



Remediation of soils contaminated with wood preserving wastes: crosscurrent and countercurrent solvent washing

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Abstract

Solvent washing was evaluated as a method to remove pentachlorophenol (PCP) from aged field soils contaminated with wood treating wastes. Several soil:solvent contact ratios were considered. Solvent washing processes were evaluated based on the removal of PCP from the soil throughout the process. Mixtures with at least 50% (mass) ethanol extracted statistically equivalent amounts of PCP, removing as much as 730 mg/kg for one soil. Kinetic experiments demonstrated that soil–solvent contact times of approximately 1 h were adequate to remove a majority of the PCP. A crosscurrent soil washing procedure was developed to determine the solvent volume required to remove PCP from field soils. Consecutive wash stages with the 50% ethanol solvent were followed by water rinse stages. The crosscurrent washes were performed in three- and two-stage processes where soils were washed with the 50% ethanol solvent in three- and two-successive stages followed by water rinse stages. Ethanol recoveries were greater than 90% for both the three- and the two-stage wash trains. In addition to PCP, hydrocarbons were removed from the field soils by the 50% ethanol solvent. Effective removal of PCP by the 50% ethanol solvent was not impeded by the presence of hydrocarbons in the soils. Three-stage countercurrent soil washing with 50% ethanol was successful in reducing PCP contamination on the soil from 785 to less than 40 mg/kg. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Crosscurrent; Countercurrent; Ethanol; PCP; Solvent washing

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1. Introduction

Used as a wood preserving agent for many years, pentachlorophenol (PCP) has been placed on the US EPA List of Priority Pollutants [1,2] and was the primary contaminant of concern in this research. In addition to PCP, several types of contaminants may be found at wood treating sites including creosote and polycyclic aromatic hydrocarbons (PAHs), petroleum hydrocarbons, and heavy metals such as copper, chromium, arsenic, and zinc [3]. The presence of these contaminants in the soil may constitute an additional hazard and may affect remedial processes through interactions such as impeding the mobilization of PCP or poisoning microbial cultures. Ex situ soil solvent washing may effectively remediate soils contaminated with wood preserving wastes [3–6], and has successfully removed several types of organic pollutants from contaminated soils [7–13].

Although soil solvent washing may be more expensive compared to bioremediation techniques such as landfarming and in situ bioremediation, it can be a desirable alternative when a rapid response to a contaminated site is necessary. Soil solvent washing can be cost effective when soil solvent washing is followed by the recovery of solvent, and biotreatment of contaminant residuals after solvent recovery. In addition, successful in situ bioremediation studies performed at bench scale inside the laboratory may not be feasible in actual field-scale in situ remediation.

The success of ex situ soil solvent washing depends on the effectiveness of the solvent extraction process. Important factors contributing to the effectiveness of the solvent extraction process include solvent type, extraction time, and the contact mode between the soil and solvent. Additional contributing factors to consider in such a process are the cost of solvent and the capital and operating costs of the soil solvent washing equipment [14–16]. Ex situ solvent washing of excavated soils is usually carried out in a semi-batch or a semi-continuous mode using a variety of soil–solvent contacting technologies [17]. Selection of the extracting solvent depends on several factors including the solubility of the organic pollutant in the solvent, the miscibility of solvent with water, and the level of moisture in the soil. Ethanol was selected as the solvent in this study due to its complete miscibility with water, high PCP solubility, and its low cost. The effectiveness of water–ethanol mixtures in removing PCP from field soils was examined in this research. In addition, crosscurrent and countercurrent solvent washing procedures were evaluated.

2. Materials and methods

2.1. Chemicals

The chemicals used in this study are listed in Table 1. The water used in the batch extraction experiments was deionized water with a resistivity greater than 18 M Ω . Various water–ethanol mixtures were prepared from different volumes of water and 95% ethanol.

Table 1
Chemicals

Chemical	Specification	Source
PCP	99%	Aldrich Chemicals, Milwaukee, WI
2,4,6 Tribromophenol	98%	Aldrich Chemicals, Milwaukee, WI
Ethanol	190 proof, USP grade	Midwest Grain Products, Weston, MO
Ethanol	200 proof, USP grade	Midwest Grain Products, Weston, MO
Acetone	Optima grade	Fisher Chemicals, Fairlawn, NJ
Hexane	Optima grade	Fisher Chemicals, Fairlawn, NJ

2.2. Soils

The field soils were obtained from a former wood treating facility in the southeastern United States. Some pertinent physical and chemical properties of the soils are presented in Table 2. The PCP contamination on field soils A and B was 785 and 246 mg/kg, respectively. The HC contamination on field soils A and B was 1730 and 438 mg/kg, respectively.

2.3. Analysis

The concentration of PCP in liquid samples was measured using a 5890 Series II HP gas chromatograph (GC) (Hewlett Packard, Palo Alto, CA) equipped with an electron capture detector (ECD); 2,4,6-tribromophenol (TBP) was used as an internal standard (PCP and TBP with 99% and 98% purity, respectively, Aldrich Chemicals, Milwaukee, WI). Samples were filtered through 0.45- μ m Magna nylon membranes (Micron Separations, Westboro, MA) and acidified to pH 2 before extraction into toluene for injection

Table 2
Field soil characterization

	Soil A	Soil B
pH ^a	4.46	5.46
Organic matter (%) ^{b,d}	2.69	2.88
Moisture content (%) ^{c,d}	12.7	8.98
Particle size distribution (% total soil)		
0.425–0.85 mm (20 \times 40 US Mesh)	5.0	1.2
0.149–0.425 mm (40 \times 100 US Mesh)	60.9	25.2
0.106–0.149 mm (100 \times 140 US Mesh)	11.7	24.0
0.075–0.106 mm (140 \times 200 US Mesh)	3.3	20.0
< 0.075 mm (> 200 US Mesh)	18.8	29.4
PCP ^d (mg/kg)	785	246
Hydrocarbons ^d (mg/kg)	1730	438

^aASTM Method D2974-87 (1992).^bASTM Method D2974-87 (1992).^cASTM Method D4972-89 (1992).^dDry weight basis.

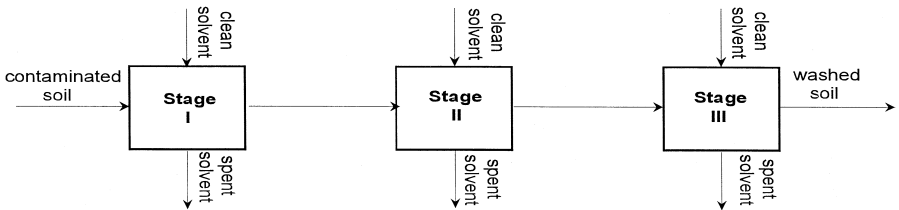
Table 3
Quantitated hydrocarbons

PAHs	Alkanes
Naphthalene	<i>n</i> C11
C1 naphthalene	<i>n</i> C12
C2 naphthalene	<i>n</i> C13
Fluorene	<i>n</i> C14
C1 fluorene	<i>n</i> C15
C2 fluorene	<i>n</i> C16
Phenanthrene	<i>n</i> C17
C1 phenanthrene	<i>n</i> C18
C2 phenanthrene	<i>n</i> C19
	<i>n</i> C20

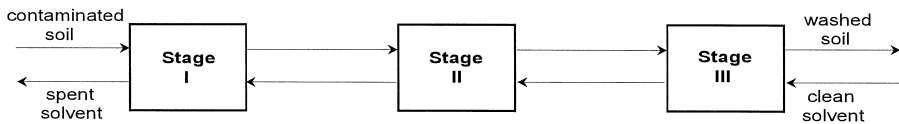
into the GC. The aqueous ethanol concentrations were determined using a 5890 Series II HP GC equipped with a flame ionization detector (FID) using *n*-propanol (Fisher Chemicals, Fairlawn, NJ) as the internal standard. The concentrations of hydrocarbons listed in Table 3 were determined with an FID detector.

2.4. Batch solvent extraction

Triplicate batch extraction experiments were conducted where various water–ethanol mixtures and soil were placed inside 160-ml glass hypovials using 1.5 to 200 ml of solvent per gram of soil washed (soil:solvent ratio of 2 g:3 ml to 1 g:200 ml). The



(a) Crosscurrent Solvent Washing



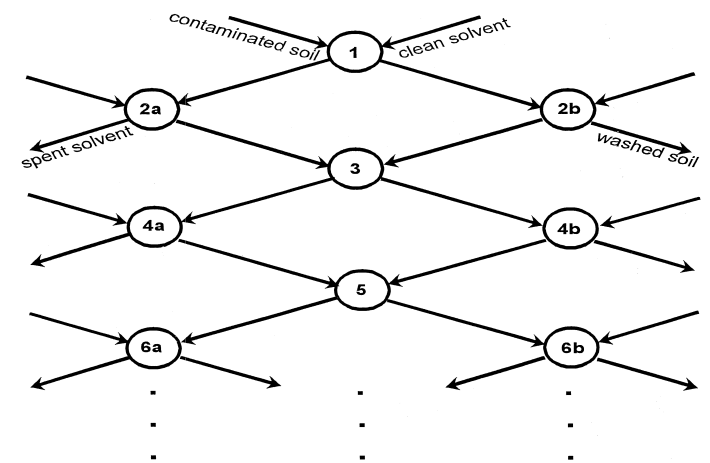
(b) Countercurrent Solvent Washing

Fig. 1. Crosscurrent and countercurrent soil solvent washing; three-stage systems.

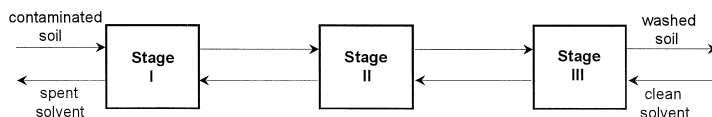
soil–solvent mixtures were contacted on a rotating tumbler at 18 rpm for 24 h. A liquid sample from each vial was filtered and analyzed for PCP on the GC. Using a similar batch extraction technique, kinetic experiments evaluated PCP removal as a function of time when soil and the 50% ethanol solvent were mixed at the soil:solvent ratios (g:ml) of 2:3, 1:8, and 1:100 for 15, 30, 60, 90, 180, and 720 min of contact time. These experiments also analyzed triplicate samples for each condition and time period.

2.5. Crosscurrent solvent washing

Fig. 1 shows a general schematic for the crosscurrent (serial) and countercurrent solvent washing of soil in three stages. Successive solvent washing of field soils with solvent followed by water rinse stages was performed in triplicate at several soil:solvent ratios (g:ml): 2:3, 1:2, 1:4, and 1:8. In each stage, the soil–solvent slurry was shaken on a rotating tumbler at 18 rpm. After 30 min, the slurry was centrifuged in a Fisher 26KM centrifuge (Fisher Scientific, Pittsburgh, PA) at 5000 rpm ($2680 \times g$) for 15 min at 20°C to separate the spent solvent from the soil. The spent solvent was decanted from the centrifuge tube, filtered, and analyzed for PCP. The next stage consisted of adding another batch of fresh solvent to the washed soil. The total contact time between the soil and the solvent for each wash stage including centrifugation was approximately 1 h. Several crosscurrent soil washing configurations were evaluated, i.e. the number of wash



(a) Experimental Procedure



(b) Continuous Stagewise Process

Fig. 2. Countercurrent soil solvent washing procedure.

stages with the solvent varied from one to three stages while the number of water rinse stages ranged from one to two.

2.6. Countercurrent solvent washing

Field soil was washed with a selected solvent in three countercurrent stages at a soil:solvent contact ratio of 1:4 (g:ml). The soil–solvent mixing and separation procedures were similar to crosscurrent solvent washing except that, used solvent replaced most of the fresh solvent. Three series of countercurrent batch experiments were performed to approximate a continuous countercurrent solvent washing in three contact stages. The three-stage countercurrent soil washing process is illustrated in Fig. 2 where contaminated soil was introduced into the process from the left side (at stages 1, 2a, 4a, 6a, 8a, and 10a), while clean solvent entered the process from the right hand side of the diagram (at stages 1, 2b, 4b, 6b, 8b, and 10b) in a countercurrent fashion. In the first wash stage (stage 1), clean (fresh) solvent was brought into contact with contaminated soil directly. In stages 2a, 4a or 6a, contaminated soil was mixed with the partially spent solvent from intermediate stages 1, 3 or 5. In stages 2b, 4b or 6b, clean solvent was contacted with the less contaminated soil from intermediate stages 1, 3 or 5. Stages 2a, 4a or 6a resembled stage I in Fig. 1, while stages 3 and 5, and 2b, 4b or 6b resembled stages II and III, respectively.

3. Results and discussion

3.1. Batch solvent extraction

Batch extraction experiments were conducted for both soils using several water–ethanol mixtures at a soil:solvent ratio of 1 g:100 ml. The extraction data presented in Fig. 3 show that for both soils, PCP removal increased gradually with increasing ethanol content of the solvent up to 0.5 mass fraction of ethanol in solution; thereafter, the removal of PCP from either soil was not further enhanced by the higher ethanol content of the solutions. The data also indicate that the 50% ethanol solvent mixture was as effective as the more concentrated ethanol solutions, removing approximately 720 and 246 mg/kg from field soils A and B, respectively. Less PCP was extracted from soil B which had a higher clay content than soil A (29.4% vs. 18.8%).

A series of batch extraction experiments was performed for a range of soil:solution contact ratios (2:3 to 1:200, g:ml). The data presented in Fig. 4 show that the lowest PCP removals were obtained with water. The 50% and 100% ethanol solutions removed comparable levels of PCP from soil A. Similar results were obtained for batch extractions of soil B.

3.2. PCP removal kinetics

The removal of PCP from both soils was studied with time using the 50% ethanol solvent at three soil:solvent (g:ml) ratios (from 2:3 to 1:100). The kinetics data presented in Fig. 5 show that the maximum PCP removal observed for soil A occurred within 1 h of contact between soil and solvent at all soil:solvent contact ratios. The kinetics data for soil A indicate that contact times longer than 1 h might have led to an irreversible

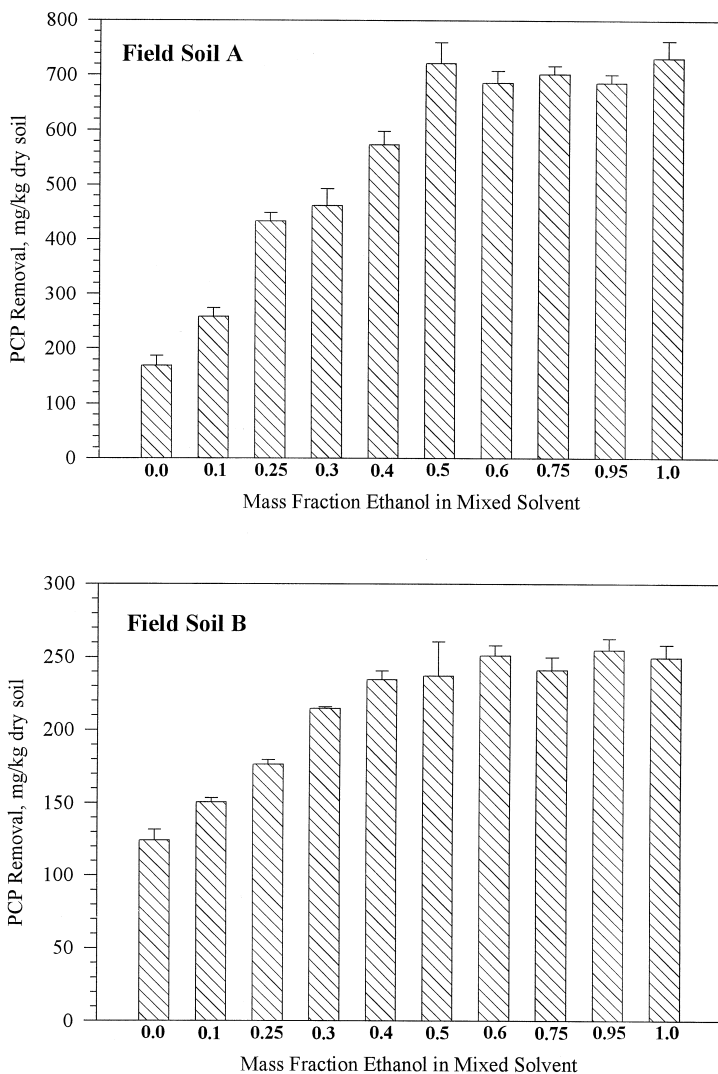


Fig. 3. Batch extraction of PCP from field soils with water–ethanol mixtures; 1 g soil:100 ml solvent, triplicate extractions.

sorption of a portion of the extractable PCP. The amount of PCP removed at the lowest soil:solvent ratio (2:3) was lower than at the other two soil:solvent ratios. For soil B, the soil with the higher clay content, maximum PCP removal occurred within 1.5 h.

3.3. Crosscurrent solvent washing

3.3.1. PCP removal

To reduce solvent volume expended in removing PCP from a given mass of soil, crosscurrent solvent washing of soil was evaluated at several soil:solvent ratios. Initially,

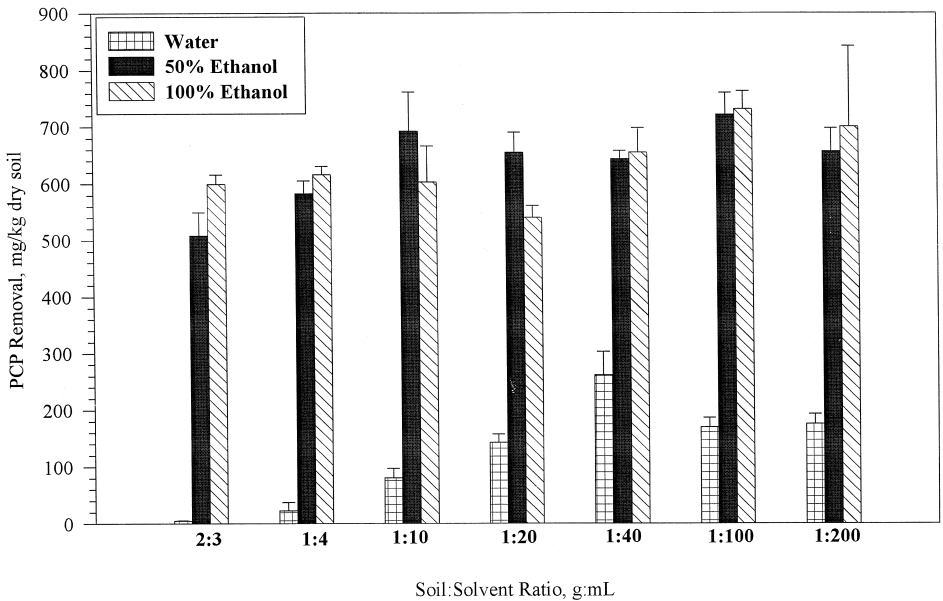


Fig. 4. Batch extraction of PCP from field soil A at several soil:solvent contact ratios with water, 50% ethanol, and 100% ethanol, triplicate extractions.

three wash stages with 50% ethanol were followed by two water rinse stages. The PCP removal data presented in Fig. 6a show that cumulative PCP removals after three wash

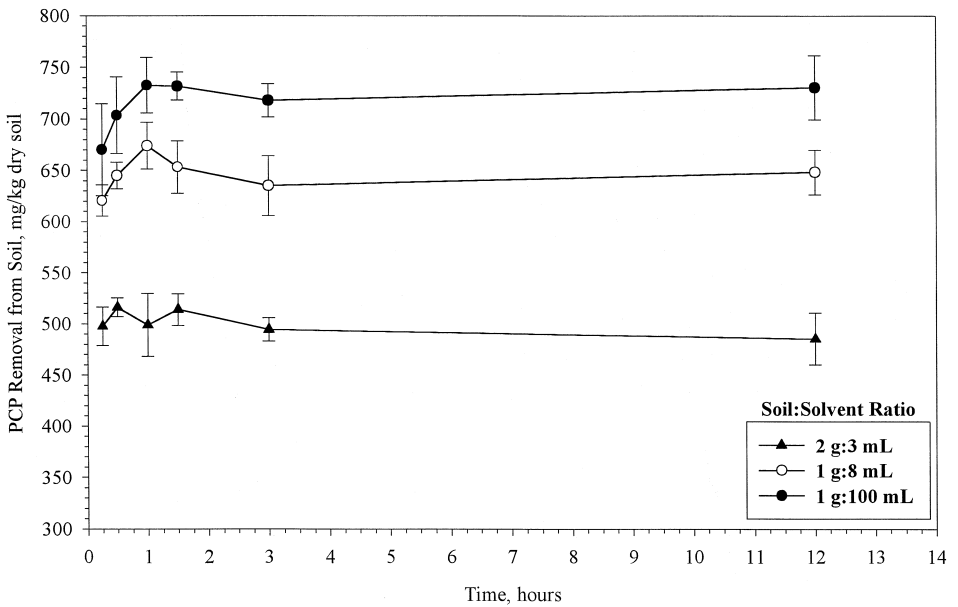


Fig. 5. Batch extraction of PCP from field soil A with time using 50% ethanol.

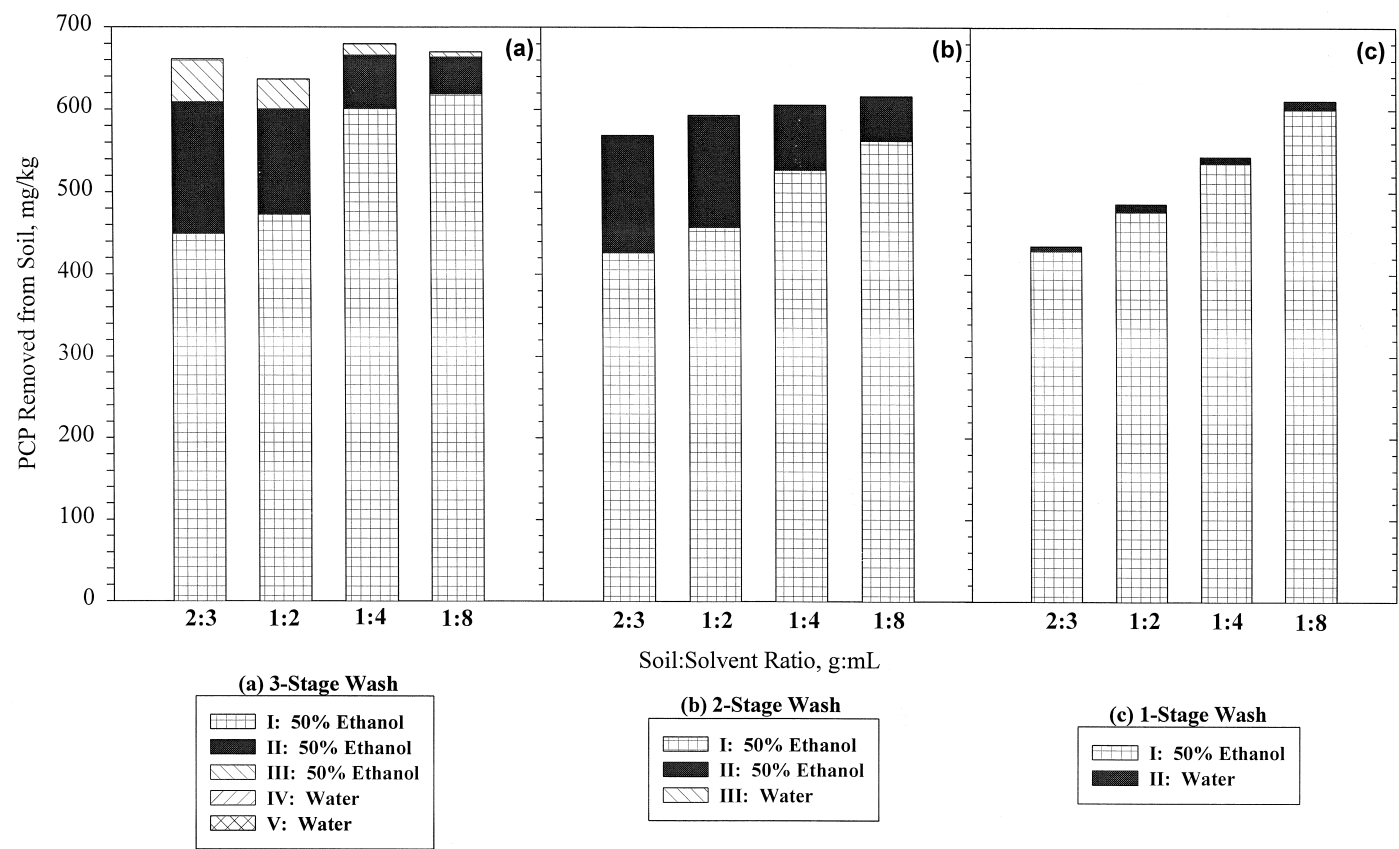


Fig. 6. PCP removal in three-, two-, and one-stage crosscurrent washing of field soil A.

stages with 50% ethanol were similar using different soil:solvent contact ratios. The data from Fig. 6a also show that insignificant levels of PCP were removed from the soil during the two water rinse stages. The data indicate that per kilogram of soil in three washes, 4.5 ml of solvent at the 2:3 soil:solvent ratio removed comparable levels of PCP to 16 ml of solvent at the 1:8 soil:solvent ratio.

In order to further reduce solvent expenditure, crosscurrent washing of soils A and B was carried out in two- and one-stage washes, each followed by a single water rinse stage. The PCP removal data presented in Fig. 6c for the one-stage wash indicate that at all soil:solvent contact ratios, the water rinse stage incrementally increased PCP removal from soil A, especially when compared to amounts removed in the water rinse stage(s) for the three- and two-stage wash trains. A comparison of PCP removal data from soil A for the three-, two- and one-stage wash trains demonstrates that at least two wash stages were necessary at the 2:3 soil:solvent contact ratio for removing greater than 75% of the PCP contamination, whereas three wash stages at the 1:4 contact ratio removed nearly 87% of the PCP contamination. Similar trends were observed for soil B.

3.3.2. Ethanol recovery

Recovery and reuse of the spent solvent is an economic necessity in soil solvent washing. An ethanol mass balance for the three-stage crosscurrent washing of soil A is shown in Fig. 7. The cumulative ethanol recovery data for soil A in the three-stage wash train were greater than 90% at all soil:solvent contact ratios. At the low soil:solvent contact ratios of 2:3 and 1:2, the water rinse stage recovered as high as 15% of the

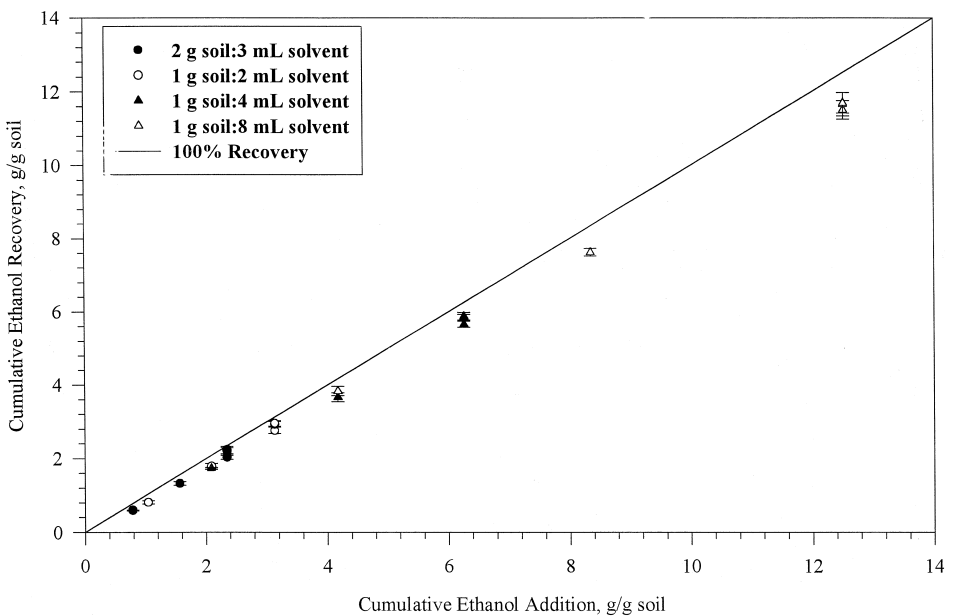


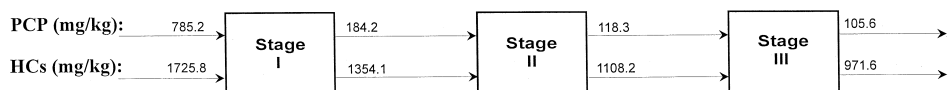
Fig. 7. Ethanol recovery in three-stage crosscurrent washing of field soil A; triplicate samples.

ethanol applied during the soil wash stages in the three- and two-stage wash trains. For example, 12.5 g were applied during three wash stages with 50% ethanol at the 1:8 soil:solvent contact ratio while 11.7 g of ethanol were recovered during the wash and rinse stages. Comparable ethanol recoveries were obtained during the three-, two- and one-stage crosscurrent solvent washing of soil B.

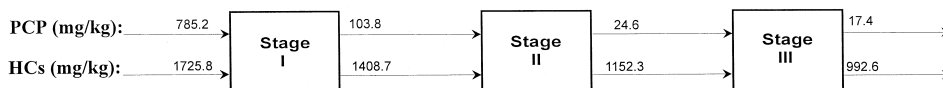
3.4. Countercurrent solvent washing

To reduce solvent expenditures further, a countercurrent solvent washing procedure was carried out for field soil A (Fig. 2). Based on the results from the crosscurrent solvent washing of soil A, an intermediate soil:solvent contact ratio of 1:4 (g:ml) and a soil–solvent contact time of 1 h were selected for the countercurrent solvent washing procedure. Three sets of countercurrent experiments were carried out. Starting with stages 6a and 6b (Fig. 2), the three contact stages leading to stages 6a and 6b (4b–5–6a and 4a–5–6b) approached a continuous countercurrent process. At stage 4a, the soil was contacted with a wash solvent that had been through two previous contact stages 3 and 2b. At stage 5, this soil was washed with a wash solvent that had been through one previous contact stage 4b. Finally, at stage 6b, a clean solvent was used to wash the soil. Similarly, at stage 4b, clean solvent was used to wash soil that had been washed twice before at stages 3 and 2a. At stage 5, this solvent was used to wash soil that had been washed once before at stage 4a. Lastly, at stage 6a, the solvent was used to wash a contaminated soil which had not been washed previously. Thus, the soil effluent from stages 4b, 5, and 6a, and the solvent effluent from stages 4a, 5, and 6a are representative of samples collected from a continuous countercurrent soil washing apparatus.

Using the procedure depicted in Fig. 2a, three additional sets of countercurrent experiments were performed to obtain additional samples of three-stage washed soil (6a, 8b, and 10b) and solvent (6a, 8a, and 10a), approaching steady-state operation in a continuous countercurrent process. The average PCP and hydrocarbon levels for these final samples are presented in Fig. 8b. In Fig. 8, crosscurrent data are provided for comparison. The PCP removal data show that the countercurrent process was more



(a) Crosscurrent



(b) Countercurrent

Fig. 8. PCP and hydrocarbon removal in three-stage solvent washing of field soil A with 50% ethanol.

efficient in solvent expenditure and generation of process residuals. For example, countercurrent washing used a total of 4 ml of solvent per gram of soil and produced 4 ml of waste solvent, while removing 767.8 mg/kg PCP from the soil. Crosscurrent washing used a total of 12 ml of solvent per g of soil and produced 12 ml of waste solvent, while removing 679.6 mg/kg PCP from the soil. The data also indicate that greater than 75% and 90% removal of the PCP occurred during the first and second countercurrent wash stages, respectively.

3.5. Hydrocarbon removal

In addition to PCP, the 50% ethanol solution removed hydrocarbons from the field soils during solvent washing. In three-stage crosscurrent solvent washing of field soil A, hydrocarbon removal was enhanced at lower soil:solvent ratios. Hydrocarbon removal levels from soil A increased in each wash stage with increasing soil:solvent ratio. Contrary to PCP removal data, successive washes with the 50% ethanol solvent continued to remove additional amounts of hydrocarbons at all soil:solvent ratios. The 50% ethanol solvent appeared to have preferentially removed PAHs (greater than 80% of total hydrocarbons) compared to alkanes. Since alkanes are more hydrophobic than the PAHs, one would expect that the 50% ethanol mixture would be more effective in removing PAHs than alkanes. The hydrocarbon data in Fig. 8 indicate similar hydrocarbon removals for the crosscurrent and countercurrent systems, where less than 45% removal of hydrocarbons was achieved after three wash stages.

4. Conclusions

The 50% ethanol solution proved to be as effective as more concentrated solutions of ethanol in removing PCP from field soils in batch extraction tests. Maximum observed PCP removal from field soils occurred within an hour of contact time between soil and solvent.

In crosscurrent washing of field soil A at soil:solvent ratios equal to or less than 1:2 (g:ml), at least two wash stages with 50% ethanol were needed to remove more than 77% of the PCP. At a 1:4 (g:ml) soil:solvent ratio, three wash stages removed nearly 87% of the PCP from field soil A. Ethanol recoveries were greater than 92% when the three- and two-stage crosscurrent washing processes were followed by water rinse stages. The 50% ethanol solution removed hydrocarbons from the field soils in addition to PCP, especially PAHs. In three-stage solvent washing process, countercurrent washing removed nearly three times more PCP per volume of solvent than a similar crosscurrent solvent washing process.

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