Effective treatment of PAH contaminated Superfund site soil with the peroxy-acid process

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Abstract

Peroxy-organic acids are formed by the chemical reaction between organic acids and hydrogen peroxide. The peroxy-acid process was applied to two Superfund site soils provided by the U.S. Environmental Protection Agency (EPA). Initial small-scale experiments applied ratios of 3:5:7 (v/v/v) or 3:3:9 (v/v/v) hydrogen peroxide:acetic acid:deionized (DI) water solution to 5 g of Superfund site soil. The experiment using 3:5:7 (v/v/v) ratio resulted in an almost complete degradation of the 14 EPA regulated polycyclic aromatic hydrocarbons (PAHs) in Bedford LT soil during a 24-h reaction period, while the 3:3:9 (v/v/v) ratio resulted in no applicable degradation in Bedford LT lot 10 soil over the same reaction period. Specific Superfund site soil characteristics (*e.g.*, pH, total organic carbon content and particle size distribution) were found to play an important role in the availability of the PAHs and the efficiency of the transformation during the peroxy-acid process. A scaled-up experiment followed treating 150 g of Bedford LT lot 10 soil with and without mixing. The scaled-up processes applied a 3:3:9 (v/v/v) solution resulting in significant decrease in PAH contamination. These findings demonstrate the peroxy-acid process as a viable option for the treatment of PAH contaminated soils. Further work is necessary in order to elucidate the mechanisms of this process.
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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are compounds made of two or more fused benzene rings and are found everywhere in the environment. In general, PAHs are hydrophobic organic compounds (HOCs), which exhibit lipophilic properties, hence their likeliness to bioaccumulate. PAHs are the products of natural pyrogenic processes and are synthesized by some bacteria, plants and fungi [1] and anthropogenic activities resulting in incomplete combustion. The latter activities include petroleum refining, transportation, former manufacturing gas plants (FMGPs), lignite pyrolysis, military installations, municipal and hazardous waste landfills [1–3] diesel or oil refinery spills, coal tar processing, and wood treatment [1,3,4]. These pollutants have also been found in foods such as edible fats and oils [5,6], products [6], smoked foods, and cereals [6,7] as well as in cigarettes and other tobacco-containing products [8].

PAHs are also persistent organic pollutants (POPs) that have been determined to exhibit mutagenic and carcinogenic properties, in both humans and animals. They may exhibit properties that differ from their pure phase properties when found in complex mixtures [1,2]. Therefore, it is imperative to find different effective PAH degradation techniques. Bioremediation is a preferred technique because of its ease of implementation but tends to be timely and often incomplete. Chemical and physical degradation techniques range from the transformation/mineralization of contaminants using ultraviolet (UV) radiation to their oxidation using compounds with high standard reduction potential [9–12]. These remediation techniques, although efficient at degrading recalcitrant compounds, can be costly especially at a large scale.

Polynuclear aromatics are also found at elevated concentrations at industrial sites, including former manufactured gas plants (MGPs), where coal tars have been produced. Many of these are now Superfund sites, which have employed a variety of remediation techniques to treat the high concentrations of PAHs. Superfund sites are any land in the U.S. that have been

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contaminated by hazardous waste and identified by the Environmental Protection Agency (EPA) as a candidate for cleanup because they pose a risk to human health and/or the environment. Between 1982 and 1995 Superfund sites predominantly used conventional remediation techniques such as soil vapor extraction and incineration to treat recalcitrant pollutants. More recently there has been an increased interest in more cost effective treatment strategies. Bioremediation is one of the most cost effective and widely used remediation techniques for treatment of Superfund sites. However, it often does a poor job treating higher molecular weight PAHs. Faster and more efficient degradation of these compounds has been observed with so called advanced oxidation processes (AOPs), which introduce a strong oxidant into the soil. However, even these new more popular techniques are poor at achieving complete removal of PAHs from aged soil. Non-homogenous soil contamination and treatment plateaus are among the problems, which need to be considered when attempting to characterize the efficiency of any abatement technique [13–15]. Therefore, the peroxy-acid process, an abatement technique, which depends on the formation of a peroxyacetic acid compound and the subsequent release of reactive species such as hydroxyl radicals can be considered as an AOP.

Peroxy-acids have been used for the epoxidation of alkenes. Bach et al. [16] proposed a mechanism for the peroxy-acid process, which involved the transfer of an oxygen atom from a peroxy-acid to an alkene. This is facilitated by electron-donating substituents on the carbon–carbon double bond on the alkene and the electron withdrawing groups on the peroxy-acid molecule. Another hypothetical mechanism for the peroxy-acid process used in this study involves the reaction of an organic acid, in this case acetic acid, with hydrogen peroxide through hydrogen abstraction and hydrogen peroxide cleavage to form a peroxyacid molecule and release a hydroxyl cation or radical from the peroxy-acid molecule. This phenomenon is partially due to the fact that certain chemical, such as acetic acid, are resistant to oxidation by hydroxyl radicals [17]. The hydroxyl radicals in turn oxidize the contaminant (*e.g.*, α-methylnaphthalene or benzo(*a*)pyrene). The resulting acetic acid/acetate is recycled to catalyze more reactions [18,19]. One can also suggest that both mechanisms described above could occur simultaneously and/or sequentially. If this suggested combined mechanism actually takes place in a peroxy-acid process it could explain why this technique has proven to be so effective.

The objective of this study was to apply the peroxy-acid process to two Superfund site soils to demonstrate the effectiveness of the proposed process on real matrices. The optimum volume of hydrogen peroxide was previously determined but not the optimum acetic acid volume. This optimization study had been performed using spiked sediment samples and focused on the degradation of single PAHs. It was therefore important to test this partially optimized process of 3:3:9 (v/v/v) hydrogen peroxide:acetic acid:deionized (DI) water on aged soils (*i.e.*, the Superfund Site soils) where PAHs have been present in a complex mixture for a long time. Furthermore, it is anticipated that this innovative peroxy-acid process is an efficient and a cost effective tool for the treatment of PAH-contaminated media such as sediments and soils.

2. Materials and methods

2.1. Materials

2.1.1. Chemicals

Standards of the 14 EPA-regulated PAHs were obtained from AccuStandard (New Haven, CT, USA). Selected properties of the 14 EPA PAHs are given in Table 1. Certified ACS plus grade glacial acetic acid, hydrogen peroxide (50%, v/v), certified ACS anhydrous sodium sulfite and anhydrous sodium sulfate were purchased from Fisher Scientific (Pittsburgh, PA, USA). Extraction solvents included hexane (HPLC grade), acetone (certified ACS grade), and dichloromethane (DCM) (HPLC grade) were all purchased from Fisher Scientific (Pittsburgh, PA, USA).

2.1.2. Soil samples

The U.S. EPA provided Superfund Site soil samples, which had been contaminated predominantly by PAHs. Both small- and large-scale experiments were conducted on unamended soil from Bedford LT and Bedford LT lot 10 plots. The Bedford LT soils were obtained from the Indiana Harbor located in East Chicago, Lake County, Indiana, on the southwest shore of Lake Michigan. This Superfund site has been contaminated by PCBs, PAHs and heavy metals.

2.2. Methods

2.2.1. Soil characterization

Soil moisture content was determined gravimetrically by drying soil samples in a 103 °C oven for 24 h. Total organic carbon (TOC) content for soil samples was determined by drying the samples at 103 °C for 24 h followed by ignition at 550 °C for another full day. Losses were determined gravimetrically. Soil pH was determined by rotating 5.0 g of dry soil with 5.0 mL of DI water for 1 day and measuring the pH of the suspension using a combination electrode connected to an AP 50 pH meter (Denver Instruments, Arvada, CO, USA) [20]. Wet sieving was used to determine the particle size distributions of the Superfund site soils investigated. In addition, Superfund site soil surface area was determined by using the gas adsorption BET method for nitrogen adsorption at −196 °C (Quantachrome Model AS-1). Soil metals were analyzed by atomic absorption spectroscopy with a Perkin Elmer AAnalyst 300 graphite furnace AA (GFAA) according to EPA method 3050B. Briefly, 1 g of dry soil was homogenized and digested first with concentrated nitric acid, followed by a 30% hydrogen peroxide solution. Digestions were carried out in 250 mL Erlenmeyer flasks covered with watch glasses and boiled gently on top of a hot plate. Samples were cooled and diluted to 100 mL with DI water, centrifuged at 820 × *g* to clear the supernatant and refrigerated until analysis.

2.2.2. Small-scale AOP process
2.2.2.1. Equilibration.
Aged Bedford LT or Bedford LT lot 10 Superfund site soil (5 g) was added to 125 mL Erlenmeyer flasks followed by the addition of 9 mL of DI water. Flasks were placed on a New Brunswick Scientific incubator shaker (Edison, NJ,

Table 1
Physico-chemical properties of the 14 PAHs used in this investigation

Name	Formula	Molecular weight (g/mol)	Density, ρ (g/cm³)	T_m (°C)	T_b (°C)	Vapor pressure, v_p (Pa)	Aqueous solubility, C_w^{sat} (mol/L)	Octanol–water partition coefficient, K_{ow}	Henry's constant, K_H (L Pa/mol)
Naphthalene	$C_{10}H_8$	128.2	1.16	80.2	218.0	1.12E+01	2.51E−04	2.14E+03	4.47E+04
Acenaphthylene	$C_{12}H_8$	152.2	0.90	92.5	270.0	8.91E−01	2.57E−05	1.00E+04	3.47E+04
Acenaphthene	$C_{12}H_{10}$	154.2	1.05	96.2	278.0	3.09E−01	2.45E−05	1.58E+04	1.58E+04
Fluorine	$C_{13}H_{10}$	166.2	1.20	116.0	295.0	9.55E−02	1.15	2.09E+04	8.32E+03
Phenanthrene	$C_{14}H_{10}$	178.2	0.98	101.0	339.0	2.19E−02	6.31E−06	3.72E+04	3.47E+03
Anthracene	$C_{14}H_{10}$	178.2	1.25	217.5	341.0	9.77E−04	2.51E−07	4.79E+04	3.89E+03
Fluoranthene	$C_{16}H_{10}$	202.3	1.25	110.5	384.0	1.23E−03	1.10E−06	1.70E+05	1.12E+03
Pyrene	$C_{16}H_{10}$	202.3	1.27	156.0	403.0	8.13E−04	6.92E−07	1.35E+05	1.17E+03
Benz(*a*)anthracene	$C_{18}H_{12}$	228.3	1.25	160.6	437.5	2.51E−05	4.79E−08	8.13E+05	5.25E+02
Chrysene	$C_{18}H_{12}$	228.3	1.28	255.0	448.0	6.03E−07	8.91E−09	6.46E+05	6.76E+01
Benzo(*a*)pyrene	$C_{20}H_{12}$	252.3	1.28	176.5	496.0	7.08E−07	7.24E−09	1.35E+06	9.77E+01
Indeno(1,2,3-*cd*)pyrene[a]	$C_{22}H_{12}$	276.3	na	162.0	na	na	na	na	na
Dibenzo(*ah*)anthracene[b]	$C_{22}H_{14}$	278.3	na	266.0	524.0	na	1.80E−09	na	na
Benzo(*ghi*)perylene[b]	$C_{22}H_{12}$	276.3	na	278.3	500.0	na	9.41E−10	na	na

Data obtained from [29]; na = not available.
[a] Data obtained from CRC Handbook of Chemistry and Physics online.
[b] Data obtained from Chemfinder.com.

USA) at 140 rpm overnight to equilibrate the soil-water solution before the reaction with acetic acid and hydrogen peroxide.

2.2.2.2. Reaction. The reaction was initiated by adding acetic acid (3 mL). Hydrogen peroxide (3 mL) was added to each tube after the 24-h equilibration period with DI water and addition of acetic acid. Samples were then placed back on the end-over-end rotator for chosen reaction times (between 0 and 24 h) after which they were quenched by adding 3 mL of a 1 M sodium sulfite solution. At least two replicates were analyzed for each experiment. In addition, four control experiments were also prepared. Controls A and B did not contain hydrogen peroxide and acetic acid, respectively. Control C contained only contaminated soil and DI water, and served also as an extraction efficiency experiment. Finally, control D contained only DI water and no soil. Table 2 illustrates the content of the different experimental tubes; each with a final reaction volume of 15 mL.

2.2.2.3. Extraction. Extraction was used to complete the mass balance. Therefore, once the reaction was quenched at the desired reaction time, 10 mL of a 50:50 (v/v) hexane or hexane and acetone mixture was added to each flask. Hexane has been used in several applications to extract PAHs, such as methylated naphthalenes and benzo(*a*)pyrene, both in aqueous and solid media [8,21–23]. Acetone is added to a non-polar or less polar extraction solvent in order to increase its polarity and the efficiency of PAH extraction from aged soil as a common practice [24–26]. The flasks were placed back on the shaker at 140 rpm for 24-h extraction. Solid and liquid phases were either extracted together or separately. The slurry was then transferred and centrifuged in 35 mL tubes at $22{,}000 \times g$ for 21 min at $-5\,°C$. Samples were ready for GC analysis after the supernatant, in this case the extraction solvent, was collected and filtered through sodium sulfate containing pipettes to remove any excess water. Samples were analyzed immediately or stored in the freezer until analysis.

2.2.3. Large-scale AOP process
2.2.3.1. Equilibration. One hundred and fifty grams of soil was added to 1000 mL beakers, followed by the addition of 270 mL of DI water. Beakers were placed on a shaker and allowed to mix overnight at 100 rpm before the reaction with acetic acid and hydrogen peroxide was initiated.

2.2.3.2. Reaction. Following the equilibration for a day, 90 mL of acetic acid followed by 90 mL of hydrogen peroxide were added to the beakers in a ratio of 3:3:9 (v/v/v) acetic acid:hydrogen peroxide:DI water. The experimental blanks were brought to volume with 180 mL of DI water. All samples were allowed to shake for 2 min on the shaker at 100 rpm. After 2 min half of the experiments were taken off the shaker and placed on the bench top in order to compare mixed and non-mixed reaction efficiencies. Table 2 illustrates additional information regarding the large-scale experimental set-up.

2.2.3.3. Extraction. Solid phase samples were taken from each vessel in triplicate. Five grams of soil were weighed and then

Table 2
Experimental conditions for the small and large-scale experiments

	Superfund Site Soil #10 (g)	Water (mL)	Acetic acid (mL)	Hydrogen peroxide (mL)	Sodium sulfite (mL)
Large-scale experiments					
E	150.0	270	90	90	
Em	150.0	270	90	90	
Controls					
B	150.0	450			
Bm	150.0	450			
Small-scale experiments					
E	5.0	9	3	3	3
Controls					
A	5.0	12	3		3
B	5.0	12		3	3
C	5.0	15			3
D		15			3

E = experiment without mixing; Em = experiment with mixing; B = background without mixing; Bm = background with mixing; A = acetic acid control; B = hydrogen peroxide control; C = DI water control; D = no soil control.

extracted with 10 mL of a 50:50 (v/v) hexane:acetone mixture for 24 h on an end-over-end rotator in the dark. Samples were ready for GC analysis after the extracts were filtered through sodium sulfate pipettes to remove excess water. As for the small-scale experiment, the samples for the large-scale study were analyzed immediately or stored in a freezer until analysis. Liquid phase samples were also taken in triplicate. Samples (15 mL) were extracted with DCM (5 mL) for 24 h on an end-over-end rotator in the dark.

2.2.4. GC analysis

Solvent extracts were analyzed using a GC equipped with a flame ionization detector (FID). The equipment used was a Shimadzu GC-17A equipped with an autoinjector AOC-20i (Columbia, MD, USA). The separation was obtained using a DB-5 capillary column (15 m with an inner diameter of 0.25 mm and a film thickness of 0.25 μm). The detector and injector temperatures were 317 °C. The oven temperature was held at 70 °C for 1 min, and then increased to 180 °C at the rate of 15 °C/min where it was held 3 min. The temperature was finally increased to 300 °C at 8 °C/min and held for 3 min. The injection volume was 1 μL. The peak areas of each injection were used to determine the concentration of each regulated PAH in the samples by comparison with a calibration curve made with external standards consisting of known amounts of the 14 EPA priority PAHs. At least three calibration standard concentrations were used for each GC run. In addition, the minimum detection limit was 3×10^{-12} g/s with a column flow rate of 0.9 mL/min.

3. Results and discussion

3.1. Soil characterization

The Superfund site soils used in this study had moisture contents of 25% and 18.5%, respectively, for Bedford LT lot 10 and Bedford LT soils. The TOC content was found to be 11% and 18.5%, respectively. The pH was near neutral (*e.g.*, 7.09 and 7.04) for both Superfund site soil samples investigated. In addition, the pH at the end of the peroxy-acid treatment was low because of the residual acetic acid left in the Superfund soil after removal of the liquid phase. These values for moisture content, TOC content and pH are average values of duplicate or triplicate measurements. The PSD revealed that the Superfund site soil collected from Bedford LT lot 10 consisted of 34.2% >850 μm and 37.2% <75 μm particles, respectively. The Bedford LT Superfund site soil PSD was found to be similar. Information on the characteristics of the Superfund site soils investigated is found in Table 3.

3.2. Metals

Selected metals were analyzed for both Bedford LT and Bedford LT lot 10 soil samples. Table 4 reports the results from iron (Fe^{3+}), calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), and sodium (Na^+) analysis. The results from Na^+, K^+, and Mg^{2+} analysis were similar for both Superfund site soils investigated. The Bedford LT lot 10 soil had approximately 41% and 85% more Fe^{3+} and Ca^{2+}, respectively. Typical background

Table 3
Selected properties of Superfund site Bedford LT soils used in this study

Soil ID	pH	OC (%)	SA (m²/g)	Moisture content (%)	Particle size distribution (%)					
					>850 μm	425–850 μm	250–425 μm	150–250 μm	75–150 μm	<75 μm
Bedford LT Lot 10	7.09	11	12.2	25	34.2	9.3	8.9	4.6	5.8	37.2
Bedford LT	7.04	18.5	7.44	18.5	45.3	8	8.1	5	5.5	28.2

Table 4
Selective metals analysis of Bedford LT and Bedford LT lot 10 soils

ID	Fe (g/kg)	Ca (g/kg)	Mg (g/kg)	K (g/kg)	Na (g/kg)
Bedford LT lot 10	87.7	78.5	3.8	1.8	0.5
Bedford LT	62.2	42.4	3.9	1.8	0.8

concentration of 63.5 g/kg iron has been found in Indiana soil [27]. A study by Kawahara et al. [28] determined the concentrations of 11 metals in PAH contaminated soil. These researcher found 17.3 g/kg, 2.17 g/kg, 1.12 g/kg and 0.185 g/kg of iron, magnesium, potassium, and sodium, respectively, demonstrating that our findings for the Bedford LT soils were similar.

3.3. Small-scale process

The partially optimized peroxy-acid process was used to treat aged Superfund site soils (*e.g.*, Bedford LT and Bedford LT lot 10) contaminated with multiple PAHs. Therefore, the partially optimized peroxy-acid used in this investigation consisted of 3:3:9 (v/v/v) or 3:5:7 (v/v/v) ratios of hydrogen peroxide:acetic acid:DI water. Fig. 1 represents an example of the small-scale study using the chromatograms of the PAHs present in Bedford LT at time 0 h (dotted line) and 24 h (bold line) in solid and liquid phases. As seen in the Fig. 1, the peroxy-acid process seemed to be quite effective in the degradation of most, if not all, of the EPA regulated PAHs.

Disappearance of naphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, benzo(*a*)anthracene, chrysene, benzo(*a*)pyrene, indeno(123-*cd*)pyrene, dibenz(*ah*)anthracene, and benzo(*ghi*)perylene were observed in Bedford LT Superfund site soil during the time-course study. Fig. 2A and B represents the results from the time-course behavior of the 14 PAHs investigated in this study using Bedford LT and Bedford LT lot 10 soils, respectively. The individual PAH concentration (mg/kg) consisted of the concentration of the 14 PAHs found in both the liquid and solid phases. The black bars represent total concentration of the 14 PAHs before the experiment (*e.g.*, 0 h) and the white bars represent the concentration after the experiment (*e.g.*, 24 h), respectively. During the period of treatment (ca. 24 h), the concentrations of 14 PAHs were observed to decline rapidly. In the case of the 3:5:7 (v/v/v) ratio of hydrogen peroxide:acetic acid:DI water, yielded approximately a 50% reduction of all 14 PAHs. In addition, in the Bedford LT soil both small (4 rings or less) and large (more than 4 rings) PAHs were found to be adequately degraded by the process (see Fig. 2A). The blanks (*e.g.*, hydrogen peroxide only, acetic acid only, DI water only and no soil) served as controls for these experiments; no applicable disappearance of the 14 PAHs were observed during the time-course study. Therefore, it was assumed that the degradation of naphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, benzo(*a*)anthracene, chrysene, benzo(*a*)pyrene, indeno(123-*cd*)pyrene, dibenz(*ah*)anthracene, and benzo(*ghi*)perylene was due to the peroxy-acid process. In the case of Bedford LT lot 10 soil, no applicable degradation of the 14 PAHs were observed (see Fig. 2B). One valid explanation for this finding was that the Bedford LT lot 10 soil had higher SA and higher fraction of smaller (*e.g.*, <75 μm) particles (see Table 3). In addition, the Bedford LT lot 10 had two to three times higher background concentration of total PAHs compared to Bedford LT. The background concentration of total PAHs for Bedford LT were between 500 and 1000 mg/kg and the Bedford LT lot 10
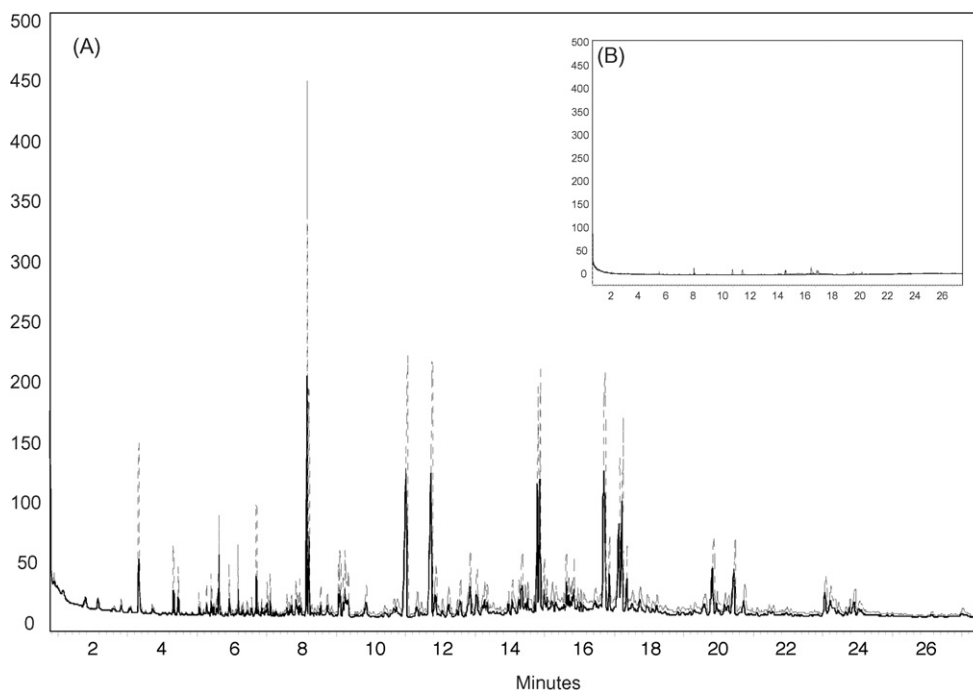

Fig. 1. Chromatograms of the small-scale (A) solid and (B) liquid samples of background (dotted line) and peroxy-acid treatment for Bedford LT soil after 24 h (solid lines).
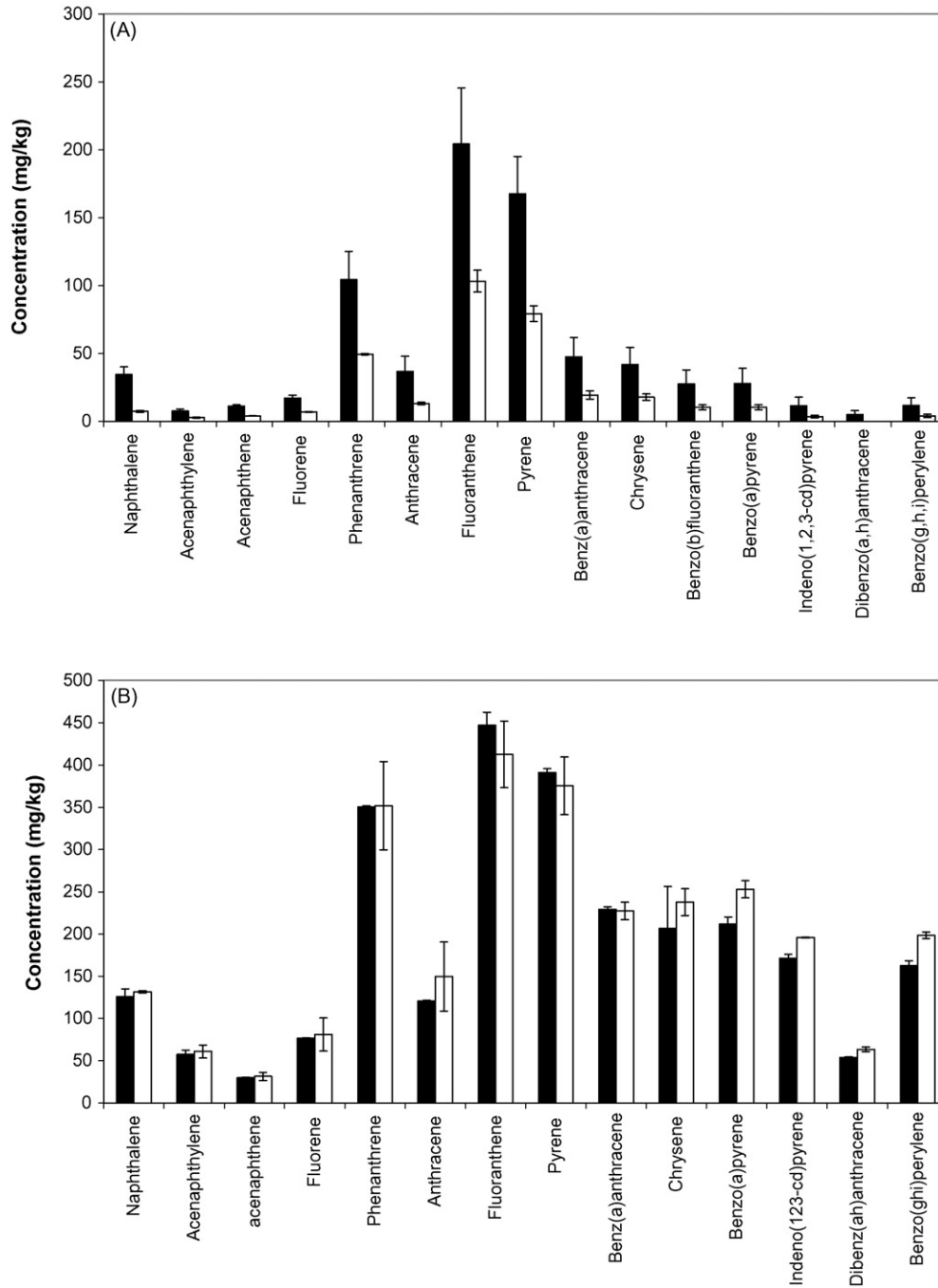
Fig. 2. Disappearance of 14 PAHs during the small-scale investigation using 5 g of (A) Bedford LT and (B) Bedford LT lot 10 Superfund site soils with 3:5:7 (v/v/v) and 3:3:9 (v/v/v) ratios of acetic acid:hydrogen peroxide:DI water, respectively. Black bars represent the background concentration of the PAHs and the white bars represent the results from the peroxy-acid treatment after 24 h. Error bars represent the deviation between triplicates.

had a background concentration of total PAHs in the order of 2000–3000 mg/kg.

To test the hypothesis that the results from Bedford LT lot 10 small-scale experiments were due to the two to three times larger total PAH concentration than Bedford LT, additional hydrogen peroxide was added to the experiment. Fig. 3A and B illustrates the findings from a double and triple dose experiments, respectively. The double dose experiments, containing 6 mL of hydrogen peroxide, resulted in a significant reduction in PAH contamination. A 32% difference in reduction of total PAHs

were found between experiments conducted with a 3:3:9 (v/v/v) ratio and those conducted with a final ratio of 3:6:9 (v/v/v) acetic acid:hydrogen peroxide:DI water (see Fig. 3A). An additional 19% reduction of the total PAH concentration resulted when the final dose was changed from 3:6:9 (v/v/v) to 3:9:9 (v/v/v) acetic acid:hydrogen peroxide:DI water (see Fig. 3B) with an overall reduction of 51% of the total PAH contamination (see Figs. 2 and 3). The process was successful at degrading each of the 14 individual PAHs studied, both small and large structures.
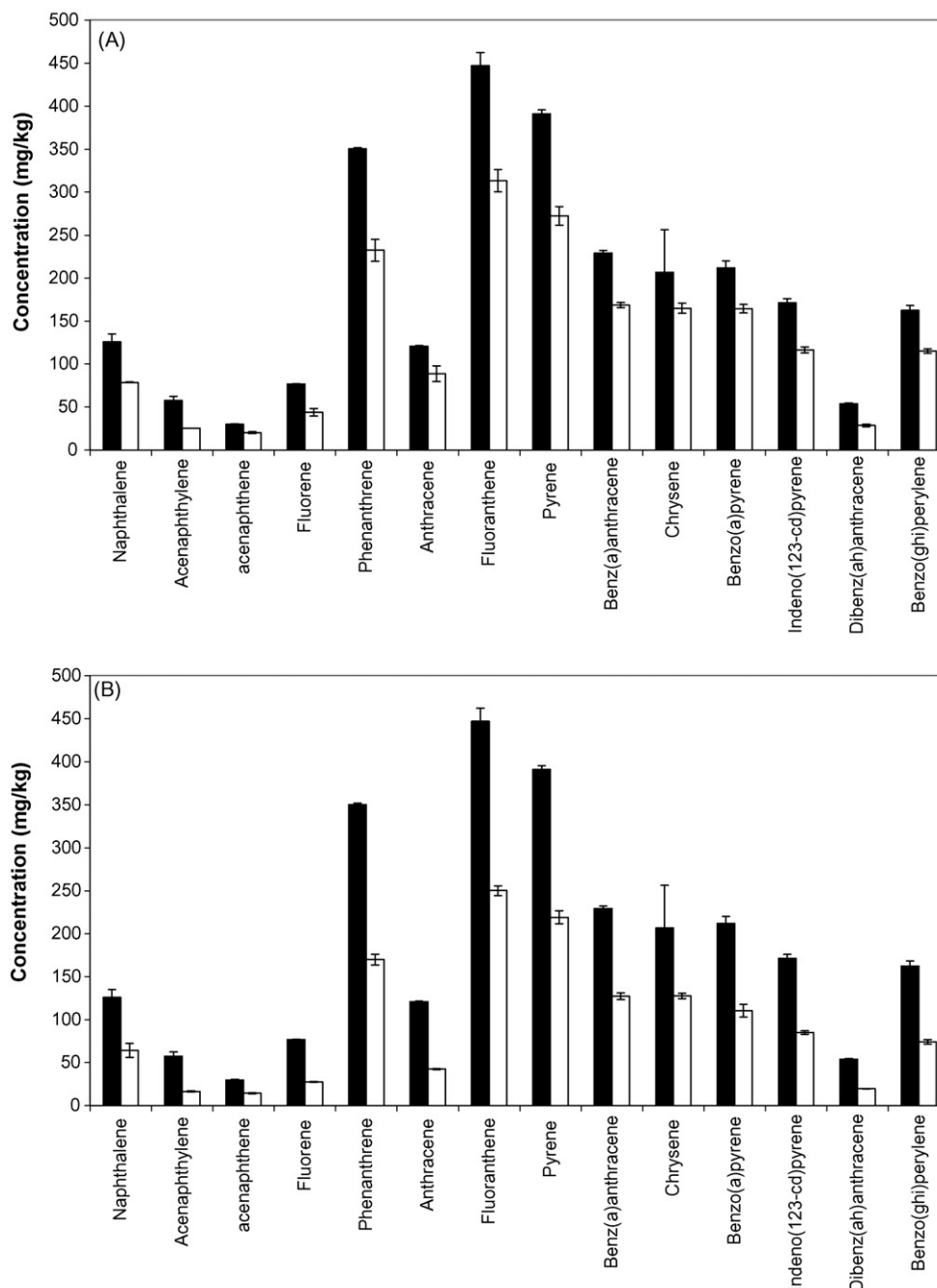
Fig. 3. Disappearance of 14 PAHs during the small-scale investigation using 5 g of (Bedford LT lot 10 Superfund site soil with (A) 3:6:9 (v/v/v) and (B) 3:9:9 (v/v/v) ratios of acetic acid:hydrogen peroxide:DI water, respectively. Black bars represent the background concentration of the PAHs and the white bars represent the results from the selected peroxy-acid treatment after 24 h. Error bars represent the deviation between triplicates.

3.4. Large-scale AOP process

Disappearance of naphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(a)pyrene, indeno(123-cd)pyrene, dibenz(ah)anthracene, and benzo(ghi)perylene was also observed in the large-scale study using the Bedford LT lot 10 Superfund site soil. Fig. 4 illustrates the results from the large-scale study. The PAHs concentration (mg/kg) is also calculated using the concentrations from both the liquid and solid

phases. In this large-scale study, the importance of mixing was also investigated. Disappearance of all 14 PAHs were observed during the 24-h reaction period. However, the disappearance of all 14 PAHs was observed to be less than what was observed during the small-scale study using the 3:3:9 ratio of hydrogen peroxide:acetic acid:DI water. The background, blanks without mixing (Bs), peroxy-acid experiments without mixing (Es), blanks with mixing (Bm) and experiments with mixing (Em) demonstrated some deviation. Mainly, the experiments without mixing did not provide evidence of disappearance of the
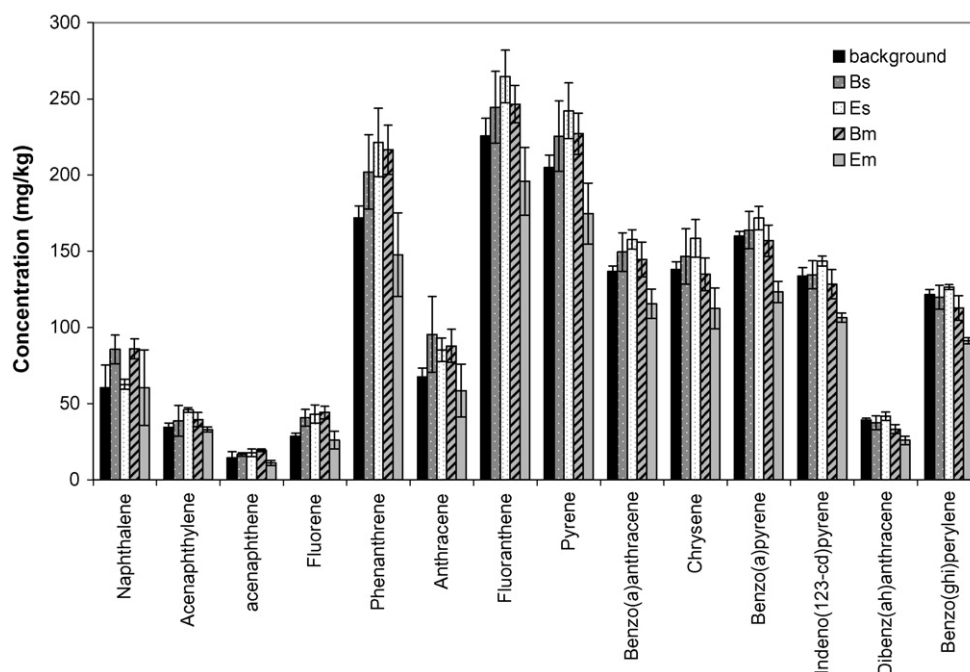
Fig. 4. Disappearance of 14 PAHs during the large-scale investigation using 150 g of Bedford LT Superfund site soil and 3:3:9 (v/v/v) ratio of acetic acid:hydrogen peroxide:DI water. Background, Bs, Es, Bm and Em correspond to background concentration of 14 PAHs in the Bedford LT lot 10 Superfund site soil without treatment, blanks without mixing, peroxy-acid treatment without mixing, blanks with mixing and peroxy-acid treatment with mixing, respectively.

14 PAHs while peroxy-acid experiments with mixing resulted in approximately 25% disappearance of the total mass of the 14 PAHs (see Fig. 4). These results suggest that mixing is needed for successful degradation of multiple PAHs during one peroxy-acid treatment cycle.

4. Conclusions

The optimum ratio of 3:3:9 of acetic acid:hydrogen peroxide:DI water was used to treat Bedford LT Superfund site soil containing aged PAHs. PAHs including naphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, benzo(*a*)anthracene, chrysene, benzo(*a*)pyrene, indeno(123-*cd*)pyrene, dibenz(*ah*)anthracene, and benzo(*ghi*)perylene were investigated in this study. The disappearance of all 14 PAHs investigated in this study was observed both in the small and large-scale studies. However, the small-scale study with effective mixing resulted in more efficient degradation of all 14 PAHs while the large-scale study demonstrated the same effect (*e.g.*, mixing is needed for a more complete degradation of PAHs). Therefore, the peroxy-acid process has shown to have great utility in treating multiple compounds at the same time. However, the need of mixing has to be explored further. These results seem to confirm the initial hypothesis, and offer a further understanding of the mechanisms of the peroxy-acid process. More tests are essential however to make certain that theses findings are attributable only to initial concentration variations, and not differences in other physico-chemical properties of the two soils mentioned above.

References

[1] U. Varanasi (Ed.), Metabolism of Polycyclic Aromatic Hydrocarbons in the Aquatic Environment, CRC Press, Florida, 1989.

[2] S.W. Rogers, S.K. Ong, B.H. Kjartanson, J. Golchin, G.A. Stenback, Natural attenuation of polycyclic aromatic hydrocarbon-contaminated sites: review, Pract. Periodic. Hazard. Tox. Radioact. Waste Manage. 6 (2002) 141–155.

[3] S.R. Wild, J.K. Cones, Polynuclear aromatic hydrocarbons in the United Kingdom environment: a preliminary source inventory and budget, Environ. Pollut. 88 (1995) 91–108.

[4] G.D. McGinnis, H. Borazjani, M. Hannigan, F. Hendrix, L. McFraland, D. Pope, D. Strobel, J. Wagner, Bioremediation studies at a northern California Superfund site, J. Hazard. Mater. 28 (1991) 145–158.

[5] S. Moret, L.S. Conte, Polycyclic aromatic hydrocarbons in edible fats and oils: occurrence and analytical methods, J. Chromatogr. 882 (2000) 245–253.

[6] J.F. Lawrence, D.F. Weber, Determination of polycyclic aromatic hydrocarbons in Canadian samples of processed vegetable and dairy products by liquid chromatography with fluorescence detection, J. Agric. Food Chem. 32 (1984) 794–797.

[7] J.P. Tuominen, H.S. Pyysalo, M. Sauri, Cereal products as a source of polycyclic aromatic hydrocarbons, J. Agric. Food Chem. 36 (1988) 118–120.

[8] J.J. Ellington, P.F. Schlotzhauer, A.L. Schepaartz, Quantitation of hexane-extractable lipids in serial samples of flue-cured tobaccos, J. Agric. Food Chem. 26 (1978) 270–273.

[9] T.A. Tuhkanen, F.J. Beltran, Intermediates of the oxidation of naphthalene in water with the combination of hydrogen peroxide and UV radiation, Chemosphere 30 (1995) 1463–1475.

[10] B.D. Lee, M. Hosomi, A hybrid Fenton oxidation-microbial treatment for soil highly contaminated with benzo(a)anthracene, Chemosphere 43 (2001) 1127–1132.

[11] S.L. luster-Teasley, J.J. Yao, H.H. Herner, J.E. Trosko, S.J. Masten, Ozonation of chrysene: evaluation of byproduct mixtures and identification of toxic constituents, Environ. Sci. Technol. 36 (2002) 869–876.

[12] E. Psillakis, G. Goula, N. Kalogerakis, D. Mantzavinos, Degradation of polycyclic aromatic hydrocarbons in aqueous solutions by ultrasonic irradiation, J. Hazard. Mater. B 108 (2004) 95–102.

[13] C.L. Potter, J.A. Glaser, L.W. Chang, J.R. Meier, M.A. Dosani, R.F. Herrmann, Degradation of polynuclear aromatic hydrocarbons under bench-scale compost conditions, Environ. Sci. Technol. 33 (1999) 1717–1725.

[14] A.J.M. Legadec, D.J. Miller, A.V. Lilke, S.B. Hawthorne, Pilot-scale subcritical water remediation of polycyclic aromatic hydrocarbon and pesticide-contaminated soil, Environ. Sci. Technol. 34 (2000) 1542–1548.

[15] S. Lundstedt, Y. Persson, L. Oberg, Transformation of PAHs during ethanol—Fenton treatment of an aged gasworks' soil, Chemosphere 65 (2006) 1288–1294.

[16] R.D. Bach, C. Canepa, J.E. Winter, P.E. Blanchette, Mechanism of acid-catalyzed epoxidation of alkenes with peroxy acids, J. Org. Chem. 62 (1997) 5191–5197.

[17] E. Chamarro, A. Marco, S. Esplugas, Use of Fenton reagent to improve organic chemical biodegradability, Water Res. 35 (2001) 1047–1051.

[18] J.S. Levitt, A.L. N'Guessan, K.L. Rapp, M.C. Nyman, Remediation of α-methylnaphthalene-contaminated sediments using peroxy acids, Water Res. 37 (2003) 3016–3022.

[19] A.L. N'Guessan, T. Carignan, M.C. Nyman, Optimization of the peroxy-acid treatment of α-methylnaphthakene and benzo(a)pyrene in sandy and silty-clay sediments, Environ. Sci. Technol. 38 (2004) 1554–1560.

[20] E.O. McLean, in: Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties, Agronomy Monograph 9, 2nd ed., 1982, pp. 159–165.

[21] O.H.J. Szolar, H. Rost, R. Braun, A.P. Loibner, Analysis of polycyclic aromatic hydrocarbons in soil: minimizing sample pretreatment using automated Soxhlet with ethyl acetate as extraction solvent, Anal. Chem. 74 (2002) 2379–2385.

[22] K.G. Furton, E. Jolly, G. Pentzke, Recent advances in the analysis of polycyclic aromatic hydrocarbons and fullerenes, J. Chromatogr. 642 (1993) 33–45.

[23] M.T.O. Jonker, A.A. Koelmans, Extraction of polycyclic aromatic hydrocarbons from soot and sediment: solvent evaluation and implications for sorption mechanism, Environ. Sci. Technol. 36 (2002) 4107–4113.

[24] K. Nam, W. Rodriguez, J.J. Kukor, Enhanced degradation of polycyclic aromatic hydrocarbons by biodegradation combined with a modified Fenton reaction, Chemosphere 45 (2001) 11–20.

[25] B.W. Bogan, V. Trbovic, J.R. Paterek, Inclusions of vegetable oil in Fenton's chemistry for remediation of PAH-contaminated soils, Chemosphere 50 (2003) 15–21.

[26] V. Flotron, C. Delteil, Y. Padellec, V. Camel, Removal of sorbed polycyclic aromatic hydrocarbons from soil, sludge, and sediment samples using the Fenton's reagent process, Chemosphere 59 (2005) 1427–1437.

[27] H.A. Elliott, N.L. Shastiri, Extractive decontamination of metal-polluted soils using oxalate, Water Air Soil Pollut. 110 (1999) 335–346.

[28] F.K. Kawahara, B. Davila, S.R. Al-Abded, S.J. Vesper, J.C. Ireland, S. Rock, Polynyclear aromatic hydrocarbon (PAH) release from soil during treatment with Fenton's reagent, Chemosphere 31 (1995) 4131–4142.

[29] R. Schwarzenbach, P. Gschwend, D. Imboden, Environmental Organic Geochemistry, Wiley InterScience Publications, New York, NY, 1993.