

## Removal of PAHs from highly contaminated soils found at prior manufactured gas operations

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### Abstract

Removal of PAHs from highly contaminated soil found at a manufactured gas site was evaluated using solvent washing with mixed solvents. The following solvents were considered as water miscible co-solvents in mixed solvents: ethanol, 2-propanol, acetone, and 1-pentanol. In batch solvent extraction of soil, ethanol and 2-propanol were selected as primary components of mixed solvents in addition to 1-pentanol. Using ternary solutions containing either ethanol or 2-propanol with a volume fraction of 1-pentanol ranging from 5 to 25% and a water volume fraction ranging from 5 to 30%, ethanol was more effective than 2-propanol in extracting PAHs from soil. A solvent mixture of 5% 1-pentanol, 10% water and 85% ethanol was selected as the extraction solvent. Using a 1 g:4 ml soil:solvent extraction ratio, extraction kinetics showed that from 65 to 90% of the extractable PAHs were removed within an hour of contact between soil and solvent. Using this 1 g:4 ml extraction ratio, PAHs were removed in a three-stage cross-current solvent washing process where the same batch of soil was extracted with clean solvent for 1 h in each stage. PAH removals in three-stage cross-current solvent washing were comparable to PAH removals obtained with Soxhlet extraction. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Co-solvent; 1-Pentanol; Ethanol; 2-Propanol; Polycyclic aromatic hydrocarbons (PAHs); Solvent washing

### 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are present in varying amounts at most abandoned manufactured gas sites, primarily as part of coal and oil tars (nonaqueous phase

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liquids, NAPLs) produced during the manufacture of town gas from coal, coke, and oil. Widespread contamination of soil and groundwater with PAHs has resulted from manufactured gas plant operations dating back to the late 19th and early 20th centuries [1,2]. Some of these PAHs are on the U.S. Environmental Protection Agency (EPA) List of Priority Pollutants [3] and the more recalcitrant of them (primarily the five- and six-ring compounds) remain virtually unchanged today in soil and groundwater many years after cessation of town gas manufacture.

Manufactured gas was produced at a site near downtown Bedford, IN, for  $\approx 30$  years (1900–1930). The soil and groundwater at the site are contaminated with PAHs. The level of contamination at the site generally varies from 400–500 to 4000–5000 mg/kg total PAHs. In several ‘hot-spot’ zones, however, total PAH concentrations range up to 30,000 mg/kg. The water-table level ranges from  $\approx 3$  to 8 ft below ground surface. PAH concentrations tend to increase with soil depth with significantly higher concentrations found in the saturated zone than in the vadose zone. Free product was encountered at the water-table interface at some sampling locations.

The ‘hot-spot’ zones with the highest soil PAH concentrations (10,000–30,000 mg/kg) were found in the vicinity of the prior process production facility and gas holder. Soils contaminated with such high PAH concentrations will not be amenable to most biotreatment approaches if pretreatment is not first employed to lower PAH concentration and toxicity. These highly contaminated soils, undiluted, would not be considered promising candidates for bioremediation. Soil cleanup alternatives currently include ex situ (but on-site) land treatment, biopile/composting treatment, and bioslurry treatment and in situ phytoremediation and natural attenuation.

This study was conducted to determine whether soil solvent washing should also be considered as a cleanup alternative for the Bedford, IN, site and, if so, under what treatment conditions. Solvent washing of contaminated soils may be a viable soil cleanup technology [4–7]. In remediation of contaminated soils, the selection of solvent for either in situ or ex situ washing of soils with solvent depends on several factors that influence the effectiveness of the solvent in contaminant removal [5]. Solubility of the organic pollutant in the solvent and miscibility of the solvent with water are important factors [8]. Ex situ soil solvent washing may be a cost effective and rapid-response alternative to on site and in situ bioremediation when soil solvent washing is followed by the recovery of solvent, and biotreatment of contaminant residuals after solvent recovery [7,9].

Previously, researchers have successfully dissolved the PAH constituents of coal tar in mixed solvents containing solutions of water and water-miscible co-solvents such as acetone and 2-propanol [10,11]. Others have shown the effectiveness of methanol, ethanol, 2-propanol, tertiary butyl alcohol and 1-pentanol in flushing and extracting constituents of jet fuel, chlorinated solvents, wood preservers, and several PAHs from wet soils found at contaminated sites [12–17]. Some of these studies were conducted inside the laboratory at bench scale, and others were carried out as in situ and ex situ field studies. Mixed solvents containing water and a water miscible solvent, a co-solvent, can be effective in ex situ extraction of organic contaminants from wet excavated soils. In this study, the removal of PAHs from highly contaminated excavated soils was evaluated using solvent washing with mixed solvents.

Table 1  
Solvents

Chemical	Specification	Source
Ethanol	190 proof, USP grade	Midwest Grain Products, Weston, MO
Ethanol	200 proof, USP grade	Midwest Grain Products, Weston, MO
2-Propanol	ACS Certified	Fisher Chemicals, Fairlawn, NJ
Acetone	ACS Certified	Fisher Chemicals, Fairlawn, NJ
1-Pentanol	ACS Certified	Fisher Chemicals, Fairlawn, NJ
Methanol	ACS Certified	Fisher Chemicals, Fairlawn, NJ
Dichloromethane	ACS Certified	Fisher Chemicals, Fairlawn, NJ

## 2. Materials and methods

### 2.1. Solvents

The solvents used in this study are listed in Table 1. MilliQ grade deionized water (DI) with a resistivity  $>18\text{ M}\Omega$  was produced inside the laboratory by processing tap water through a Millipore purification system (Millipore Corporation, Bedford, MA).

### 2.2. Soil

A sandy loam contaminated soil was obtained from the ‘hot-spot’ area at the Bedford, IN, site. Table 2 lists some of the ‘hot-spot’ soil properties. This soil had an organic matter content of 19.8% and a moisture content of 18.7%.

### 2.3. Extraction and PAH analysis of liquid samples

Table 3 lists the 19 PAH analytes that were measured. The standard PAH mixtures were obtained from AccuStandard, Inc. (New Haven, CT) with a purity of 99% or higher. Liquid samples were filtered through 0.45- $\mu\text{m}$  membranes (Micron Separations Inc., Westboro, MA) and diluted in ethanol. Water was added to the diluted samples and the aqueous samples were acidified to pH 2 with concentrated hydrochloric acid. Aqueous samples

Table 2  
Soil properties

Sand (%)	83
Silt (%)	16
Clay (%)	1
Bulk density (g/ml)	0.95
Cation exchange capacity (meq/100 g)	12.4
Moisture (%)	18.7
Organic matter (%)	19.2
pH	8.2

Table 3  
Quantitated PAHs

PAH	Number of aromatic rings
Naphthalene	Two
2-Methyl naphthalene	
Acenaphthylene	Three
Acenaphthene	
Dibenzofuran	
Fluorene	
Phenanthrene	
Anthracene	
Fluoranthene	Four
Pyrene	
Benzo(a)anthracene	
Chrysene	
Benzo(b)fluoranthene	Five
Benzo(k)fluoranthene	
Benzo(e)pyrene	
Benzo(a)pyrene	
Dibenzo(ah)anthracene	
Indeno(123-cd)pyrene	Six
Benzo(ghi)perylene	

were extracted with hexane to transfer PAHs from the aqueous phase to the organic phase for gas chromatograph (GC) analysis. During solvent exchange, 2-fluorobiphenyl was used as a surrogate. PAH concentrations in liquid samples were analyzed with a J&W 30-m long, 0.53-mm I.D. DB-5 fused silica capillary column (J&W Scientific, Folsom, CA) using a 5890 Series II HP (Hewlett-Packard, Palo Alto, CA) GC with a flame ionization detector (FID). Nitrogen was used as carrier gas.

#### 2.4. Solvent extraction of soil samples: shaking extractions

Soil was extracted in triplicates with pure or mixed solvent using soil:solvent extraction ratios ranging from 1:100 to 1:2 (g:ml). Contaminated soil was placed inside 160 ml glass bottles, solvent was added to the soil at different soil:solvent extraction ratios, the bottles were capped and placed inside a rotating shaker at 16 rpm at 24°C. Solvent extraction lasted from 1 to 72 h.

#### 2.5. Cross-current solvent washing

Soil was washed in multiple wash stages for the same period of time (determined by the shaking extraction procedure) at each wash stage. Fig. 1 shows a three-stage cross-current solvent washing train where a batch of contaminated soil came in contact with three batches of clean solvent. In stage I, contaminated soil was washed (extracted) with

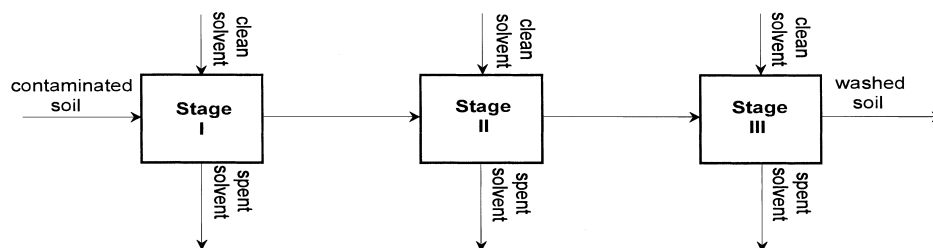


Fig. 1. Solvent washing of soil in three cross-current stages (multi-stage extraction).

clean solvent at a given soil:solvent extraction or contact ratio (g:ml). In stage II, the once-washed soil from stage I was washed with clean solvent a second time. In stage III, the twice-washed soil from stage II was washed a third time with clean solvent. After each wash stage, spent solvent was separated from the washed soil by centrifuging the soil slurry for 30 min at 2600 g. The entire three-stage solvent washing process was performed in triplicates.

### 2.6. Soxhlet extractions

In Soxhlet extraction experiments, 0.5–1.0 g of soil was extracted with 100 ml of methanol for 1 day followed by 150 ml of dichloromethane for 3 days. Triplicate experiments were performed for Soxhlet extractions.

## 3. Results and discussion

### 3.1. Selection of mixed solvent

Samples of soil from the ‘hot-spot’ were extracted using neat 1-pentanol, ethanol, 2-propanol, and acetone. Extraction experiments were performed using a soil:solvent extraction ratio of 1 g:100 ml for 24 h. The extraction data for several PAH compounds presented in Fig. 2 indicate that, while 1-pentanol was most effective in removing naphthalene and less effective with 4-ring PAHs, removals were generally comparable for ethanol, 2-propanol, acetone, and 1-pentanol. Since extraction performance with acetone was not superior to the other solvents, acetone was not further considered in solvent selection due to cost and safety. In selecting the solvent mixture, 1-pentanol was not considered as a primary solvent due to high cost. Instead, 1-pentanol was considered as a complementary co-solvent (higher removal of naphthalene) in mixtures with either ethanol or 2-propanol as the primary solvent, due to lower cost and possible recovery and reuse.

Since water was present in excavated soil as moisture, and since ethanol was mostly available commercially as a mixture of 95% ethanol and 5% water, water was considered as a component of the extracting solvent in ternary mixtures of water, 1-pentanol,

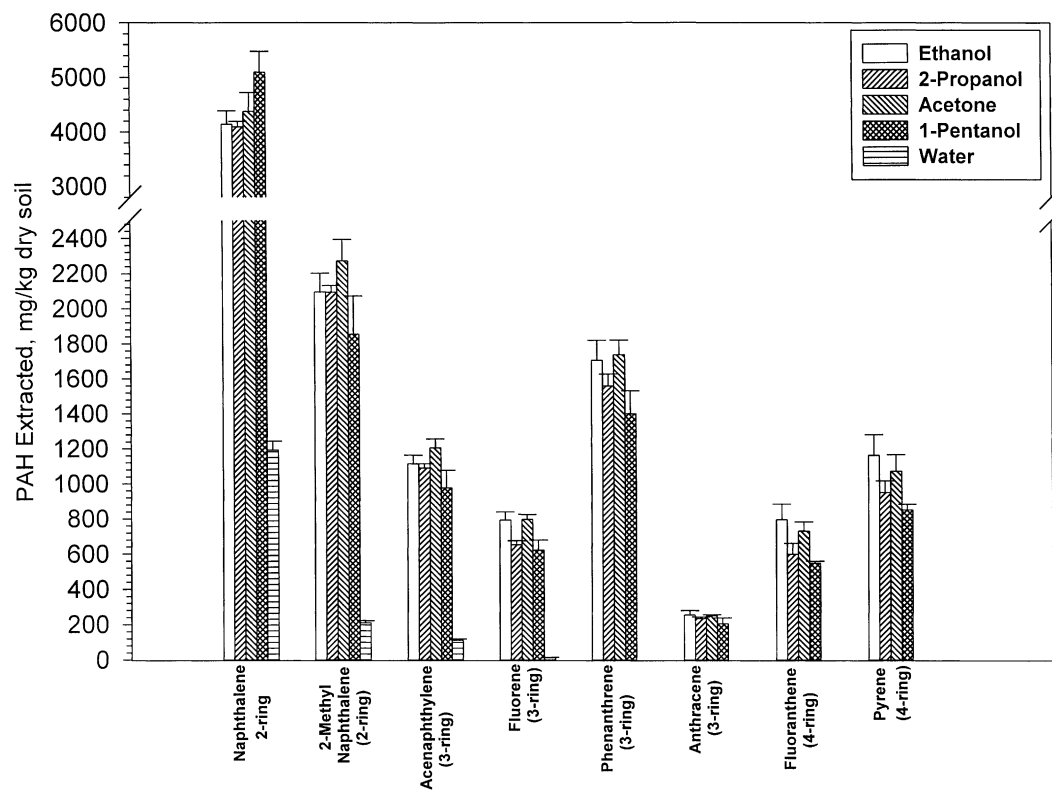


Fig. 2. Extraction of PAHs with pure solvents using an extraction ratio of 1 g:100 ml.

and either ethanol or 2-propanol. Soil was extracted for 24 h using a soil:solvent extraction ratio of 1 g:100 ml. The proportion of 1-pentanol in the mixed solvent varied from 5 to 25% by volume, while the proportion of water in the mixed solvent varied from 5 to 30% by volume, with either ethanol or 2-propanol making up the rest of the mixed solvent.

The extraction data for representative 2-, 3-, 4-, 5- and 6-ring PAH compounds are presented in Fig. 3 for mixed solvents containing 5% 1-pentanol and mixtures of water and ethanol. These extraction data show a general decrease in extraction of PAHs with more than four rings when the mixed solvent contained 30% water. This decrease became less significant for higher fractions of 1-pentanol in the mixed solvent. Similar results were obtained for mixed solvents containing 10 and 25% 1-pentanol and mixtures of water and ethanol. The extraction of representative PAHs are presented in Fig. 4 as a function of the water fraction in mixed solvents containing 10% water. These data indicate an increase in naphthalene extraction with increasing fraction of 1-pentanol, but no significant increases in extraction of the 3-, 4-, 5- and 6-ring PAHs. Similar results were obtained for mixtures of 1-pentanol, water, and ethanol containing 5, 15, 20 and 30% water.

The extraction data for mixed solvents containing 5% pentanol, 10% water, and either ethanol or 2-propanol presented in Fig. 5 show better removals using ethanol in the mixture. For all sets of extraction experiments with ternary mixtures, extractions using ethanol produced either higher or equal removals than 2-propanol. From the various mixtures of solvents containing ethanol, the following solvent mixture was selected as the extraction solvent for further optimization of the extraction process: 5% pentanol–10% water–85% ethanol.

### 3.2. Soil:solvent contact ratio and extraction time

In order to reduce solvent expenditures in later solvent washing of soil, an extraction ratio of 1 g:4 ml was selected for optimization of the solvent washing process. PAH extraction kinetics for single-stage extraction were determined using a soil:solvent extraction ratio of 1 g:4 ml. The information from the kinetics data was used to design subsequent multiple-stage extraction experiments.

### 3.3. PAH removal kinetics

The extraction kinetics data for the 5% pentanol–10% water–85% ethanol mixture presented in Fig. 6 show that maximum PAH removal was obtained after 12 h of extraction for the 2-, 3-, and 4-ring PAHs, while maximum PAH removal was obtained after 24 h of extraction for the 5- and 6-ring PAHs. The following average PAH removal fractions in 1 h were calculated based on the extraction data for 72 h: 89.7% for 2-ring PAHs, 87.8% for 3-ring PAHs, 81.0% for 4-ring PAHs, 69.8% for 5-ring PAHs, and 64.4% for 6-ring PAHs. The extraction kinetics data indicate that the 4-, 5- and 6-ring PAHs — the more hydrophobic PAH compounds — desorbed more slowly from the soil than the less hydrophobic PAHs (2- and 3-ring ones).

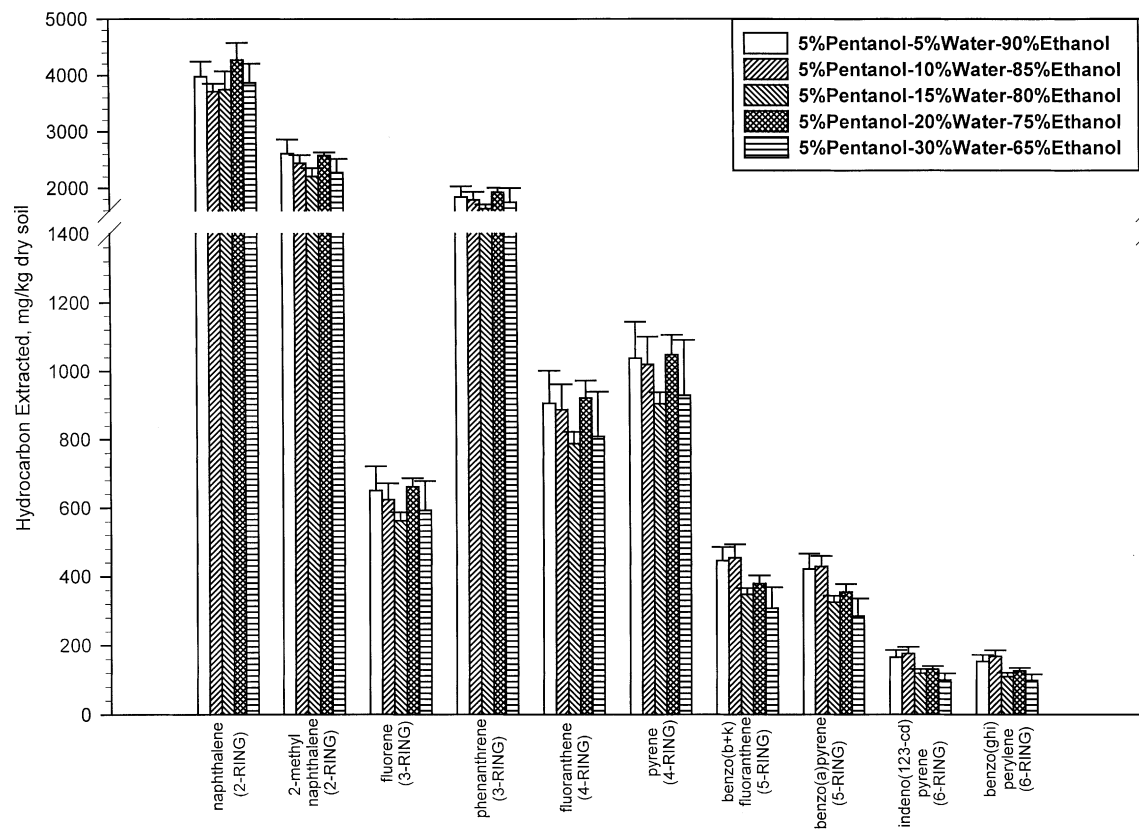


Fig. 3. Extraction of PAHs using mixed solvents: 5% pentanol and mixtures of ethanol and water.



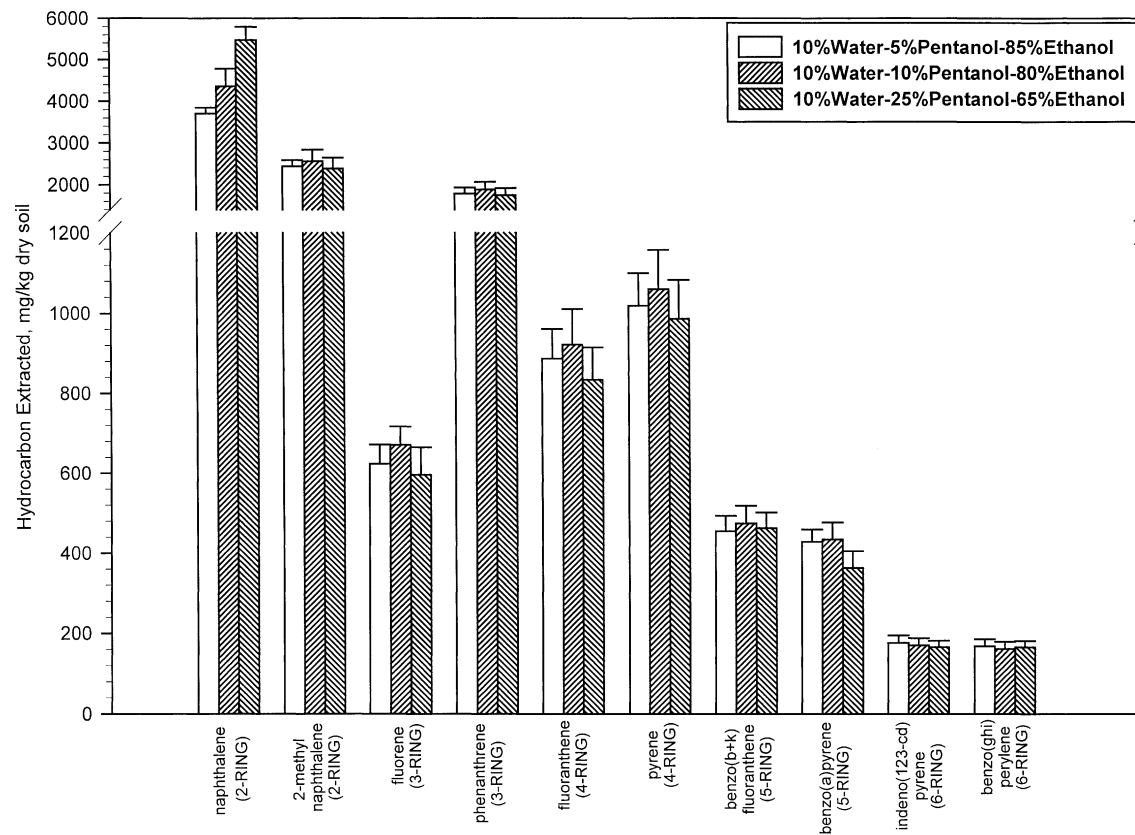


Fig. 4. Extraction of PAHs using mixed solvents: 10% water and mixtures of 1-pentanol and ethanol.

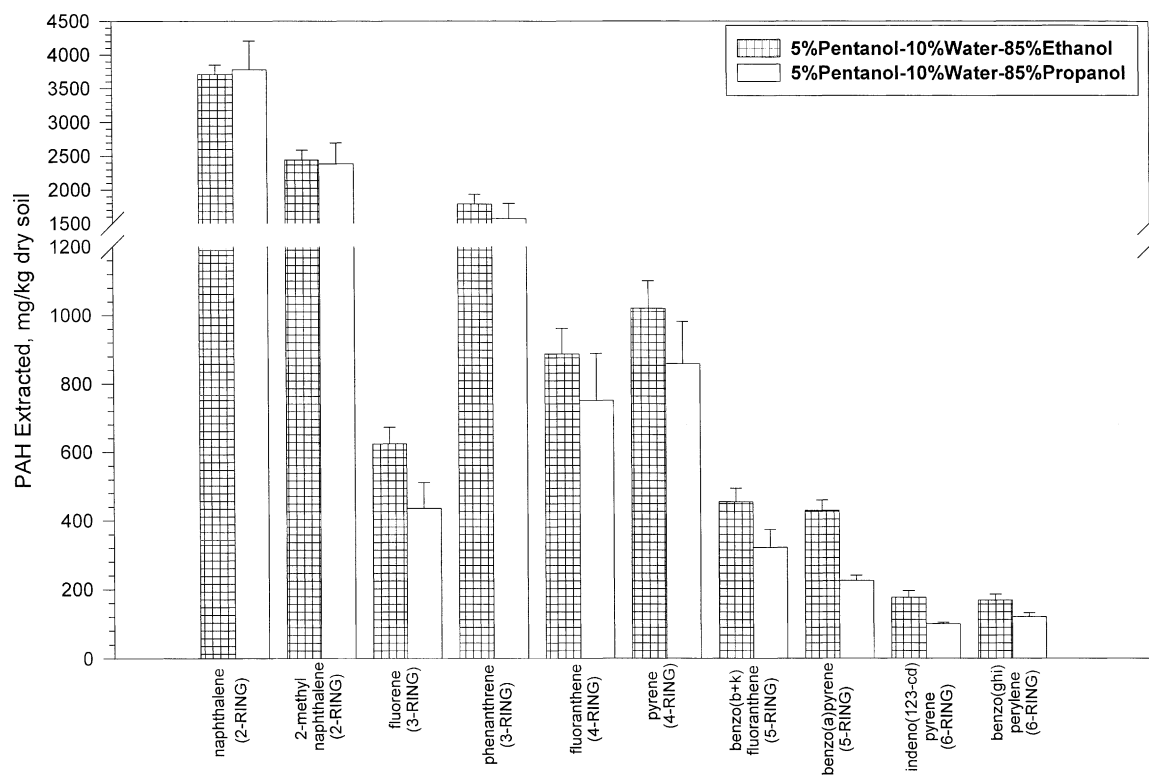


Fig. 5. Extraction of PAHs using mixed solvents with 5% pentanol and 10% water: ethanol vs. 2-propanol.

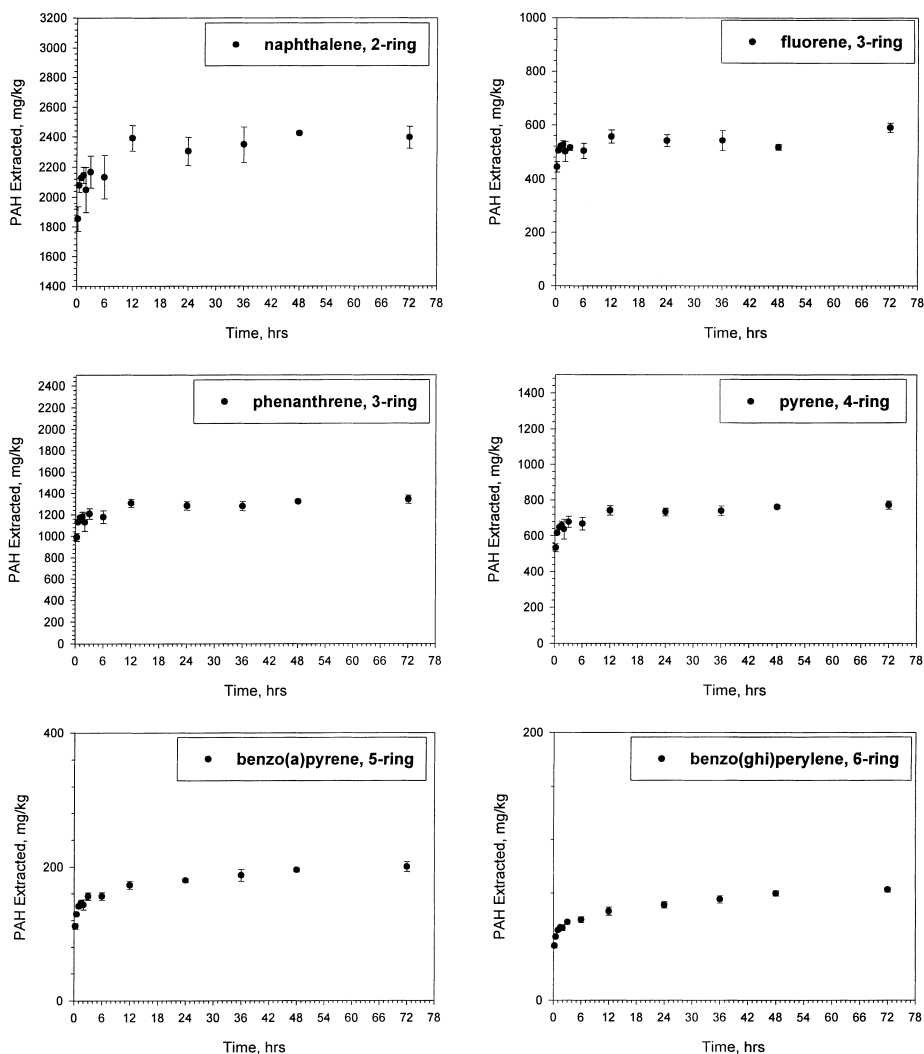


Fig. 6. Extraction of PAHs with time using 5% pentanol–10% Water–85% ethanol.

### 3.4. Solvent washing

The removal of PAHs was evaluated in three crosscurrent wash (extraction) stages using a soil:solvent contact ratio of 1 g:4 ml, where 1 g of soil was extracted with 4 ml of clean (fresh) solvent for 1 h at each wash stage. The extraction data presented in Fig. 7 show additional removal of PAHs from the soil during the second and third wash stages. The PAH data from Fig. 7 show that the additional removal of PAHs during the second and third wash stages was more substantial for the 4-, 5- and 6-ring PAHs, indicating that, for the

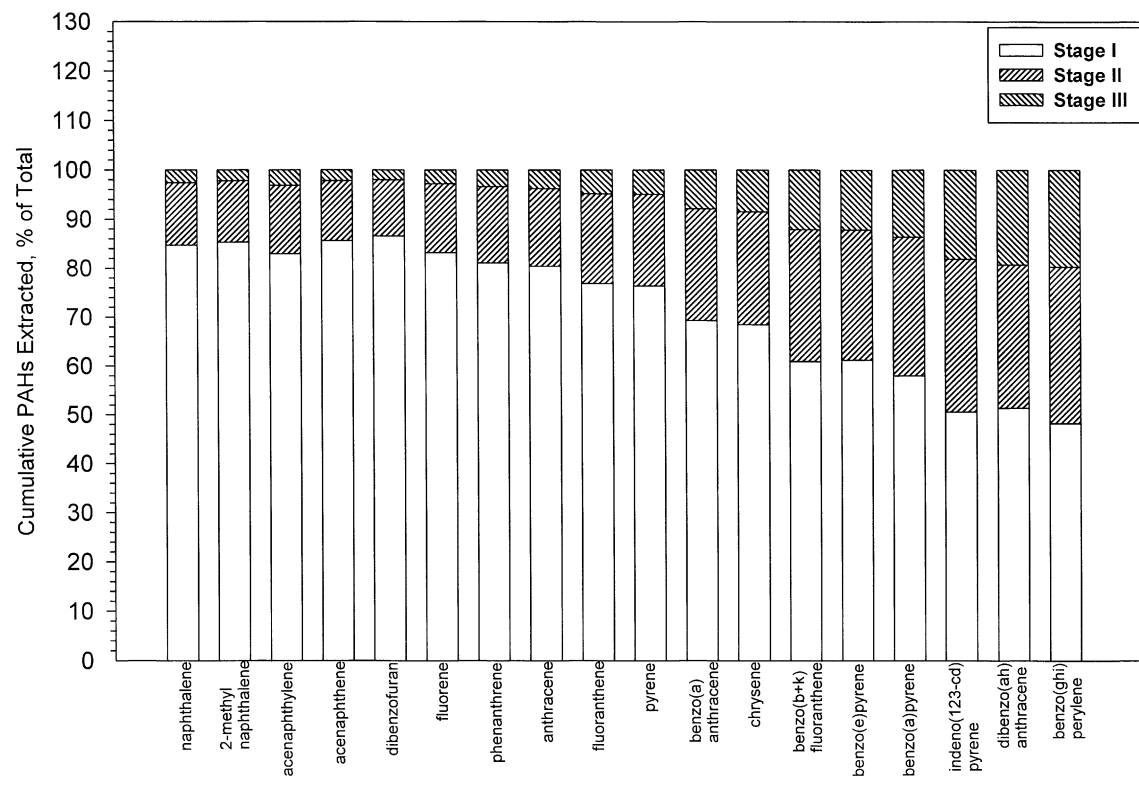


Fig. 7. Average PAH removal in three-stage cross-current solvent washing of soil at 1g:4ml soil:solvent contact ratio with 5% pentanol–10% water–85% ethanol.

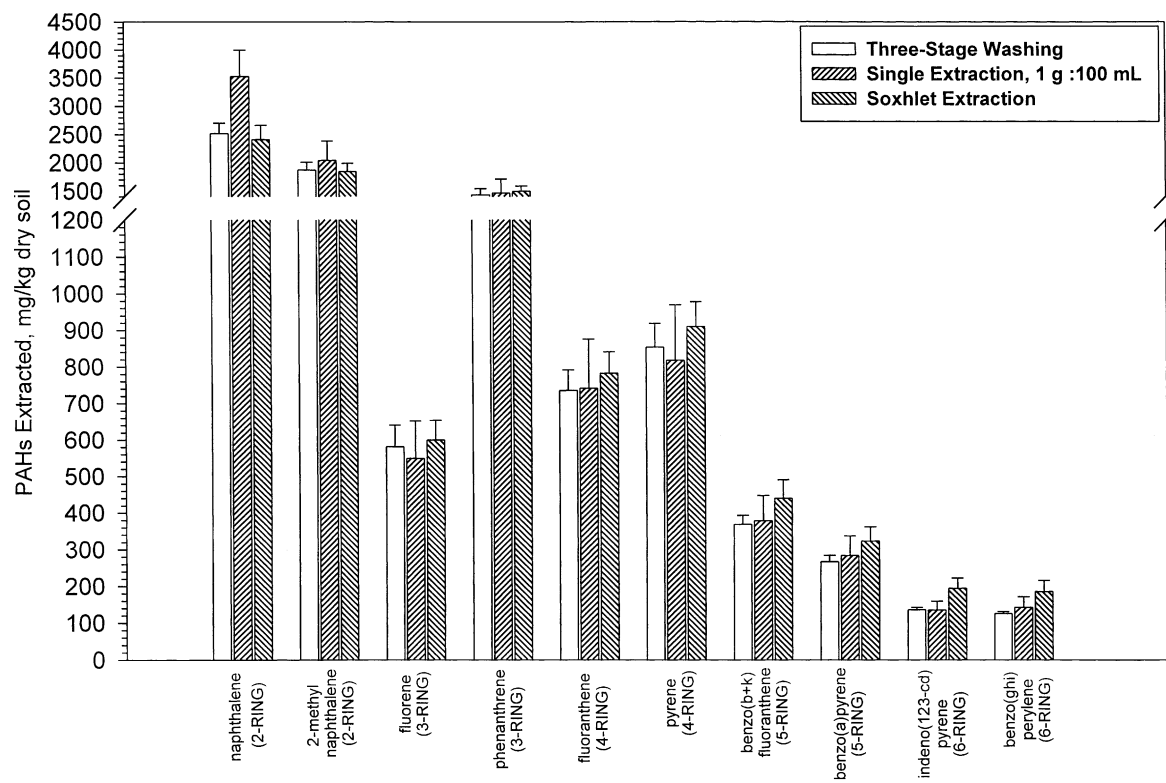


Fig. 8. Single and three-stage extraction with 5% pentanol–10% water–85% ethanol vs. Soxhlet extraction.

Table 4  
PAH removal for groups of PAHs (mg/kg)

	Soxhlet extraction	Three-stage solvent washing	Removal by solvent washing (%)
2-Ring PAHs	4250.7±397.2	4386.5±320.0	103.2
3-Ring PAHs	3685.3±260.4	3558.4±279.2	96.6
4-Ring PAHs	2313.4±185.3	2156.1±160.8	93.2
5-Ring PAHs	1021.4±123.7	853.9±55.6	83.6
6-Ring PAHs	379.6±57.4	261.9±12.0	68.9
Small PAHs (2-, 3-ring)	7936.2±635.1	7944.9±597.5	100.1
Large PAHs (4-, 5-, 6-ring)	3714.4±363.0	3271.9±227.9	88.1
Total PAHs	11650.4±980.9	11216.8±825.3	96.3

same extraction time, the additional batches of wash solvent were effective in removing the more hydrophobic PAHs which have sorbed more strongly onto the soil organic matter [18].

Soxhlet extraction of soil was performed to determine the extractable level of PAHs from this soil using methanol and dichloromethane. The data from Soxhlet extraction, from single extraction for 24 h using a 1 g:100 ml soil:solvent ratio of the optimized solvent mixture, and from three-stage cross-current solvent washing using a 1 g:4 ml ratio of the optimized solvent mixture for 1 h in each stage are shown in Fig. 8. These indicate that the removal of PAHs in three-stage cross-current solvent washing using a total of 12 ml of solvent per gram of contaminated soil was comparable to both the single-stage solvent washing using 100 ml of the same solvent mixture and Soxhlet extraction procedures. The total removals for groups of PAHs are presented in Table 4 for Soxhlet extraction and three-stage solvent washing, showing that the PAH removals obtained with three-stage solvent washing were 96.3% of the Soxhlet removals. The data from Table 4 also show that for 2-, 3- and 4-ring PAHs, the PAH removals were >93% of the PAH removals with Soxhlet extraction, and that for small and large PAHs, the removals were 100.1 and 88.1% of Soxhlet removals, respectively.

### 3.5. Solvent recovery

To recover the spent solvent from the three-stage cross-current solvent washing process, the washed soil after the third wash stage was rinsed with water in several water rinse stages. To separate the PAHs from the spent liquid, the pH of the spent wash solution (spent solvent plus rinse water) solvent was adjusted after each water rinse stage. The pH of the solution was adjusted to a pH >10 by the addition of 10 N sodium hydroxide solution. Fig. 9 shows the reduction in PAH levels in the spent wash solution (spent solvent plus rinse water), indicating that >90% of the all the PAHs were removed from the spent wash solution by adjusting the pH after three rinse stages. After separating the PAHs from the spent wash solution, the co-solvent fraction of the mixed solvent can be recycled by feeding the wash solution to a distillation column [9].

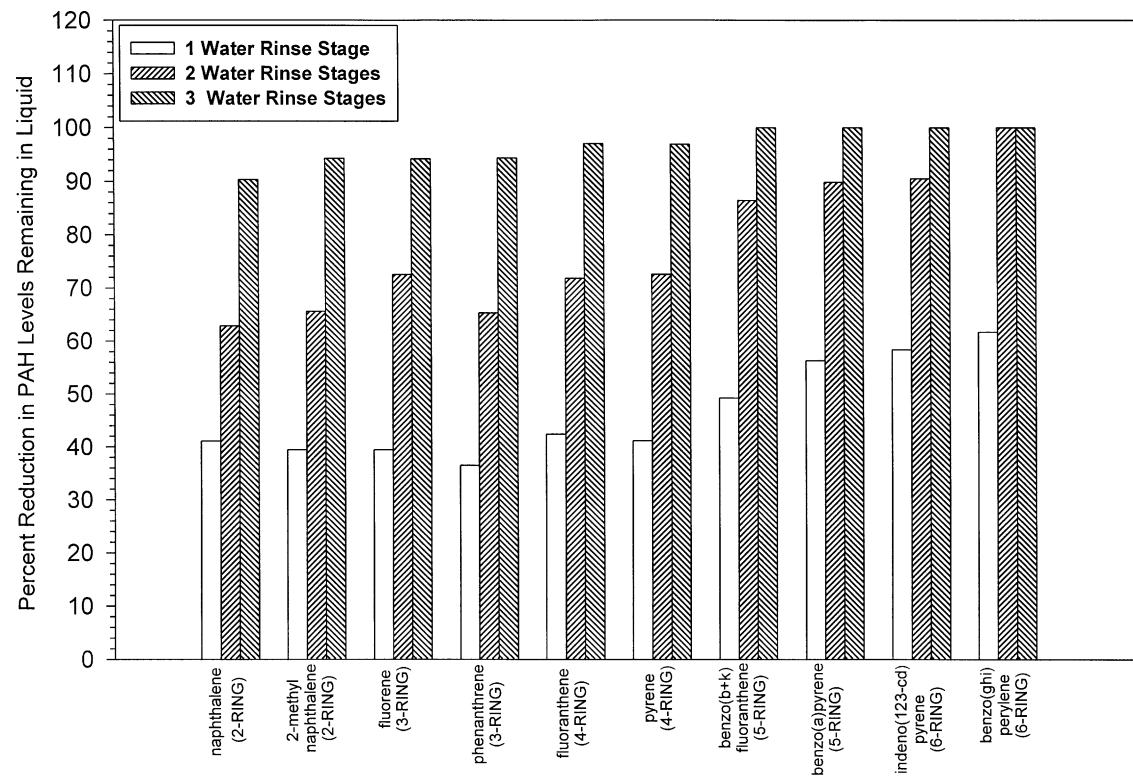


Fig. 9. Average reduction of PAH levels in spent wash liquids after pH adjustment to pH >10.

#### 4. Conclusions

A ternary mixture of 5% 1-pentanol, 10% water, and 85% ethanol was effective in solvent washing of a PAH contaminated soil found at a former manufactured gas facility. A three-stage cross-current solvent washing train was capable of removing >95% of the PAH contamination from highly contaminated field soils.

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