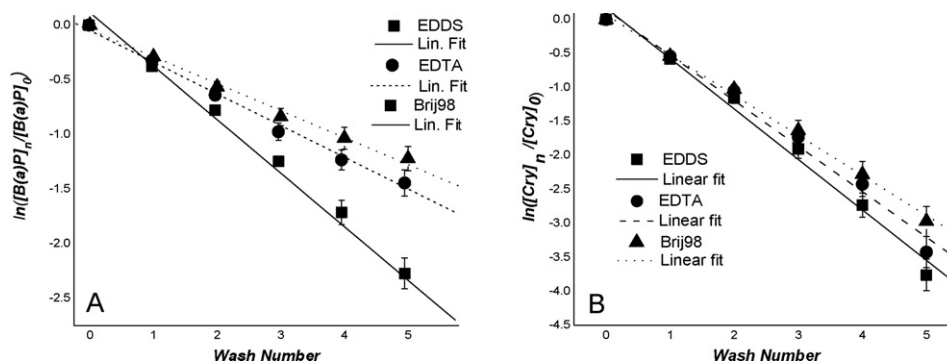


Fig. 5. Decay curves for B(a)P or Cry remaining with the soil particulate fraction ($\ln[\text{toxicant}]_n/[\text{toxicant}]_0$) after sequential equilibrations with various washing solutions.

Table 3

The mean cumulative percent recovery ($\pm 1\text{RSD}^a$) of B(a)P or Cry in the organic extracts after five washing cycles or (b) analyte soil residues ($\mu\text{g g}^{-1} \pm 1\text{RSD}$) after 9 successive washes with the same dosage of mobilization aids.

Successive washes	B(a)P		Cry	
	5	9	5	9
Brij98	78 \pm 11%	60 \pm 8%	93 \pm 5%	ND ^b
EDDS–Brij98	93 \pm 8%	ND	97 \pm 8%	ND
EDTA–Brij98	NP ^c	46 \pm 7%	NP	ND

^a Relative standard deviation.

^b None detected, limit of quantitation = 0.3 $\mu\text{g g}^{-1}$ soil for Cry and 0.2 $\mu\text{g g}^{-1}$ soil for B(a)P

^c Not performed.

in nine extracts) of the B(a)P, whereas EDTA or surfactant alone had removed 80% or 73%, respectively.

In contrast to B(a)P solubilization, Cry extraction by all three solutions were similar. The cumulative quantity of Cry recovered in all three solutions was virtually quantitative: 100% with EDDS, 102% with EDTA, and 99% with surfactant. The similar and high mobilization efficiencies among the three washing solutions suggested that metal extraction in the presence of chelating reagent did not influence chrysene mobilization.

By plotting the quantity of analyte (B(a)P or Cry) that remained in the soil vs. the number of equilibrations, a decay curve for B(a)P or Cry associated with the soil particulate fraction was obtained (Fig. 5). The Y-axis in Fig. 5A represents the \ln of the ratio of $[\text{B(a)P}]_n$ (after n washes) relative to the initial concentration ($[\text{B(a)P}]_0$) remaining in the soil ($\ln[\text{B(a)P}]_n/[\text{B(a)P}]_0$). Similarly, the Y-axis of Fig. 5B represents the \ln of the ratio of Cry remained after n equilibrations over the initial concentration ($\ln[\text{Cry}]_n/[\text{Cry}]_0$). The \ln of this ratio was anticipated to decrease linearly as the number of washes (n) and is related through a constant of proportionality (k).

$$\ln\left(\frac{[\text{B(a)P}]_n}{[\text{B(a)P}]_0}\right) = -kn \quad (1)$$

The goodness of fit of the exponential decay model to the data (R^2 , Table 4) was satisfying high in all cases. Comparisons of the logarithmically transformed mean analyte levels in each organic

Table 4

Measures of the goodness of fit (R^2) of the exponential decay model to the data, estimates of the decay constant (k) and the number of washes predicted to decrease the total burden of B(a)P or Cry in the soil by half ($n_{1/2}$) for various reagents.

Mobilizing solution	B(a)P			Cry		
	R^2	k	$n_{1/2}$	R^2	k	$n_{1/2}$
EDDS–Brij98	0.985	0.459	1.5	0.994	0.697	1.0
EDTA–Brij98	0.971	0.286	2.4	0.980	0.630	1.1
Brij98 alone	0.964	0.241	2.9	0.981	0.572	1.2

extract revealed that for B(a)P mobilization, differences between the EDTA–Brij98 vs. EDDS–Brij98 treatment or vs. Brij98 alone were statistically significant at the 95% level of confidence (but not at the 99% level) but differences between EDTA–Brij98 and Brij98 alone were not significant. As for chrysene, there were no statistically significant differences among the three treatments.

An interesting property of the constant of proportionality is that it can be used to compare the number of washes that are predicted to be required to decrease the toxicant burden to one-half of its initial value ($n_{1/2}$).

$$n_{1/2} = \ln\frac{2}{k} \cong \frac{0.693}{k} \quad (2)$$

The estimated values of k and $n_{1/2}$ for B(a)P and Cry with various washing solutions have been summarized in Table 4. To decrease the B(a)P initial concentration by half by soil washing, fewer equilibrations were needed in the case of EDDS–Brij98 (1.5) than for the EDTA–Brij98 formulation (2.4) or for the Brij98 (2.9): the washing process was more efficient in comparison with EDTA or with Brij98. For Cry mobilizations, the differences between the three predicted numbers of washes ($n_{1/2}$) were not appreciable (1.0, 1.1, and 1.2 for EDDS–Brij98, EDTA–Brij98 and Brij98, respectively).

Trace element extraction using the optimized mobilization conditions, also decreased the levels of Cr, Mn, Ni, Pb and Zn to conform with CCME recommendations but the levels of As and Cu remained in excess. This was not surprising in that soil fractionation trials [42] indicated that the levels of Cu in the soil residual fraction ($21\% \times 560 \mu\text{g g}^{-1}$ soil = 118) exceeded the CCME guideline of $90 \mu\text{g g}^{-1}$ soil. In soil, As occurs principally as oxyanions (arsenate or arsenite) that are not predicted to react with complexing reagents.

4. Conclusions

Process optimization studies indicated that pH, concentrations of the mobilization aids (EDDS and surfactant), duration of the ultra-sonication stage and the solution/soil ratio all influenced the mobilization of B(a)P, Cry and trace elements appreciably. The optimized conditions for the soil washing process were chosen as follows: 0.1 M EDDS in 6% (v/v) Brij98 adjusted to pH 9.0, 30 min of ultrasonication using a solution/soil ratio of 6.6. EDDS was more efficient than EDTA at extracting B(a)P, but Cry recoveries were similar. Alkaline pH increased Fe and Al extraction from the organic fraction and caused more organic matter dissolution, which enhanced B(a)P and Cry mass transfer from soil organic fraction into aqueous mobilizing solution. Not only was the higher pH beneficial to B(a)P solubilization, it also increased both As recovery and the selectivity of trace element complexation/mobilization relative to macro-elements [43].

Modeling of the extraction process for PAH compounds that were mobilized indicated that the number of washes needed to decrease the initial concentration of B(a)P by half were significantly fewer for EDDS–Brij than for either EDTA–Brij98 or Brij98 alone. In contrast to B(a)P mobilization, the optimized procedure did not show any perceptible influence on Cry removal when compared with EDTA or Brij98. The modeled decay curves for Cry were similar for the three mobilizing solutions. EDDS solution extracted slightly more Cry than solutions containing EDTA or Brij98 alone, but the differences were not statistically significant.

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