



Dioxin removal from contaminated soils by ethanol washing

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ABSTRACT

The aim of this study was to investigate the potential utility of ethanol washing for remediating soils contaminated with polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), as a cost-efficient alternative to conventional remediation methods of PCDD/F-contaminated soils. Initially, screening experiments were performed with a two-level full factorial design to examine the effects of temperature, extraction time and ethanol concentration on the removal efficiency. The screening experiments showed that the ethanol concentration was the most important parameter. In addition, repeated washing cycles considerably improved the results. Ethanol washing conditions were then selected (10 wash cycles with 75% ethanol at 60 °C), and applied to four soils with different soil characteristics and contamination levels to test the robustness of the selected method. Treatment efficiencies of 81% and 85% were obtained for a lightly contaminated sandy-silty soil and a highly contaminated clay soil rich in graphite particles, respectively. Even higher treatment efficiencies ($\geq 97\%$) were obtained for two other highly contaminated soils, one of which contained high amounts of organic matter. PCDD/Fs were found to both dissolve in the solvent and migrate into it as species adsorbed to particles. The relative contributions of these mechanisms and the overall efficiency of the removal seem to depend on contaminant concentration, the types of carbon in the soil matrix and the particle size distribution. The study shows that ethanol washing has effective remediation potential for a variety of PCDD/F-contaminated soils.

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1. Introduction

Chlorinated aromatic compounds like polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are highly persistent organic pollutants of great environmental concern. In fact, dioxins are amongst the most toxic anthropogenically dispersed pollutants in the environment, although their toxicity is highly dependent on the positions of the chlorine substituents in the PCDD/F molecules. This is reflected in their Toxicity Equivalency Factors (TEFs), which provide indications of their toxicities relative to that of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. The TEFs can be multiplied by the respective congeners' concentrations to obtain Toxic Equivalent Quantity (TEQ) values [1], which are often summed to obtain Total-TEQ values and used by monitoring organisations as indicators of the degree of PCDD/F pollution in soils at investigated sites.

Pentachlorophenol (PCP) agents, which were frequently used as wood preservatives in the past, often contained high concentrations of PCDD/F contaminants. Pentachlorophenol (PCP) was placed on the U.S. Environmental Protection Agency (EPA) list of priority

pollutants in 1979 [2] and its use was banned in several countries in the same year. However, although use of PCP has ceased, many soils remain heavily contaminated with PCDD/Fs because of earlier wood preservation activities. Furthermore, PCDD/Fs in soils may also originate from other contaminating industrial activities, e.g. chlorine bleaching of pulp and paper, the chlor-alkali process and the production of iron and steel. Soils at many sites of such industrial activities have been polluted with PCDD/Fs so heavily that remediation is required.

The Swedish EPA has issued recommended maximum residue levels (MRLs) for PCDD/Fs in soil [3], expressed as TEQs per gram dry weight, which are used to determine whether or not polluted sites need remediation, and to check if remediation activities have been successful. The most effective technique to reduce PCDD/F levels to below the MRLs is high-temperature incineration [4]. However, since this approach is costly, alternative, more cost-efficient, remediation methods are needed.

Historically, soil washing has mostly been performed as an "extraction technique" using water-based solvents for the removal of inorganic contaminants. Soil washing which is a relatively inexpensive method has been documented to work well on soils with coarse material but less well on soils with higher silt, clay and/or organic matter contents [5,6]. The reason for this is that coarse soils are more permeable for the liquid and can bind lower amounts of

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contaminants since they have smaller particle surface areas per unit volume [7,8]. Hence, separating fine soil (clay and silt) from coarse soil (sand and gravel) prior to or during soil-washing treatments can significantly reduce the volume of the most contaminated materials [7–10]. Recently alternative soil-washing processes have been developed and the use of surfactants or other additives has shown to be a feasible method to extract more hydrophobic compounds from soils such as organic contaminants [5]. For instance, Yeom et al. reported the separation of PAHs from soil using surfactants [11] and Cathum et al. investigated the desorption of dioxins and furans in the presence of cyclodextrins [12]. Also desorption of dioxins from soil in the presence of vegetable oils has been reported in several studies [13,14]. Since the water solubility of many organic contaminants is the controlling removal mechanism, the additives are being used to increase the solubility of the organic contaminant in the washing liquid. For that reason, the use of solvents has also been investigated and shown promising results, often using low molecular alcohols. The solvents should be relatively inexpensive, easy to recycle, capable of dissolving the targeted contaminants and have acceptable impacts on human health and the environment. Lee and Hosomi performed a comparison of extraction ability of benzo[a]pyrene from soil between several solvents. Ethanol was then found to be the most suitable washing solvent based on health effects and acceptable removal efficiencies [15].

PCP has been successfully removed by the use of ethanol [16,17]. Khodadoust et al. reported in a PAH removal comparable to Soxhlet extraction using a three-stage cross-current solvent washing, with a mixture of low molecular weight solvents, at ambient temperatures [18]. Ethanol washing has also been investigated for treating PCDD/F-contaminated soil where a 76% dioxin removal was reported at the boiling point of ethanol (78.3 °C) [19]. Since tetra through octa chlorinated dioxins and furans possess relatively low water solubility [20], they may be harder to extract from the soils when using a relatively weak solvent. However, compared to incineration which often is being used for the remediation of PCDD/F-contaminated soils, solvent washing must be considered as a cost-efficient alternative even if it may need to be performed at elevated temperatures.

Therefore, the aim of this study was to assess the potential utility of solvent washing as a remediation technique for dioxin-contaminated soils. The influence of various washing parameters (temperature, ethanol concentration and extraction time), for the removal of PCDD/Fs from soil, was examined using experimental design. Screening experiments allow a systematic investigation of the importance of the washing parameters with maximum information with a limited number of experiments. Thereafter the method was applied to four markedly different soils, from three different sites, to test its robustness and potential.

2. Materials and methods

2.1. Chemicals

All solvents used (acetone, dichloromethane, ethanol, hexane, methanol, tetradecane and toluene) were of analytical or glass distilled grade. Silica gel (60 mesh) and sodium sulphate were purchased from Merck (Darmstadt, Germany) and were activated at 130 °C (24 h) and 550 °C (48 h), respectively. Celite 545 was purchased from Fluka Chemie (Buchs, Switzerland), AX-21 carbon from Anderson Development Company (Michigan, USA), copper granulate from Sigma-Aldrich (St. Louis, USA), potassium hydroxide and sulphuric acid from VWR International AB (Stockholm, Sweden) and hydrochloric acid from Fisher Chemicals AG (Zurich, Switzerland). Glassware was machine-washed with alkaline detergent and rinsed with solvent prior to use. [¹³C₁₂]-

labelled 1,2,3,4-TeCDD and 1,2,3,4,7,8,9-heptaCDF were used as recovery standards (RS) and all [¹³C₁₂]-labelled 2,3,7,8-substituted PCDD/Fs (except 1,2,3,4,7,8,9-heptaCDF) as internal standards (IS), obtained from Cambridge Isotope Laboratories (Andover, MA, USA), in gas chromatography/high-resolution mass spectrometry (GC/HRMS) analyses. A standard solution containing the 17 native 2,3,7,8-substituted PCDD/Fs, obtained from Wellington Laboratories (Ontario, Canada), was used for the quantification of the analytes.

2.2. Experimental setup

In all, four soils from three sites were investigated in this study, as listed in Table 1. The soils differed in their amount of organic matter (measured as loss-on-ignition, LOI), water content, and PCDD/F concentrations (determined by exhaustive Soxhlet extraction with toluene for 15 h followed by GC-MS analysis, as described below). Prior to the clean-up process the extracts were spiked with IS. The volume was reduced to 0.5 ml by rotary evaporation and 40 μl of tetradecane was added prior to the volume reduction to prevent the analytes from evaporation. The extracts were then cleaned-up and analysed as described in Sections 2.3 and 2.4.

2.2.1. Soil-washing experiments

Portions (20 g) of the contaminated soils were added with 60 ml of washing liquid (ethanol and water in pre-determined proportions) to 250 ml glass bottles with Teflon-lined screw caps. The bottles were shaken by hand, to ensure that the resulting slurries were properly mixed, then placed in a shaking water bath during the washing process. After completion of the treatment the particles in the slurry were allowed to settle before the liquid phase was vacuum-filtered through a 0.45 μm hydrophilic membrane filter (Millipore, Billerica, USA), IS was added to the filtrate and the PCDD/Fs were extracted using liquid-liquid extraction with three portions of 15 ml *n*-hexane. In some screening experiments, in which high percentages of ethanol were used, the washing liquid blended completely with the *n*-hexane. Water was then added to increase the difference in polarity between the phases, thereby improving phase-separation. The organic phases from each experiment were combined, after which 40 μl of tetradecane was added as keeper and the volume was reduced to 0.5 ml, under a gentle stream of nitrogen gas.

2.2.2. Screening experiments

A factorial design was used during the screening experiments to identify parameters that had the greatest influence on the washing process, and to exclude insignificant parameters. The objective of the design of experiments (DOE) is to generate as much relevant information as possible from as few experiments as possible, by systematically changing more than one parameter between each experiment, and varying these parameters across ranges that span the total variation in the experimental domain [21]. In experimental designs the parameters are often varied between extreme high and low values. When three factors are chosen, the resulting design can be viewed a cube, with one of the experiments at each of its corners. "Centre point" experiments, with factors set at mid-points of the ranges, may also be included to assess the linearity of observed relationships, the levels of experimental error and the fit of models describing the relationships between the varied factors and measured response(s). The factors included must be independently adjustable, uncorrelated with each other, but correlated to the response.

In this study a two-level full factorial design with three centre points was used to screen the influence of three variables (temperature, extraction time and ethanol concentration) on the removal efficiency, here measured as the percentage of TEQ removed from

Table 1
Field soils used in the solvent-washing experiments.

Soil	Location	Coordinates	Contaminating activity	Soil description	LOI (%)	Water content (%)	Concentration (pg-TEQ g ⁻¹ d.w.)
1	Hansons sawmill, Luleå	N 63°35' E 22°09'	Wood preservation 1961–1975	Sandy-silty	3.4	5.9	30
2	Hansons sawmill, Luleå	N 63°35' E 22°09'	Wood preservation 1961–1975	Sandy-silty	3.4	5.9	950
3	Öbacka waterside, Umeå	N 63°50' E 20°15'	Wood preservation 1960–1975	High concentration plant parts/organic matter	40	51	2300
4	Eka Chemicals, Bohus	N 57°51' E 12°01'	Chlor-alkali industry	Fine particle clay-silty soil, graphite particles	3.7	15	8100

the soil. The experiments were performed with a sandy-silty soil from a former sawmill site (30 pg-TEQ g⁻¹) and the factor settings in each experiment are listed in Table 2. The results were evaluated using MODDE 5.0 (Umetrics, Umeå, Sweden).

2.2.3. Evaluation of the effect of the number of washing cycles

The results from the screening experiments showed that a single washing cycle would not be sufficient to extract most of the PCDD/Fs from the test soil under any conditions within the experimental domain. Therefore, the effect of employing more than one washing cycle was then investigated. An ethanol concentration of 75% was chosen for these experiments (even though 95% provided higher extraction efficiencies and technical grade, 95% v/v, ethanol is commonly used for soil washing), for the following reason. Under real remedial conditions, in which the solvent would be recycled and the pollutants would be continuously removed (e.g. by carbon filtration), the soil moisture would dilute the washing liquid, and thus reduce its efficacy for removing hydrophobic compounds, during the extraction process. Therefore, a concentration of 75% was chosen to avoid overestimating the efficiency of the treatment. The temperature was set at two levels, 20 °C and 60 °C, in these experiments, and the length of each washing cycle was set to a constant 30 min to ensure that steady-state conditions were reached. The experiments were performed on the soil originating from Hanson's sawmill site, which had a starting concentration of 30 pg-TEQ g⁻¹. Ten washing cycles were applied to this soil, but due to time and resource constraints, only the filtrates from washing cycles 1, 2, 3, 5, 7 and 10 were analysed. The total removal efficiency was determined by analysing the PCDD/F contents in the soil before and after applying the 10 washing cycles.

2.2.4. Performance assessment

Additional experiments were performed with three highly contaminated soils (Soils 2–4, Table 1), all of which had different characteristics and contamination levels, to assess the performance and robustness of the soil-washing procedure. Ten washing cycles (30 min each) were applied with a 75:25 (v/v) ethanol:water mixture. The temperature was set to 60 °C. The filtrates from washing cycles 1, 3, 5, and 10 were analysed for all soils, and the total removal

Table 2

Factor settings in the two-level screening experimental design, with three centre points, applied to assess the influence of temperature, time and ethanol concentration on the efficiency of ethanol washing.

No.	Temperature (°C)	Time (h)	Ethanol (%)	Extraction (%)
1	21	0.25	50	15
2	23	5	50	15
3	21	0.25	95	23
4	23	5	95	56
5	60	0.25	50	17
6	60	5	50	21
7	60	0.25	95	33
8	60	5	95	27
9	37	1.11	72	19
10	37	1.11	72	31
11	37	1.11	72	22

efficiency was determined by analysing the PCDD/F content in the soils (by exhaustive Soxhlet extraction and GC-MS) before and after applying 10 washing cycles.

2.2.5. Estimated particle removal

The fraction of PCDD/F removed from the soil through particle separation (i.e. PCDD/Fs adsorbed to small particles that were entrained in the liquid and subsequently trapped by filtration) was estimated by subtracting the dissolved fraction of PCDD/Fs (calculated from extraction curves for each soil based on the PCDD/Fs found in the filtrates) from the total amount of PCDD/Fs in the initial soils. Although the resulting fractions are calculated rather than directly measured they may provide interesting information regarding differences in the processes involved in PCDD/F removal from the soil.

It should be noted that the fraction removed by particle removal from Soil 4 could not be estimated, because the estimated PCDD/F content in the washing fluid and soil residue exceeded the total initial concentration in the soil. This discrepancy was probably due to the inhomogeneous character of sub-samples of Soil 4.

2.3. Clean-up

The PCDD/F clean-up procedure started with the removal of sulphur from the extracts by adding acid-washed copper granules. The extracts were then transferred in 3 × 2 ml *n*-hexane to a 16 mm i.d. multi-layer silica column (pre-cleaned with two column volumes of *n*-hexane), packed with glass wool, 3 g KOH-silica (20% by weight), and 3 g silica (activated at 130 °C), 6 g H₂SO₄-silica (40% by weight) and 3 g of Na₂SO₄ (activated at 500 °C). Each extract was eluted with 60 ml *n*-hexane and its volume was reduced to 1 ml by rotary evaporation. The concentrated sample was transferred in 3 × 1 ml *n*-hexane to a 0.5 g AX-21 activated carbon column – 9.1% carbon by weight on Celite 545, activated at 130 °C and washed with 4 ml dichloromethane/methanol/toluene (15/4/1, v/v/v), 1 ml dichloromethane/*n*-hexane (1/1, v/v) and 5 ml *n*-hexane – and was eluted with 40 ml dichloromethane/*n*-hexane (1/1, v/v) to remove non-planar PCBs. The columns were then back-flush eluted with 40 ml toluene to recover the PCDD/Fs. Finally, the extracts were prepared for GC-MS analysis by adding RS and 30 µl tetradecane, removing the volatile solvents by rotary evaporation, and transferring them to GC vials with 200 µl inserts. The RS was added to the extracts to assess IS recovery.

2.4. Instrumental analysis

PCDD/Fs were identified and quantified by high-resolution gas chromatography (HRGC)–high-resolution mass spectrometry (HRMS) using a Hewlett Packard 5890 gas chromatograph coupled to a Fisons Instruments VG Autospec mass spectrometer. Three microliter portions of the samples were injected (split-less), using an HP 7673 A auto sampler. Target compounds were separated on a 60 m × 0.32 mm, 5% phenyl-methylpolysiloxane column (0.25 µm DB-5 film, J&W Scientific, Folsom, CA, USA). The injector and transfer line temperature was set at 280 °C, the oven temperature was

initially held at 200 °C for 2 min then increased by 3 °C min⁻¹ to 300 °C, and held isothermally for 8 min. The HRMS was operated with electron impact ionization, electron energy of 35 eV, and ion source temperature of 250 °C in Single Ion Monitoring (SIM) mode to enhance the sensitivity. In each analysis, two intense ions of the molecular ion isotope distribution cluster were monitored and the SIM descriptor was time-segmented (with one segment per homologue level) to further enhance the sensitivity. PCDD/Fs were identified using relative retention times and quantified using the internal standard technique, by comparing peak areas in samples and reference standards.

3. Results and discussion

3.1. Screening experiments

The proportion of PCDD/Fs removed, expressed in terms of the percentage reduction in TEQ per gram dry weight soil following the washing, was used as the response variable in the screening experiments. The washing efficiencies in the factorial experiments varied between 15% and 56% PCDD/F removal (Table 2). The centre points showed that there were relatively large variations in the removal efficiency (Table 2), probably due to the heterogeneity of the soils. Nevertheless, several general conclusions could be drawn from the screening experiments. Most importantly, the variable with the strongest effect on removal efficiency was the ethanol concentration, i.e. higher concentrations of ethanol resulted in higher removal efficiencies, but the effects of time and temperature were weak (and statistically insignificant) within the experimental domain. This was surprising, particularly for the temperature, since increasing the temperature generally enhances the solubility of hydrophobic compounds [22,23] and Nakamiya et al. found a significantly higher removal efficiency of dioxins by increasing the extraction temperature [19]. However, temperature effects were further investigated when evaluating the effect of the number of washing cycles (see below), in order not to rule out its significance at an early stage.

3.2. Evaluation of the effect of the number of washing cycles

As the removal efficiencies obtained from single washing cycles in the screening experiments (15–56%) were too low for practical remediation of highly contaminated soils, the effect of increasing the number of washing cycles was also tested, in experiments with Soil 1. Ten 30-min washing cycles were applied (a short washing time, but sufficient to ensure that steady-state conditions were reached), at two temperatures; the low and high temperatures used in the screening experiments (20 °C and 60 °C, respectively). This was done to further investigate temperature effects on the removal efficiency, and the possibility that applying multiple washing cycles could provide compensatory improvements if low-temperature washes proved to be less efficient than high-temperature washes.

The ethanol concentration in the washing liquid was set to 75% (although the screening experiments had shown that a higher concentration would have provided higher extraction efficiencies), to avoid overestimating the efficiency of the technique in field applications, in which the ethanol that was used would be diluted by soil moisture, as mentioned above.

The total removal efficiency was considerably improved by applying multiple washing cycles rising from 15–56% with one washing cycle to 81% after 10 washing cycles at both extraction temperatures, 20 °C and 60 °C (Fig. 1). Increasing extractability with several washing cycles has been observed in previous studies [24,25]. However, since several washing cycles were performed at two different temperatures in this study, further conclusions

can be drawn. For instance, it can be concluded that although higher amounts of PCDD/Fs were released in early stages at the higher extraction temperature, i.e. during the first three washing cycles (indicated by the extraction curves shown in Fig. 1), the temperature does not appear to have a positive effect on the total removal efficiency, as the remaining PCDD/F concentration was 5.8 pg-TEQ g⁻¹ after 10 washing cycles at both temperatures.

These results are important since remediation costs increase with increases in temperature, treatment time and ethanol consumption. Therefore the treatment temperature should ideally be kept as close to the ambient temperature as possible. In addition, as few washing steps should ideally be used as possible, since each washing step consumes time and ethanol. The extraction curves in Fig. 1 indicate that by compensating for a lower extraction temperature an increasing number of washing cycles may be needed. However, after the application of a certain number of washing cycles the limit of solvent-washing extraction was reached, indicated by flat extraction curves after 5 and 3 washing cycles at 20 °C and 60 °C, respectively. This indicates that applying more washing cycles after this will not significantly contribute to better removal efficiency.

Instead, alterations of the washing process could increase the removal efficiency. For instance, in a study by Khodadoust et al. it was shown that changing from cross-current washing process to counter-current washing process, the same removal efficiency could be achieved with significantly lower solvent volumes [26], and thus lower costs. Applying a water rinse between the washing cycles could also further reduce costs [16].

3.3. Performance assessment

Based on the results of the screening experiments and the experiments with repeated washing cycles, the selected soil-washing procedure (10 washing cycles with 75% ethanol at 60 °C) was applied to three additional soils (Soils 2, 3 and 4; Table 1) with varying characteristics and contamination levels to assess the robustness of its performance.

The PCDD/Fs were most efficiently removed from Soil 2 (Table 3), a sandy-silty soil with low amounts of organic matter (3.4%) but relatively high concentrations of PCDD/F (1000 pg-TEQ g⁻¹ dry weight). About 98% of the TEQ was extracted from this soil after five extraction cycles (following which there were no further reductions, Fig. 2). Close to this removal efficiency (97%) was obtained for Soil 3, which was rich in organic matter (40%) and contained about 2000 pg-TEQ g⁻¹ dry weight. The soil with the lowest extractability was Soil 4 (85% removal efficiency); a highly contaminated clay soil (8100 soil pg-TEQ g⁻¹ dry weight), rich in graphite particles.

The sandy character can most likely explain the high removal efficiency from Soil 2, since extraction techniques such as solvent washing are often most efficient when applied to coarse soils [6], because the solvent can penetrate the particles in such soils more thoroughly, and thus more effectively desorb the contaminants. In addition, as the size of the soil particles increases, their relative surface area declines, thereby reducing the abundance of contaminant sorption sites and the adsorptive capacity of the soil. These relationships were explored by Khodadoust et al. who sieved samples of pentachlorophenol-contaminated soil into three size fractions, and found the least amount of pentachlorophenol was desorbed from the finest soil fraction, in accordance with the hypothesis that this fraction has more abundant sorption sites per unit mass [27]. Another observation in the cited study was that less of the contaminant was desorbed in soils that had high organic matter contents than in soils with low contents. This is consistent with the high extraction yields for Soil 2, which had low organic matter contents, but not with the high extraction efficiency observed for

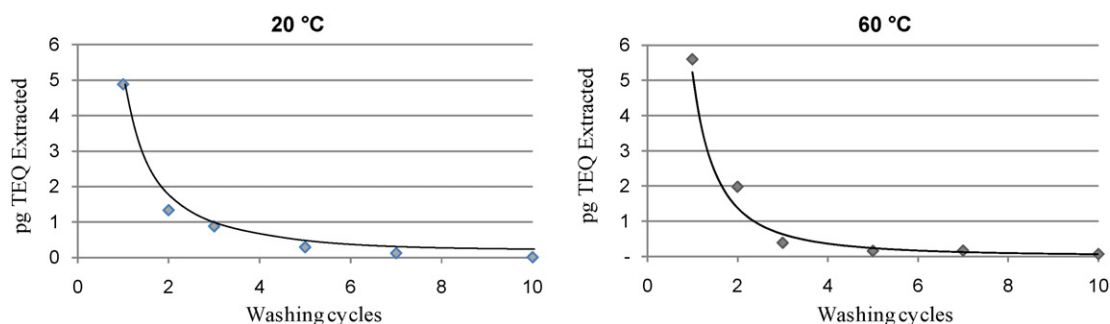


Fig. 1. PCDD/F extraction curves obtained from experiments with samples of Soil 1, based on PCDD/F levels detected in extracts after washing cycles 1, 2, 3, 5 and 10 at 20 °C and 60 °C.

Soil 3, which had the highest organic content of the investigated soils. This apparent discrepancy may have been due to most of the organic matter in Soil 3 consisting of wood fibres (the soil originated from a former sawmill site), since Frankki et al. have found wood fibres to have lower sorption capacity than other types of organic matter [28].

Of the three soils investigated in this series of experiments the removal efficiency was the lowest for Soil 4, a clay soil containing graphite particles of industrial origin, probably due to entrapment of contaminants in clay and silt conglomerates, and the strong affinity of PCDD/Fs for the graphite particles. Clay and silt soils do not respond well to washing techniques [6] and hydrophobic compounds are known to be strongly adsorbed to organic carbon, particularly to graphite and soot [29]. This was likely the reason for the strongly deviating results in extraction efficiencies for Soils 3 and 4. The removal efficiency was clearly not influenced by the high amount of organic matter in Soil 3, but seemed to be considerably influenced by the graphite in Soil 4.

The removal efficiencies from Soils 1 (investigated in the experiments described in Section 3.2) and 2 strongly differed, although these soils had very similar characteristics, except that they contained 30 pg-TEQ g⁻¹ and 952 pg-TEQ g⁻¹ dry weight of PCDD/Fs, respectively (Table 1). The removal efficiency from Soil 1, which contained much lower levels of PCDD/Fs, was substantially lower

than that from Soil 2 (81% and 98%, respectively). Hence, the removal efficiency, in terms of amounts of pollutants removed, also seems to be influenced by the degree of pollution (although it should be noted that the residual levels of PCDD/Fs were still lower in Soil 1 than in Soil 2). The relative ease of removing most pollutants from heavily contaminated soils has previously been observed in several studies [30–32], and suggested to be due to the saturation of strong sorption sites in soils with high concentrations of pollutants [33].

The removal efficiency of the different congeners from the soils was relatively even and the solvent extraction procedure seems to perform equally well for all 2,3,7,8-substituted PCDD/Fs. The only exception was for Soil 4, in which the residual level of 2,3,7,8-TCDD was higher than the initial concentration. However, this only accounted for 4% of the residual PCDD/F levels and the inhomogeneity of soil samples probably explains the deviating result.

3.4. Estimated contribution of particle separation to contaminant removal

The estimated contribution of particle separation to PCDD/F removal varied between soils more than the total removal efficiency. For instance, as much as 53% of the contaminants are estimated to have been removed by particle separation from

Table 3

Initial and residual concentrations of PCDD/Fs in samples of Soils 2, 3 and 4, and percentage removals after 10 washing cycles at 60 °C.

Congeners	Soil 2		Soil 3		Soil 4	
	Initial	Residual	Initial	Residual	Initial	Residual
2378-TCDD	3	a	15	a	32	48
12378-PeCDD	19	a	44	1	19	4
123478-HxCDD	a	a	19	1	1	a
123678-HxCDD	15	a	279	3	1	a
123789-HxCDD	6	a	39	1	1	a
1234789-HpCDD	4	a	126	6	1	1
OCDD	c	a	c	a	c	a
2378-TCDF	55	a	27	a	2402	450
12378-PeCDF	10	a	9	1	458	60
23478-PeCDF	96	1	82	2	3728	405
123478-HxCDF	42	1	105	a	890	160
123678-HxCDF	37	a	40	2	190	32
234678-HxCDF	76	1	92	a	77	9
123789-HxCDF	12	a	30	a	260	2
1234678-HpCDF	576	12	1377	55	22	5
1234789-HpCDF	1	1	9	1	7	2
OCDF	c	a	c	a	c	a
Total pg-TEQ g ⁻¹	952	16	2293	73	8089	1178
Dissolved in solvent (%)	82	69	b			
Estimated particle removal (%)	16	27	b			
Total removal efficiency (%)	98	97	85			

^a <0.5 pg-TEQ g⁻¹.

^b Estimation of particle removal contribution not possible.

^c Missing data.

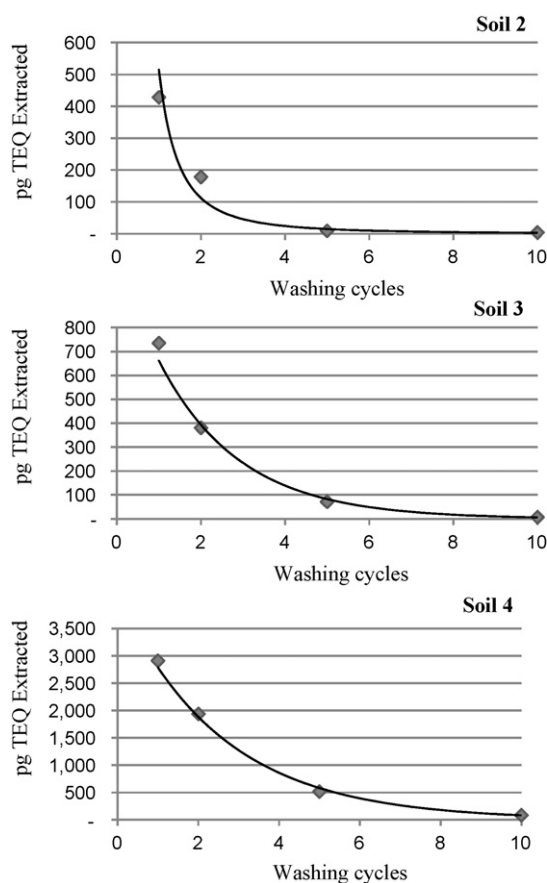


Fig. 2. PCDD/F extraction curves obtained experiments with samples of Soils 2, 3 and 4, based on PCDD/F levels detected in extracts after 1, 2, 5 and 10 washing cycles at 60 °C.

Soil 1, compared to only 16% from Soil 2, while the total removal efficiencies ranged from 81% to 98% (Tables 3 and 4). The large difference between Soils 1 and 2 is somewhat surprising, since they both came from the same site and, consequently, had very similar characteristics; both being sandy soils with very low organic contents. However, since Soil 2 contained much higher levels of contaminants than Soil 1, the proportions of contaminants that were adsorbed to fine particles were probably much higher in Soil 1 than in Soil 2, which probably explains why the proportion removed by particle separation was higher for Soil 1 than Soil 2. Previous results, has been shown that only 24% of the cadmium in a polluted soil appeared to be adsorbed to sand particles, although such particles accounted for 70% of the total soil mass [7]. Sorption to the fine soil fraction is likely to be the dominating process for organic hydrophobic compounds like PCDD/Fs as well. Hence, sorption sites in the fine fraction may have been saturated due to the higher concentrations in Soil 2, and the lower particle-associated removal from this soil indicates that substantial proportions of the contaminants were adsorbed to the coarser fraction, and thus more readily removed by the dissolution in the solvent.

The estimated contribution of particle removal to the total PCDD/F removal from Soil 3 was lower than that of Soil 1 but higher than that of Soil 2. As mentioned earlier, a possible explanation for the unexpectedly high total removal efficiency from Soil 3 is the relatively low sorption capacity of the organic matter it contains. However, there may be another contributory factor. Since the wood fibres did not settle as well as soil particles, they may have been removed by filtration to a greater extent than the soil particles, at least partially explaining why the particle-associated removal was higher from Soil 3 than from Soil 2. For Soil 4 it was not possible

to estimate particle removal contributions from the acquired data, most likely due to the inhomogeneity of the soil sample. The following conclusions can be drawn regarding particle removal from the results of this study: contaminants bound to minerals (especially the coarse fraction) are more likely to be removed by dissolution in the solvent, while those bound to organic matter or the fine fraction of the soil are more likely to be removed sorbed to particles.

The treatment reduced the PCDD/F levels to below 10 pg-TEQ g⁻¹ in Soil 1 (5.8 pg-TEQ g⁻¹), and below 250 pg-TEQ g⁻¹ in Soils 2 and 3, which are the current Swedish EPA regulatory limits for sensitive and less sensitive land uses, respectively. The residual level of PCDD/Fs in Soil 4 was above these limits. However, the levels in this soil (1200 pg-TEQ g⁻¹ dry weight) are of the same magnitude as the maximum residue limits in many other countries, which are often around 1000 pg-TEQ g⁻¹ dry weight [34]. Thus, solvent washing seems to be a promising alternative to incineration and thermal stripping techniques.

The estimates of the contributions of particle removal and contaminant dissolution to overall removal reveal that both processes occur simultaneously and neither should be neglected. A commonly recommended strategy is to separate the coarse fraction mechanically and then treat the fine and coarse fractions separately [8]. This can reduce costs significantly [7]. However, other options are also available. For instance, Yeh and Young found that rates of removal of total petroleum hydrocarbons from a sandy loam soil with low silt and clay contents increased with increases in the fine/coarse fraction, and could be further enhanced by the use of a surfactant [35]. These findings illustrate the great need for process optimisation before applying solvent washing to any soils.

It should also be noted that for efficient, cost-effective operation, the solvent would have to be recycled and PCDD/Fs would have to be separated from it. Further, in full-scale operations the ethanol concentration would either have to be continuously kept at a high level, e.g. by the recirculation of the washing liquid through a bed of molecular sieves, or continuously monitored during remediation. The ethanol concentration could then be increased to a satisfactory level, e.g. by distillation or passage through molecular sieve beds, when it dropped below a critical limit (which would have to be determined for each soil).

4. Conclusions

Despite the low water solubility of PCDD/Fs, the results of this study show that it is possible to remediate PCDD/F-contaminated soils. Using screening experiments it was possible to reveal that that temperature had limited effect on the total removal efficiency of dioxins and furans from the investigated soil. Instead, the principal factor affecting the efficiency of the washing process was found to be the ethanol concentration, and the efficiency could be improved by applying multiple washing cycles, even at ambient temperature. The characteristics of the soils also affected the extraction results, notably increases in particle size and contaminant levels had a positive effect on the removal efficiency, while clay and graphite particles had negative effects. Regarding the organic matter in soil, the extraction efficiency was found to be affected more by the type of organic matter than its absolute levels in the soil. Dissolution of the contaminants in the solvent and particle size separation occurs concurrently, and both processes need to be considered when using solvent washing for remediation. The contamination level appears to have a considerable effect on the relative importance of these two removal processes. Contaminants sorbed to the coarse fraction will be removed by dissolution to a greater extent than contaminants sorbed to the fine fraction. Nevertheless, although different soil characteristics and contamination levels affected the removal efficiency in the investigated soils, this study clearly shows that

solvent washing possesses potential as remediation method for a wide variety of soils.

All 2,3,7,8-substituted PCDD/F congeners were evenly extracted and thus all contributed to similar degrees to the total degradation efficiency. It seems reasonable to assume that the technique could also be applied to other organic compounds with similar properties.

The findings that efficient washing can be performed at low temperatures are encouraging, since it is significantly reducing the costs, fire hazards and occupational exposure associated with the process, due to the volatility of the solvent. However, before solvent washing could be used to remediate soils in practice, effective ways to recycle the solvents (while simultaneously removing water) and to remove and/or degrade the extracted contaminants from the solvent must be developed. The latter is the subject of an ongoing study.

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