



Research article

Laboratory and pilot scale soil washing of PAH and arsenic from a wood preservation site: Changes in concentration and toxicity

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ABSTRACT

Soil washing of a soil with a mixture of both polycyclic aromatic hydrocarbons (PAH) and As was evaluated in laboratory and pilot scale, utilizing both single and mixtures of different additives. The highest level of decontamination was achieved with a combination of 0.213 M of the chelating agent MGDA and $3.2 \times \text{CMC}^*$ of a non-ionic, alkyl glucoside surfactant at pH 12 ($\text{Ca}(\text{OH})_2$). This combination managed to reach Swedish threshold values within 10 min of treatment when performed at elevated temperature (50°C), with initial contaminant concentrations of $\text{As} = 105 \pm 4 \text{ mg/kg}$ and US-EPA $\text{PAH}_{16} = 46.0 \pm 2.3 \text{ mg/kg}$. The main mechanisms behind the removal were the pH effect for As and a combination of SOM ionization as a result of high pH and micellar solubilization for PAHs. Implementation of the laboratory results utilizing a pilot scale equipment did not improve the performance, which may be due to the shorter contact time between the washing solution and the particles, or changes in physical characteristics of the leaching solution due to the elevated pressure utilized. The ecotoxicological evaluation, Microtox[®], demonstrated that all soil washing treatments increased the toxicity of soil leachates, possibly due to increased availability of contaminants and toxicity of soil washing solutions to the test organism.

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1. Introduction

Soil contamination is an increasing problem worldwide and in cases where a mixture of different contaminants is present, more advanced remediation methods are likely needed, resulting in higher remediation costs. *In situ* remediation methods, where the soil is left in place for treatment, may be advantageous since the handling costs (excavation and transportation) are kept down, however, long treatment times may render the site unusable during the treatment period and for example delay the redevelopment of brownfield sites. Thus, excavation of the soil is at times preferred, which both renders redevelopment possible and where other treatment possibilities are accessible. Soil washing is a commonly utilized soil remediation technology which is performed on excavated soil, preferably with a moderate clay content [1]. It has very large potential since it can be adapted to fit different masses and different contaminant content by changing the composition

of the soil washing fluid. Much research has therefore been carried out to find additives that release certain target compounds. If a mixture of different contaminants is present, multiple washing cycles or mixtures of washing solutions [2–4] may be required to fulfill treatment goals. Soil originating from old wood preservation industries is often contaminated by a mixture of polycyclic aromatic hydrocarbons (PAH) and heavy metals, from the simultaneous utilization of creosote and CCA salts (copper, chromium, arsenic), respectively. In addition, utilization of real, industrial soil introduces the effect of ageing, which renders historical pollutants less available [5,6].

Remediation of PAH from soil has been extensively evaluated in the scientific literature. Soil washing of PAH has been evaluated using additives, including humic acids [7], vegetable oils [8] and chelating agents [9,10]. Among the most well-studied additives are different surface active agents, surfactants [11–14]. Surfactants act by decreasing the surface tension in combination with a creation of micelles. These micelles have a hydrophobic interior and a hydrophilic exterior which enhance mobilization of hydrophobic compounds into the solution, and they start to form at a certain concentration called the critical micelle concentration (CMC). For

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efficient PAH removal, especially of high molecular weight PAH, earlier experiments have shown that high concentrations of surfactants are needed [15,16]. This is mainly due to the adsorption of surfactants onto the soil particles. Therefore, the efficient CMC (CMC*) is often utilized in soil remediation contexts, which is the concentration when micelles are formed in the presence of soil (and the soil particle adsorption is accounted for).

The removal of arsenic from soil is difficult, and much research has therefore focused on stabilization and solidification instead of leaching [17,18]. Efforts made to mobilize arsenic often include leaching of iron–arsenic complexes, utilizing for example oxalic acid [19], but also chelating agents, such as citric acid [20] have been used. Concerning cationic heavy metals, more complex biodegradable chelating agents are also interesting in soil washing applications due to their capacity to complex heavy metals. [S,S]-ethylene diamine disuccinate (EDDS) and methylglycine diacetic acid (MGDA) are two biodegradable chelating agents which have been given some attention for their positive effect on mobilization of cationic heavy metals from contaminated soils [21].

Simultaneous removal of PAH and heavy metals has been evaluated using mixtures of different additives. Maturi and Reddy [2] and Khodadous et al. [4] utilized a sequential flushing procedure where they combined non-ionic surfactants (Tween 80 or Igepal CA-720) with complexing agents (e.g. citric acid, EDTA or DTPA). The surfactants were mainly efficient for PAH whereas the complexing agents were able to mobilize heavy metals. In addition, the authors observed that utilization of the sequential leaching procedure could facilitate the mobilization of contaminants by extractants that were not as efficient in single compound systems. More complex processes were thought to occur when different chemical extractants are utilized in combination, since remains of the pre-treatment extractant are present in the soil at the second leaching step.

In Swedish risk assessment, the future land use at the investigated site is a key factor and there exist different threshold values based on different land use scenarios. KM (*känslig markanvändning*; sensitive land use) is applied in residential areas and MKM (*mindre känslig markanvändning*; less sensitive land use) is applied in industrial areas [22]. For PAH, the threshold values also depend on the molecular weight. MKM values for PAH are: Light weight PAH (PAH-L; naphthalene, acenaphthene and acenaphthylene) 15 mg/kg, medium weight PAH (PAH-M; flourene, phenanthrene, anthracene, flouranthene and pyrene) 20 mg/kg and high weight PAH (PAH-H; benzo[a]anthracene, chrysene, benzo[b]flouranthene, benzo[k]flouranthene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene) 10 mg/kg. Accordingly, PAH-H includes all carcinogenic PAHs (US-EPA) plus benzo[g,h,i]perylene. MKM value for arsenic is 25 mg/kg. These MKM values are also applied as remediation goals in this study.

In general, risk assessment only includes measurement of total concentration of target compounds. Therefore, utilization of an ecotoxicological evaluation may provide the risk assessment and treatment selection with valuable data on the effect of degradation products and changes in bioavailability which may arise during the remedial action. One such ecotoxicological test is Microtox®, where the effect of soil water leachates on the test organism, the marine bacterium *Vibrio fischeri* is studied in acute toxicity tests. *V. fischeri* has been used to assess the toxicity of PAH and arsenic, both as single compounds [23–25], in soil [26,27] and following a soil remediation process [28–30].

The aim of this study was to evaluate the utilization of different additives for the simultaneous soil washing of a mixed contaminated soil, containing PAH and As, a combination of contaminants which, though commonly detected at contaminated sites, has rarely been in the literature. Additives suitable for PAH (surfactants) and As (oxalic acid and complexing agents) were evaluated alone or in

Table 1

Selected chemical and physical properties of the Elnaryd soil.

pH	6.6
Water content (%)	5
TOC (%)	1.1
Particle size distribution (%)	
1 mm	17
500 µm	36
250 µm	28
125 µm	7
63 µm	3
<63 µm	9
Metals (mg/kg d.w. ±SE)	
As	105 ± 4
Zn	96 ± 10
Cr	14 ± 0.4
PAH (mg/kg d.w. ±SE)	
PAH-L	0.4 ± 0.1
PAH-M	19 ± 1.2
PAH-H	27 ± 0.7

combination and at different pH values. To investigate the implementation in large scale, a pilot scale soil washing equipment was utilized. Treatment success was thereafter assessed using both chemical and ecotoxicological analysis.

2. Materials and methods

2.1. Soils

Soil was collected at an old wood preservation site in Elnaryd, south east Sweden. The site had been used for preservation of railway ties between 1945 and 1968. Soil samples were taken from ~4 m depth, and main contaminants were PAH and arsenic. The soil was sieved through a 2 mm mesh and thoroughly homogenized prior to the experimental startup. Selected chemical and physical characteristics of the soil are presented in Table 1.

2.2. Experimental setup

2.2.1. Laboratory scale

The laboratory scale experiments were divided into two phases, where the first phase included a kinetic study of eight single compound solutions and the second phase involved mixtures of the best solutions from the first phase. In all experiments, 300 g of soil was put in 1 l Teflon®-lined plastic containers and 300 ml of solution (L:S 1:1) was added. Soils were extracted on a reciprocating shaker in the dark (to avoid photodegradation) and after predetermined times (10, 20, 30 and 60 min, 24 h and 10 days in the first phase and 10 min in the second phase), approximately 5 g of soil and 5 ml of solution was withdrawn. The samples were centrifuged at 4000 rpm for 5 min and the supernatant was decanted. The supernatant was transferred to a new tube, diluted 10 times and preserved by addition of 100 µl HNO₃ (65%; Scharlau, Barcelona, Spain) before analysis for mobilized arsenic in the solution. The soil was dried in a 40 °C oven until completely dry and thereafter put in the freezer before analysis of remaining PAH in the soil. All samples were run in triplicates.

The soil washing solutions were chosen for their anticipated extraction efficiency for either PAH or As. For PAH, one non-ionic surfactant with the active agent alkyl polyglucoside-C6 (AG 6202, Akzo Nobel, Stenungsund, Sweden; hereafter denoted "AG") and one chelating surfactant with the active agent sodium cocoamphopolycarboxy glycinate (Ampholak 7CX/C, Akzo Nobel, Stenungsund, Sweden; hereafter denoted "Amph"), were tested. The concentration was set to 3.2 × CMC* after determination of CMC and CMC* by stalagmometer measurements. For As, oxalic

acid buffer (0.47 M pH 3.4) prepared from oxalic acid (Alfa Aesar GmbH & Co KG, Germany) and di-sodium oxalate (Scharlau Chimie, Barcelona, Spain) was evaluated. Chelating agents [S,S]-EDDS (Enviomet™ C140, Innospec Ltd., Cheshire, UK) and MGDA (TrilonM powder, BASF, Germany) were also used for As-removal. Both chelating agents were evaluated at a concentration of 0.213 M, corresponding to a concentration of 5 times the concentration of heavy metals, As and Fe in the soil [20], and adjusted to neutral pH. In addition the effect of pH was evaluated using either NaOH (Merck, Darmstadt, Germany), adjusted daily to pH 12 or HNO₃ (Scharlau Chimie, Barcelona, Spain) adjusted daily to pH 3. Tap water without pH adjustment was used as control.

After evaluation of the best leaching solutions from phase one, different mixtures of additives were evaluated in the second phase. The same concentrations as in the first phase were utilized, with the exception of oxalic acid, where the concentration had to be decreased to 0.025 M due to the low solubility in the mixed solutions. In addition, Ca(OH)₂ replaced NaOH during the second phase due to problems to maintain constant pH. Therefore, 1%_{w/w} of Ca(OH)₂ (powder; Riedel-de Haën, Seelze, Germany) was mixed into the soil before the addition of soil washing fluid. A pH of 12–12.5 would be expected in the presence of Ca(OH)₂ as buffering agent. The effect of temperature on the leaching was evaluated utilizing solutions that had been heated up in a water bath to 50 °C. During the second phase, only one sample was withdrawn from the containers, after 10 min, since the contact time was considered relevant in relation to an industrial soil washing application.

2.2.2. Pilot scale

To further evaluate the soil washing efficiency, a pilot scale soil washing equipment (water treatment construction, WTC) constructed and patented by Solventic AB (www.solventic.com) was utilized (Fig. 1). Approximately 5 kg of soil was put in the soil chamber from the top and kept in place by a coarse-meshed stainless steel net. The WTC device is aimed for continuous feeding of soil, but was used in a “batch” mode in this study. The soil washing solution was thereafter introduced from below utilizing a high pressure pump (2.5 MPa). Nine dies dispersed the soil washing solution into droplets and distributed the solution evenly on the soil surface, which created a fluidized bed in the soil-net interface. The soil particles then passed through the net while in contact with the upward flowing soil washing fluids, and were collected in a plastic tub below. When all the soil had fallen down, three samples were immediately taken from the collection tub.

2.3. Analysis of PAH

To 2 g of dried soil, 100 μl of a 10 μg/ml internal standard solution (PAH-mix 31; naphthalene-d₈, acenaphthylene-d₁₀, phenanthrene-d₁₀, crysene-d₁₂ and perylene-d₁₂), prepared from a stock solution of 1000 μg/ml (Dr. Ehrenstorfer GmbH, Augsburg, Germany) was added. The soil was extracted with 10 ml of dichloromethane (DCM; Merck, Darmstadt, Germany) and acetone (Fischer Scientific, Leicestershire, UK) at a ratio of 1:1, for 24 h on a shaker. After centrifugation (4000 rpm for 5 min) the liquid phase was transferred to amber glass vials and evaporated under a gentle stream of nitrogen and the solvent was changed to *n*-hexane (Fisher Scientific, Leicestershire, UK). Cleaning of soil extracts was performed using disposable glass pasteur pipettes. A piece of glass wool was put in a glass pipette and 6 cm (~0.7 g) 10% deactivated silica (70–230 mesh for column chromatography, Scharlau chimie, Sentmenat, Spain) was put on top. The silica was dried in a 550 °C oven for 3 h and 10%_{v/v} of distilled water (Milli-Q-grade, Millipore) was added after cooling in a desiccator. On top of the silica, 1 cm of dried Na₂SO₄ (150 °C for 24 h; Fisher Scientific, Leicestershire, UK) was added. The soil extracts were put on the column

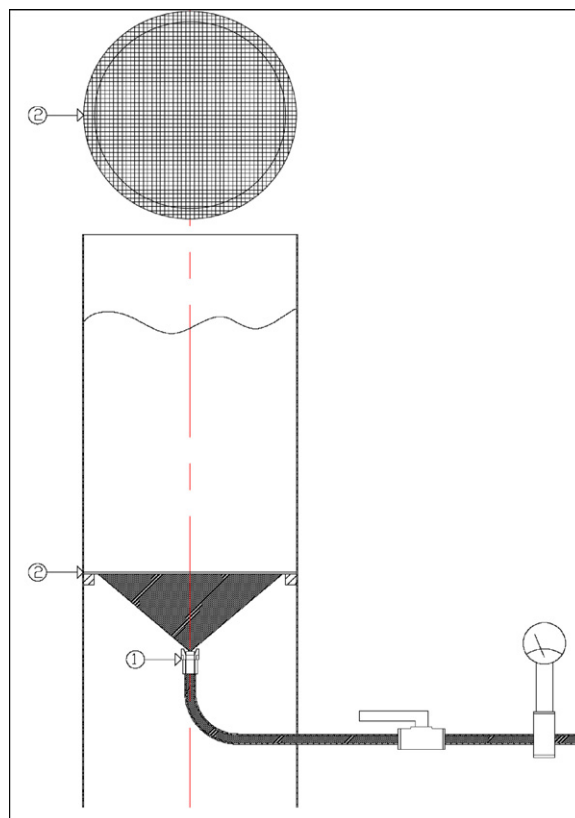


Fig. 1. Principal drawing of the pilot scale equipment (WTC). The soil washing solution (dark color) is evenly distributed using a set of dies (1) into the soil which is placed on the net (2). The soil then falls through the net and is collected in a tub below.

(pre-eluted with 3 ml *n*-hexane) and eluted by 3 ml *n*-hexane and 3 ml *n*-hexane:DCM (3:1_{v/v}). Extracts were again evaporated and the solvent was changed to toluene before transferring to amber GC/MS vials and spiked with 100 μl of a 10 μg/ml recovery standard (flouranthene-d₁₀), prepared from 100 μg/ml stock solution (Dr. Ehrenstorfer GmbH, Augsburg, Germany). Samples were analyzed on a GC/MS (PerkinElmer GC 500 MS) equipped with a J&W Scientific DB-5MS column (30 m × 0.25 mm; 25 μm; Agilent technologies). 1 μl of the samples were injected (290 °C) in splitless mode and helium (1 ml/min) was used as carrier gas. The starting temperature in the oven (75 °C) was held for 1 min, increased by 25 °C/min to 250 °C and by 3 °C/min to 310 °C, held for 7 min. A calibration standard consisting of 16 US-EPA priority PAHs (100 μg/ml in toluene, LGC Promochem GmbH, Wesel, Germany) and IS and RS was utilized for peak identification and quantification. Quantification was performed using the software MassLynx V4.0.

2.4. Analysis of arsenic and heavy metals

Distribution of heavy metals in the soil was evaluated in agreement with Elgh-Dalgren et al. [31], using a sequential extraction procedure, modified from Tessier et al. [32]. Extracts, adjusted to pH < 2 using HNO₃, were analyzed by ICP-OES (Plasma 4000 DV, PerkinElmer). The sum of all fractions is referred to as the total acid leachable metal.

2.5. Ecotoxicological characterization

The ecotoxicological evaluation was performed on selected samples using a Microtox®, in accordance with the international standard ISO 11348-3. To produce the soil leachates, the ISO/TS

method 21268-1, utilizing a 0.001 M CaCl₂ solution at a L/S ratio of 2, was followed. After 24 h of extraction, the samples were centrifuged for 8 min at 4000 rpm. The bioluminescent test organism, *V. fischeri* was thereafter exposed to the CaCl₂ extracts during 30 min. Thirty minutes IC₅₀ values (the concentration where 50% light inhibition of the sample was detected) were calculated using the software MicrotoxOmni™ (Azur Environmental, USA). To verify the results, three control substances (potassium dichromate, 2,4-dichlorophenol and zinc sulphate heptahydrate) with known responses were run in parallel.

2.6. Statistical analysis

The statistical analysis was performed using software Minitab® 15.1.1.0. Final concentrations of PAH and As were compared between different treatments and calculated IC₅₀ values were statistically evaluated. Means of three replicates were compared. Two-way analysis of variance (ANOVA; 5% significance) was executed in the kinetic study (treatment; time) and one-way ANOVA (Tukey's test, 5% significance) was utilized for phase two and the ecotoxicological evaluation. All results are presented as mean ± SE.

3. Results and discussion

In the untreated soil, the total acid leachable As-concentration was above the Swedish MKM values and the sequential extraction revealed that As was mainly associated with the Fe- and Mn-(hydr)oxides and in the residual, tightly bound soil fraction (Fig. 2). For PAH, the only fraction exceeding MKM was the PAH-H. Initial PAH-M concentrations were just below MKM, whereas PAH-L concentrations were very low (Table 1). The fraction of PAH-L may decrease over time, due to the higher volatility, water solubility and biodegradation rate of these compounds compared to medium and high molecular weight PAH, wherefore accumulation of heavy and medium molecular weight PAH in aged soil is common. Henceforth, only results for PAH-M and PAH-H are presented and discussed.

3.1. Phase one

The most efficient leaching solution for As was the 0.47 M oxalic acid buffer, which mobilized 61 mg/kg already after 10 min of extraction (Table 2), significantly better than all other treatments. The maximum removal capacity was achieved after 24 h, when 84 mg/kg was mobilized. The efficiency of oxalic acid for As-

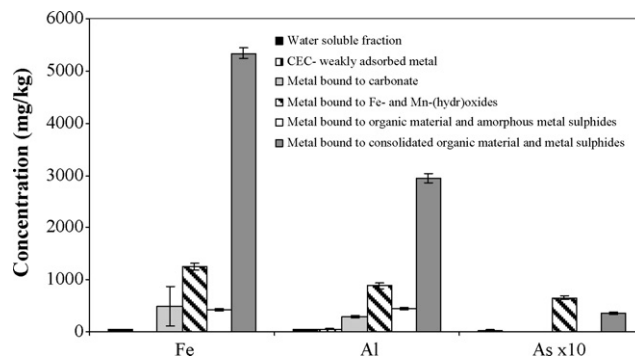


Fig. 2. Distribution of Fe, Al and As in different soil fractions after sequential extraction based on Tessier et al. [30]. Error bars represent SE ($n = 3$). Concentrations for As are multiplied by 10.

removal has also been pointed out in earlier research [19]. NaOH (pH 12) also showed high removal capacity, removing 37 mg/kg after 10 min, while HNO₃ (pH 3) was the least efficient. This is in line with earlier studies, which have demonstrated that either very high (>pH 11) or very low (<pH 2) pH were required for efficient arsenic leaching [20,33].

For PAH, the differences between different treatments were not as pronounced as for As (Table 2). The overall best performing treatments were EDDS, MGDA, AG and NaOH, although the best treatment for each fraction at different times varied. For AG, EDDS and MGDA, the treatment goal of 10 mg PAH-H/kg was met after 24 h treatment, but even the less efficient treatments showed decreasing PAH concentration, which lead to almost all treatments managing to reach treatments goal after 10 days. This could probably be explained by the physical scrubbing and mobilization of soil fines.

3.2. Phase two

In the second phase, the best performing treatments from the first run were combined and mixtures of different agents were evaluated. pH 12 showed good removal capacity for both PAH and As and was therefore applied as standard pH. At first, NaOH was utilized to adjust the solution pH, in agreement to the phase one tests, but the soil buffering capacity was found to be too high (pH was not even sustained for 10 min; Fig. 3). Consequently, the pH-adjusting agent was changed to Ca(OH)₂. The design of the pH

Table 2
Remaining concentrations of As, PAH-M and PAH-H after the first phase (mg/kg).

		AG	Amph	0.47M Ox	EDDS	MGDA	NaOH	HNO ₃	H ₂ O
As	10 min	99 ± 0.2	102 ± 0.2	44 ± 0.2	102 ± 0.0	103 ± 0.1	68 ± 0.6	104 ± 0.0	103 ± 0.0
	20 min	98 ± 0.4	101 ± 0.1	35 ± 1.5	102 ± 0.0	102 ± 0.1	69 ± 0.7	104 ± 0.0	103 ± 0.1
	30 min	95 ± 0.4	101 ± 0.6	31 ± 0.9	101 ± 0.1	102 ± 0.1	68 ± 0.5	104 ± 0.0	102 ± 0.0
	60 min	93 ± 0.2	99 ± 0.6	27 ± 1.7	100 ± 0.1	101 ± 0.1	68 ± 0.4	104 ± 0.0	102 ± 0.1
	24 h	80 ± 0.6	98 ± 2.8	15 ± 0.6	92 ± 0.8	76 ± 0.7	66 ± 0.8	104 ± 0.1	91 ± 1.0
	10 days	62 ± 0.9	79 ± 0.5	37 ± 2.0	83 ± 0.6	69 ± 1.4	66 ± 0.6	104 ± 0.1	81 ± 1.1
PAH-M	10 min	18 ± 5.2	14 ± 0.9	21 ± 8.2	14 ± 0.0	16 ± 2.6	11 ± 1.8	19 ± 2.6	15 ± 2.6
	20 min	13 ± 1.1	15 ± 2.4	21 ± 9.4	13 ± 2.3	11 ± 0.5	13 ± 4.9	18 ± 3.6	12 ± 0.3
	30 min	11 ± 1.0	16 ± 0.7	17 ± 1.6	12 ± 0.5	13 ± 1.1	8 ± 0.7	20 ± 1.8	20 ± 5.0
	60 min	12 ± 0.9	21 ± 6.6	15 ± 1.0	12 ± 0.8	15 ± 1.7	14 ± 1.7	17 ± 2.4	15 ± 2.1
	24 h	8.2 ± 1.2	12 ± 0.7	14 ± 0.8	12 ± 1.2	9.2 ± 0.7	11 ± 1.2	14 ± 1.6	13 ± 1.2
	10 days	6.9 ± 0.6	10 ± 1.1	10 ± 0.6	6.1 ± 0.3	6.4 ± 0.1	6.0 ± 0.6	7.3 ± 0.6	9.3 ± 2.1
PAH-H	10 min	20 ± 3.3	17 ± 1.5	16 ± 1.8	13 ± 0.1	15 ± 0.7	12 ± 1.2	21 ± 2.4	17 ± 1.5
	20 min	16 ± 1.0	18 ± 0.5	16 ± 3.5	12 ± 1.1	12 ± 0.9	11 ± 2.0	21 ± 4.1	14 ± 1.4
	30 min	15 ± 2.2	19 ± 0.3	17 ± 1.6	12 ± 1.4	14 ± 1.5	8.8 ± 0.5	19 ± 1.0	18 ± 2.4
	60 min	16 ± 1.7	24 ± 5.5	17 ± 1.3	12 ± 0.1	17 ± 1.2	12 ± 1.6	21 ± 3.3	17 ± 0.5
	24 h	10 ± 1.7	14 ± 0.5	13 ± 0.7	10 ± 0.8	9.5 ± 0.6	13 ± 0.7	16 ± 1.8	12 ± 1.1
	10 days	6.9 ± 0.5	10 ± 1.1	8.9 ± 0.6	5.0 ± 0.4	5.6 ± 0.2	6.4 ± 0.4	12 ± 2.4	11 ± 1.7

Values represent mean ± SE ($n = 3$).

adjustment was also shifted and 1% $\text{Ca}(\text{OH})_2$ was mixed into the soil before addition of the leaching solution in order to create a pH-sustaining alkaline buffer. In combination with the elevated pH, oxalic acid (for As) and AG and MGDA (for PAH) were selected.

3.2.1. Arsenic removal

Fig. 3a shows remaining As in the soil after the laboratory and pilot scale treatments with different soil washing solutions. The most efficient treatments for As-removal all included MGDA and AG at alkaline pH (either NaOH or $\text{Ca}(\text{OH})_2$). To establish which factors influenced the mobilization of arsenic, the distribution coefficient between soil and water (K_d) was calculated and plotted against pH (Fig. 4). The value for WTC- $\text{Ca}(\text{OH})_2$ was excluded since no arsenic was detected in the solution and no K_d value could be calculated. In this plot, a clear pH dependence of the arsenic removal can be seen, with arsenic being more present in the water phase at elevated pH (low $\log K_d$). The original pH in this soil was 6.6 (Table 1). Earlier studies have demonstrated that arsenic is strongly bound to the soil at around neutral pH and that either very high (>12) or very low (<2) pH is necessary to mobilize arsenic [20]. Treatments strongly correlated to the pH effect (black markers) were utilized in the linear regression, whereas treatments that demonstrated effects non-correlated to pH were excluded (gray markers). Exclusion of selected treatments implied an increase of the coefficient of determination (R^2) from 0.05 to 0.82.

Treatments to the right of the line (lower mobilization than the pH effect) included treatments with $\text{Ca}(\text{OH})_2$ but without MGDA ($\text{Ca}(\text{OH})_2$, Temp- $\text{Ca}(\text{OH})_2$, AG- $\text{Ca}(\text{OH})_2$) and treatments utilizing the WTC equipment. The first phenomenon could be explained by the complexation of arsenic with calcium, which has previously been demonstrated [34,35]. Utilization of $\text{Ca}(\text{OH})_2$ drastically decreased mobilization of As compared to NaOH (Table 2 and Fig. 3a), which is due to the precipitation of Ca-As-complexes. In treatments with combinations of AG, MGDA and $\text{Ca}(\text{OH})_2$, the negative effect of the $\text{Ca}(\text{OH})_2$ decreases, probably due to complexation of Ca^{2+} ions by MGDA, thereby preventing the precipitation of Ca-As-complexes. The low mobilization of arsenic with the WTC process may be due to the shorter contact time (0 min vs. 10 min in the other treatments), and will be discussed in more detail in Section 3.3.

Only two treatments showed a higher removal of arsenic when compared to the pH effect alone: oxalic acid buffer (pH 3.4) from phase one and the combination of AG-MGDA- $\text{Ca}(\text{OH})_2$ at elevated temperature. The effect of oxalic acid buffer on the removal of arsenic has already been discussed above (Section 3.1). The other treatment exceeding the pH effect demonstrates the importance of temperature on the As-mobilization, since all other combinations utilizing AG, MGDA or both could be explained by the pH effect alone. This is in agreement with assumptions regarding MGDA and AG efficiency for As-removal, where neither the carboxylic acids of the MGDA, nor the non-ionic surfactant head group ought to lead to any significant As-mobilization. Therefore the main conclusion is that the temperature increase leads to faster kinetics of Fe mobilization and thereby adds to the positive effect of the elevated pH.

3.2.2. PAH removal

No single treatment was superior in comparison to the other for PAH removal. For both PAH-M and PAH-H, elevated pH in combination with AG and MGDA had the largest removal efficiency (Fig. 3b and c). All combinations, including NaOH, $\text{Ca}(\text{OH})_2$ and elevated temperature, managed to reach Swedish threshold values of 10 mg PAH-H/kg soil after 10 min treatment. Several different factors may underlie the results observed, even though the exact processes can be difficult to describe.

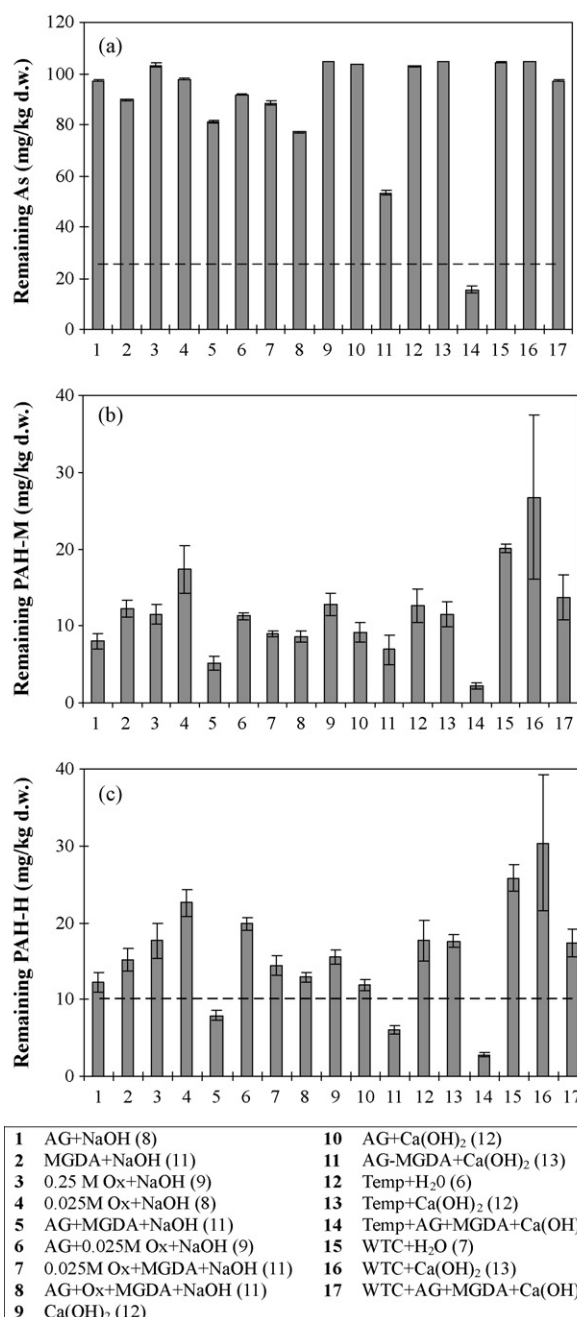


Fig. 3. Remaining concentration of As (a) PAH-M, (b) and PAH-H (c) after the second phase and WTC (mg/kg d.w.). Sampling time was 10 min for laboratory scale and 0 min for WTC. Initial concentrations were As = 105 ± 4 , PAH-M 19 ± 1.2 and PAH-H 27 ± 0.7 mg/kg d.w. The dashed lines represent the MKM values (for As = 25 mg/kg and PAH-H = 10 mg/kg). Error bars represent SE ($n=3$). Legend is the same for all panels and the numbers into parentheses are pH values at samples withdrawal. Please note the different scales.

SOM is ionized and subsequently dissociated in alkaline solutions [36]. PAH, which are often associated with SOM, are also released into solution at high pH. The addition of certain amendment has also been reported to mobilize SOM, and may explain the differences observed between the treatments with pH adjustment only (NaOH or $\text{Ca}(\text{OH})_2$) and the treatments with pH adjustment, AG and MGDA. Yang et al. [9] and Subramaniam et al. [10] have both demonstrated that PAH mobilization can be achieved through addition of complexing agents (e.g. sodium citrate, EDTA and sodium oxalate), possibly through the disruption of humic-metal-mineral linkages in the soil, through complex-

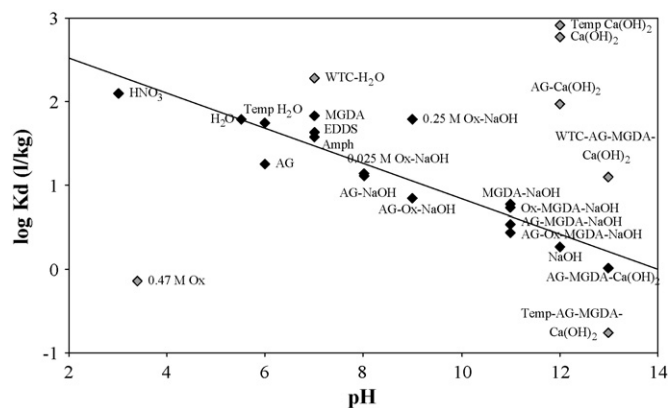


Fig. 4. Log K_d values as a function of pH. Values are 10 min treatments from both the first and second phase laboratory experiments and WTC runs. The line is the linear regression of treatments with black markers ($R^2 = 0.82$), whereas the gray markers are left out of the regression.

ation of the metals [10]. In the present study, the treatments managing to mobilize the most of the soil constituents Fe and Al (data not shown) all include either MGDA or oxalate, which could indicate disruption of humic-metal–mineral linkages, and be an indirect sign of SOM release. However, a similar correlation between pH and log K_d values as for As is also observed for Fe and Al, thus the complexing capacity of the MGDA and oxalate is probably smaller than the pH effect. Therefore, if MGDA is not responsible for the PAH removal observed, the clear difference in PAH removal between treatment with MGDA and AG and those without must be attributed to the AG present. Non-ionic surfactants have earlier been shown to efficiently mobilize PAH [14,37]. The main mechanism of action is through reduction of the oil–water interfacial tension in combination with the formation of micelles [38]. Hydrophobic contaminants are captured into the hydrophobic inner of the micelles and dissolved. In the present study, utilization of elevated temperature further enhanced the PAH mobilization, even though the results were not statistically different from the treatments at room temperature. Enhancement of surfactant facilitated mobilization of hydrophobic contaminants with elevated temperature is well known, and the main function is the expansion of the micelles and the subsequent enlargement of the micelle core, managing to mobilize more hydrophobic contaminants [11,39]. A common soil washing procedure, with basic soil particle size separation, costs around €40/ton [40] and by applying different additives and/or high temperature, the treatments costs are likely to increase. It is thus important to also include the environmental gain of removing the contaminants from the soil and create a soil which could be recycled. Soil washing has the advantage of producing well-defined soil fractions (down to particle sizes $>63 \mu\text{m}$), which could have an economic value and thus likely find its application as construction material following a proper risk assessment. In addition, it is desirable to find ways to reuse the washing solutions, which would further improve the economy of the soil washing treatment.

3.3. Pilot scale

Efforts to implement the results from the laboratory scale to pilot scale were made utilizing the WTC equipment. The WTC process did not improve either As or PAH removal compared to laboratory scale leachings (Fig. 3). The mixture with AG, MGDA and $\text{Ca}(\text{OH})_2$ in the WTC equipment, was equally efficient as utilization of H_2O in laboratory scale for both PAH and As. One reason for this might be the shorter contact time observed during the WTC process compared to the laboratory scale soil washings. In

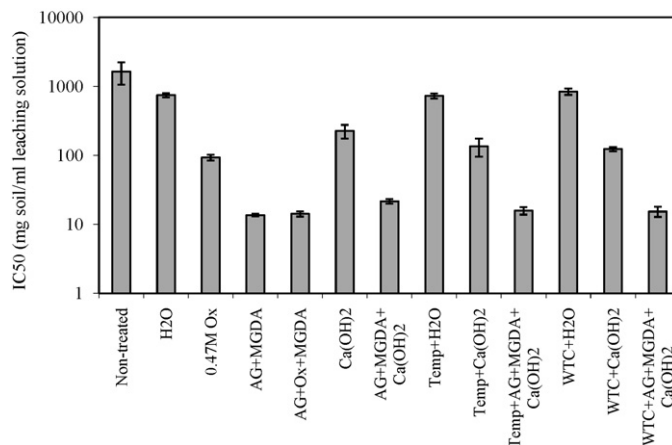


Fig. 5. IC_{50} values (the concentration where 50% reduction in luminescence is observed) before and after selected treatments (mg soil/ml CaCl_2 -solution). Error bars indicate SE ($n = 3$). Please note the logarithmic scale.

the WTC process, samples were withdrawn directly after that soil had fallen down into the collection jar, which could be compared to less than a minute of extraction in the lab. Even though the soil is attacked multiple times during the downward movement in the WTC equipment, the longer contact between liquid and solids in the batch tests most likely lead to enhanced contaminant mobilization [41,42]. Possibly, a different result could have been achieved if the sample withdrawal had been performed after longer time, to allow kinetically slow processes to take place.

In addition, the pilot scale experiments were performed in a non-heated room, where the ambient temperature was $\sim 10^\circ\text{C}$, and this may have contributed to the slowness of the chemical reactions. The lower effect of the WTC treatment could also be explained by changes in the physical characteristics of surfactants as a consequence of the elevated pressure utilized for the introduction of the soil washing solution into the soil. In a surfactant solution exposed to elevated pressure, the CMC increases up to pressures around 150 MPa [43,44]. A higher CMC demands a higher concentration of surfactant before micelles start to form, resulting in a lower solubilization of hydrophobic contaminants. In addition, the radius of the micelles decrease if exposed to elevated pressure, especially at low temperature [45]. These physical changes can however only explain the lower efficiency of the WTC to some degree, since also both the water and $\text{Ca}(\text{OH})_2$ treatments showed much lower removal capacity in the WTC compared to the laboratory scale. Therefore, more research is needed for utilizing the WTC process, to elucidate which processes that are the most important for soil washing performance, such as treatment time, temperature, washing solution composition and their interactive effects.

3.4. Ecotoxicological evaluation

The ecotoxicological evaluation was performed on soil leachates on selected samples (Fig. 5). The IC_{50} values were not in agreement with the results obtained by the chemical analysis and most noticeable was that the least toxic of the samples was the non-treated soil. The samples showing the highest toxicological effect to *Vibrio fischeri* were the samples with combinations of elevated pH, MGDA and AG, the samples with the lowest remaining concentrations of both As and PAH. In samples where the only additive was water, only a slight decrease in toxicological response was observed.

PAH are very strongly sorbed to the soil and the water solubility is limited [26,46]. In addition, earlier research has shown that the toxicity of As to *V. fischeri* is low [23], and at concentrations much higher than what was released during the first step of the sequen-

tial extraction (water soluble fraction; Fig. 2) are needed. These two factors in combination are the most probable reasons for the low toxicity observed in the non-treated soil. Even though the total concentration of contaminants is high, they are not mobilized by the CaCl_2 -leaching procedure and consequently the microorganisms in the bioassay are not exposed.

The reason for the higher soil toxicity in the treated soil can be due to contaminants becoming more bioavailable during the treatment procedure, a phenomenon which has been observed earlier [29,47]. Toxicity of the additives utilized may also contribute to the observed increase in toxicity. Therefore, solutions containing AG, MGDA and $\text{Ca}(\text{OH})_2$ only, were run in the Microtox[®]. The toxic response observed was in the same range as when the soil leachates were evaluated (data not shown), which indicates that the additives utilized for the soil washing procedure were themselves toxic. *V. fischeri* is pH-sensitive, and according to the standard protocol, the pH in the samples should be adjusted to around neutral (pH 6–8) before exposure. This was however not done, based on the goal to study the overall effect of the soil washing procedure, including contaminant and additives remains. The effect of pH could cause the higher toxicity noted in treatments utilizing $\text{Ca}(\text{OH})_2$ and oxalic acid (pH 3.4), but the results suggest that treatments with elevated pH and MGDA and AG cause a higher toxicity than the pH effect alone. No earlier studies on the toxicity of MGDA have been found. However the toxicity of other chelating agents, such as EDTA [48], DTPA [49] and NTA [50] after 15 min exposure to *V. fischeri* has been reported. The concentrations utilized in these previous studies were much lower than the concentration in the present study, wherefore a toxic response to the MGDA is possible. In addition, complexes between both DTPA and NTA showed increased toxicity to *V. fischeri* when complexed with different heavy metals [49,50]. On the contrary, EDTA toxicity was shown to decrease in water with high hardness [48]. In the present study, both compounds that have been shown to increase (As) and decrease (Ca) the toxicity of chelating agents were present. In addition to complexing agents, Mazidji et al. [48] demonstrated that non-ionic surfactant sodium dodecyl sulphate (SDS) showed a toxic response in the Microtox[®] test. The surfactant concentration studied was much lower than in the present study. Sherrard et al. [51] speculated that the toxicity observed for non-ionic surfactants is due to a minimum surface tension requirement of the microorganisms. The surfactant concentration in the soil leachates is probably higher than CMC, wherefore the surface tension is very low, which may lead to irreversible cell damage.

4. Conclusions

The combination of elevated pH, chelating agent MGDA and biodegradable, non-ionic surfactant AG showed very good removal capacity for both As and PAH after only 10 min of washing at elevated temperature (50 °C). The main mechanism behind the As-removal was thought to be the pH effect, even though the presence of MGDA was necessary when $\text{Ca}(\text{OH})_2$ was utilized as pH-adjusting agent, in order to complex Ca^{2+} ions and prevent As–Ca-complexation and precipitation. For PAH, ionization of SOM at elevated pH and dissolution of PAH into surfactant micelles were considered the main mobilization mechanisms. In addition, both As and PAH removal was positively affected by high temperature. It should however be noted that combinations of chemical extractants could lead to unexpected results as a consequence of different interactive processes, and the most important process could therefore be difficult to establish. Implementation of the laboratory results in a pilot scale soil washing equipment did not improve contaminant mobilization. The main reasons for this was probably the shorter contact time between soil and washing solution and possibly the negative effect of the high pressure on the CMC.

Monitoring of toxicity changes in the remediation experiments indicated that soil contaminants were tightly bound to the soil in the non-treated soil. All treatments therefore lead to increase in soil toxicity in comparison with the non-treated soil, possibly due to increased contaminant availability. Moreover, results indicate that some of the additives, despite being selected on the basis of their biodegradability, may have contributed to the observed increase in soil toxicity. Especially the very high concentrations of MGDA and the very low surface tension as a result of the surfactant addition are thought to be the cause of the observed results.

Future research should include efforts to remove remains of both contaminants and washing solution after the soil washing procedure. This could be achieved through post-rinsing of the treated soil or by “maturing” the soil, whereby soil washing remains and possibly also easily available contaminants are degraded. In addition, further evaluation of the WTC equipment is necessary, possibly as a first step in a soil washing treatment, where the thorough mixing of soil and washing fluid is demanded. With subsequent static leaching of the soil, more kinetically slow contaminants could be mobilized and the overall soil washing efficiency increased.

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