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Enhanced Degradation of Polycyclic Aromatic Hydrocarbons in Soil Treated with an Advanced Oxidative Process — Fenton's Reagent

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ABSTRACT: Polycyclic aromatic hydrocarbons (PAHs) are resistant to present bioremediation practices. This study was conducted to determine if pretreatment with an advanced oxidative process (Fenton's reagent; H_2O_2 + $FeSO_4$) could enhance PAH degradation in soil that had previously been exposed to crude oil. PAHs were more readily degraded after incubation for 56 d when treated with H_2O_2 (2.8 *M*) plus $FeSO_4$ (0.1 *M*) compared with degradation rates without the addition of Fenton's reagent during the same time period. Overall, the use of Fenton's reagent as a pretreatment promoted the mineralization of the nine spiked PAHs by an average of 87%. Degradation of native PAH parent compounds (180 to 840 μg of PAH per kilogram of soil) in the same soil incubated with Fenton's reagent for 7 d was enhanced 44 and 39% for phenanthrene and fluoranthene, respectively, but only 5 and 1% for pyrene and chrysene, respectively, when compared with no addition of Fenton's reagent. Pretreatment of the soil with a surfactant (10 m*M* sodium dodecylsulfate) before the addition of Fenton's reagent increased the native PAH degradation rate 84, 83, 55, and 32% for the parent compounds phenanthrene, fluoranthene, pyrene, and chrysene, respectively, compared with no addition of Fenton's reagent. Degradation of PAHs was confirmed by HPLC-UV analyses. The use of Fenton's reagent ($OH^{\bullet}$) appears to have applications in bioremediation practices of the most recalcitrant chemical compounds in nature (PAHs), particularly with the use of surfactants.

KEY WORDS: bioremediation, surfactants, hydroxyl radicals, anthracene, benzo(*a*)pyrene, chrysene, fluorene, naphthalene, phenanthrene, pyrene.

I. INTRODUCTION

Polycyclic (nuclear) aromatic hydrocarbons (PAHs) are an environmental concern because of their microbial recalcitrance and high bioaccumulation potential in the food chain (Park *et al.,* 1990). PAHs have been identified in soils in uncontrolled

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disposal sites, including wood preservation, petroleum, oily wastes, and coal gasification sites (Mahmood, 1989; Sims and Overcash, 1983). There is considerable human health concern about the fate of PAHs in the environment because many of these compounds are toxic, and some have been shown to be potent mutagens and carcinogens (Miller and Miller, 1981). Due to their chemical properties such as low water solubility and microbial toxicity of the multiring PAHs, bioremediation processes such as composting, anaerobic digestion, or use of white rot fungi (*Phanerochate chrysosporium*) have resulted in little success for rapid PAH mineralization in soil.

Indigenous microbial populations have been reported to degrade PAHs. Park *et al.*, (1990) estimated that the half-life ($t_{1/2}$) of PAHs can range from as short as 2 d for naphthalene to almost 400 d for fluoranthene in soil. They found extensive degradation of two- and three-ring PAHs, with little decomposition of four- and five-ring compounds, in soils incubated for more than 100 d.

PAHs present in the atmosphere or natural waters are believed to be degraded to a limited extent by indigenous hydroxyl radicals ($OH^\bullet$) (Seinfeld, 1989). The use of $OH^\bullet$ generated from the mixing of H_2O_2 and $FeSO_4$ (Fenton's reagent) has shown promise for the degradation of a wide range of environmental contaminants, including chlorophenols (Barbeni *et al.*, 1987), PCBs and chlorobenzene (Sedlack and Andren, 1991; Sedlack and Andren, 1991), chlorophenoxy herbicides (Pignatello, 1992), and formaldehyde (Murphy *et al.*, 1989) in aqueous systems. Fenton's reagent has also shown promise for enhancing the degradation of pentachlorophenol (Watts *et al.*, 1990) and trifluralin (Tyre *et al.*, 1991) in soil slurry reactors. These results led us to believe that the addition of Fenton's reagent may be applicable for the oxidation of refractory soil contaminants such as PAHs to a more biodegradable compound for further degradation by soil microorganisms. The generation of $OH^\bullet$ from mixing H_2O_2 and $FeSO_4$ (Equation 1) has been evaluated for nearly 100 years, and a summary of the resulting reactions has been reviewed previously (Walling, 1975; Clifton and Savall, 1986).

$$H_2O_2 + Fe^{2+} \text{-->} OH^\bullet + OH^- + Fe^{3+} \quad (1)$$

The use of Fenton's reagent for the degradation of PAHs has not been reported in the literature, although Kunai *et al.* (1986) have found that $OH^\bullet$ generated from H_2O_2 and $FeSO_4$ rapidly decomposed benzene in aqueous solution. The mechanism involved in the $OH^\bullet$-mediated decomposition of benzene is the initial addition of the $OH^\bullet$ to form a hydroxycyclohexadienyl radical, with further oxidation by Fe^{3+} or O_2 to phenol. The formation of the benzene radical is the limiting step in this reaction sequence due to the initial low water solubility of benzene. The oxidation to phenol increases the reaction rates with the $OH^\bullet$ to form compounds of increased water solubility such as catechols, which are in turn degraded very rapidly by $OH^\bullet$.

Recent evidence suggests that if PAHs can be metabolized or oxidized to more polar compounds in the microbial environment, increased mineralization may occur (Heitkamp *et al.,* 1987). The major limitations in microbial degradation of PAHs are their water solubility and large molecular structures. One means of increasing the water solubility of lipophilic compounds is by use of surfactants. Kile and Chiou (1989) reported that surfactants can greatly enhance the solubilities of pesticides such as DDT and 1,2,3-trichlorobenzene in aqueous solution. Jafvert (1991) found that the use of sodium dodecylsulfate (SDS) at concentrations as low as 10 m*M* resulted in rapid desorption of PAHs from soil and sediments. The objectives of this study were to determine the effectiveness of Fenton's reagent as a pretreatment process for bioremediation of PAHs and to evaluate the use of a surfactant (SDS) to enhance the availability of PAHs in promoting this chemical/biological treatment train.

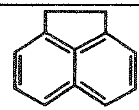
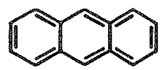
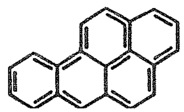
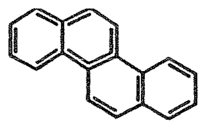
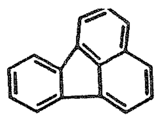
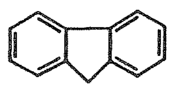
II. EXPERIMENTAL SECTION

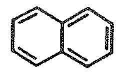
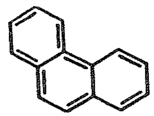
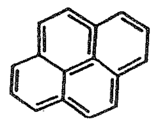
PAHs (acenaphthene, anthracene, benzo(*a*)pyrene, chrysene, fluoranthene, fluorene, naphthalene, phenanthrene, and pyrene) were obtained from Aldrich Chemical Co. (Milwaukee, WI). The soil (Haplic Durixeralf) was obtained from a former manufacture gas plant in Riverside, CA, that had been exposed to crude oil. The soil properties were determined as follows: particle size analysis by the hydrometer method (Gee and Bauder, 1986), organic C by a wet combustion method (Nelson and Summers, 1982), total N by a semi-Kjeldahl steam distillation method (Bremner and Mulvaney, 1982), inorganic NO_3^- and NH_4^+ by the method of Keeney and Nelson (1982), P by the method of Olsen and Summers (1982), and pH in a 1:2.5 soil:water paste.

A. Mineralization of Spiked PAHs

Degradation of the nine spiked PAHs in soil was determined in microcosms as follows: 30 g of moist soil (air-dry basis) were placed in a 500-ml Erlenmeyer flask and 400 mg of the specified PAH (see Table 1) per kilogram of soil was added to each flask. The soil-PAH mixture was mixed thoroughly and allowed to equilibrate for 72 h. PAHs were not added with solvents such as acetone or methylene chloride to minimize disturbance of the soil microbial population (Lethbridge *et al.,* 1985). Fenton's reagent (5 ml 2.8 *M* H_2O_2; 5 ml 0.1 *M* $FeSO_4$) was mixed in a 50-ml test tube and immediately added to the PAH-contaminated soil, the contents gently mixed and incubated at 20 ± 2°C for 56 d. The CO_2 evolved from the treatments with and without Fenton's regent was trapped in a 10-ml beaker (5 ml 0.5 *M* KOH) attached to a glass rod suspended from a rubber stopper. At specified time intervals, the KOH was titrated to a phenolphthalein endpoint with 0.5 *M* HCl. The

TABLE 1
Chemical Properties of Polycyclic Aromatic Hydrocarbons Used

	Chemical name	Formula weight	Boiling point (°C)	Log K_{oc}	Log K_{ow}	Water solubility 25°C (mg/l)	Vapor pressure (mm)	Specific density
	Acenaphthene	154.2	279.0	1.25	3.92	3.47	1.55×10^{-3}	1.02
	Anthracene	178.2	339.9	4.27	4.45	0.045	1.95×10^{-4}	1.24
	Benzo(*a*)pyrene	252.3	494.0	5.60	5.99	0.004	5.49×10^{-9}	1.35
	Chrysene	228.3	448.0	5.39	5.60	0.006	6.3×10^{-9}	1.27
	Fluoranthene	202.3	375.0	4.62	5.22	0.265	1.0×10^{-2}	1.25
	Fluorene	166.2	298.0	3.70	4.12	1.69	1.0×10^{-3}	1.20

	Naphthalene	128.1	217.9	3.11	3.36	30.0	2.3×10^{-1}	1.16
	Phenanthrene	178.2	340.0	4.36	4.52	1.180	6.8×10^{-4}	1.18
	Pyrene	202.3	393.0	4.81	5.18	0.135	6.85×10^{-7}	1.27

percentage of the PAH mineralized was calculated based on the total mg PAH-C added for the specified compound. Soil controls included Fenton's addition or water alone without the added PAH compounds. CO_2-C evolution rates from the background controls were subtracted from the treatment CO_2-C values to account for native organic carbon mineralization during the experiment. The results reported are averages of quadruplicate determination.

B. Effectiveness of a Surfactant with Fenton's Reagent

The effect of SDS in combination with Fenton's reagent was determined by the addition of 5 ml of 10 m*M* SDS to 20 g of the native PAH-contaminated soil. Three hours later, Fenton's reagent was added to the microcosms. To maintain optimum moisture levels in the soil, Fenton's reagent was added in concentrated solution to the SDS-treated soil, resulting in the same concentration as specified in the previous experiment with two applications.

C. Extraction of Native PAHs from Crude Oil-Exposed Soil

The amounts of PAHs present in the crude oil-exposed soil were determined by a method described by Grimmer *et al.* (1978) for extraction of PAHs from sewage sludge. Briefly, 20 g of soil (air-dry basis) were extracted twice (shaken 2 h at 160 cycles per minute) with 100 ml of acetone, and the combined extracts were evaporated on a rotary evaporator. The residue was then taken up with 4 ml of 100% acetonitrile and filtered through a nylon 0.22-mm filter (Gelman Sciences, Ann Arbor, MI).

D. High-Performance Liquid Chromatography of PAHs

An isocratic HPLC analysis was performed on a Beckman 330 liquid chromatograph (Beckman, Fullerton, CA) equipped with a Model 110A pump, a Model 210 sample injector equipped with a BioRad (Richmond, CT) ODS-5 guard column (30 × 4.6 mm) in place of the sample loop, a R-Sil (250 × 4.6 mm) reverse phase separator column (Alltech Associates, Deerfield, IL), and a Beckman Model 165 absorbance monitor set at 254 nm (0.01 absorbance units full scale, AUFS). The mobile phase was optimized at 75% acetonitrile:25% deaired HPLC-grade water (18 MΩ) (Grimmer *et al.,* 1978). Separations were conducted at ambient temperatures at a flow rate of 1 ml/min.

An on-line direct column procedure was used to concentrate PAHs for HPLC analysis, as recently described by Martens and Frankenberger (1991). Briefly, 60 μl of the acetonitrile solution was injected with a calibrated syringe (Hamilton, Reno, NV) into 0.4 ml of H_2O and injected onto the ODS-5 guard column, followed by rinses of 0.4 ml of H_2O and a 0.5-ml mobile phase to remove all nonretained compounds. The PAHs were then eluted from the concentrator column onto the separator column by injection for subsequent separation and UV analysis.

Correlation and multiple regression analyses between PAH degradation rates and soil chemical properties were conducted using the SuperAnova statistical program (Abacus Concepts, Berkeley, CA).

III. RESULTS AND DISCUSSION

The nine PAHs included in this study (Table 1) were chosen to represent a wide range in water solubility (0.0038 to 30.0 mg/l), log K_{ow} (3.36 to 5.99), and vapor pressure (6.3×10^{-9} to 0.23 mm) (Montgomery and Welkom, 1990). The chemical and physical properties of the soil used were as follows: pH 7.0; organic C, 3.3 g/kg; NH_4-N, 6.0 mg/kg; NO_3-N, 2.2 mg/kg; total N, 0.36 g/kg; orthophosphate-P, 4.7 mg/kg; sand, 675 g/kg; and clay, 100 g/kg. The soil was contaminated from previous exposure to PAHs from the use of crude oil for the generation of manufactured gas and had an indigenous microbial population that could mineralize PAH-like compounds. Heitkamp and Cerniglia (1987) found that PAH residues persisted from two- to fourfold longer in a pristine ecosystem than in an ecosystem exposed to low levels of PAHs. The effectiveness of Fenton's reagent is highly dependent on the volume and concentration of the H_2O_2 and $FeSO_4$ reagents added (Watts et al., 1990; Tyre et al., 1991). The soil:volume ratio used in this study (1:0.3 ml of Fenton's reagent) approximated field capacity (–0.034 kPa). Moisture levels above saturation were avoided to aid bioremediation and reduce the formation of anoxic conditions. Martens and Frankenberger (1994) reported that moisture levels in excess of field capacity did not significantly increase Fenton's enhanced degradation rates of phenoxyherbicides in soil. We used the same concentration of H_2O_2 and $FeSO_4$ in this study as was used for the soil degradation of *p*-chlorophenoxyacetic acid in various soil types (Martens and Frankenberger, 1994).

Pretreatment with Fenton's reagent resulted in a sigmoidial shape or a lag phase of PAH mineralization during the initial sampling periods (Figures 1 to 3). We reported previously that Fenton's reagent will initially decrease the soil bacterial and fungal populations in soil, but these populations recover over an extended time period of 5 to 10 d (Martens and Frankenberger, 1994). This initial decrease in microbial numbers may explain the lag time noted for CO_2-C evolution from PAH contamination. The soil pH dropped slightly after the addition of Fenton's reagent but the pH change was negligible during the 56-d incubation period.

Naphthalene was the most readily mineralized PAH of this study (Figure 1; Table 2). After 56 d, 62 and 53% of the added naphthalene was recovered as CO_2-C after treatment with and without Fenton's reagent, respectively. In compari-

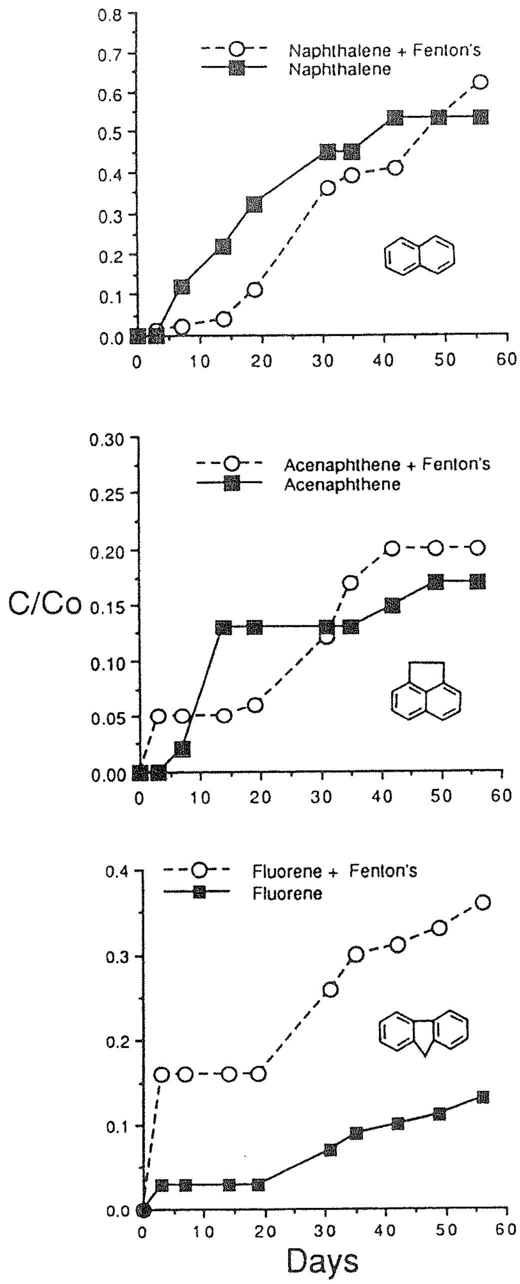


FIGURE 1. Mineralization of 2-ring PAHs determined by CO_2-C evolution rates in a spiked soil after treatment with and without Fenton's reagent (5 ml 2.8 *M* H_2O_2; 5 ml 0.1 *M* $FeSO_4$) incubated at 20°C for 56 d.

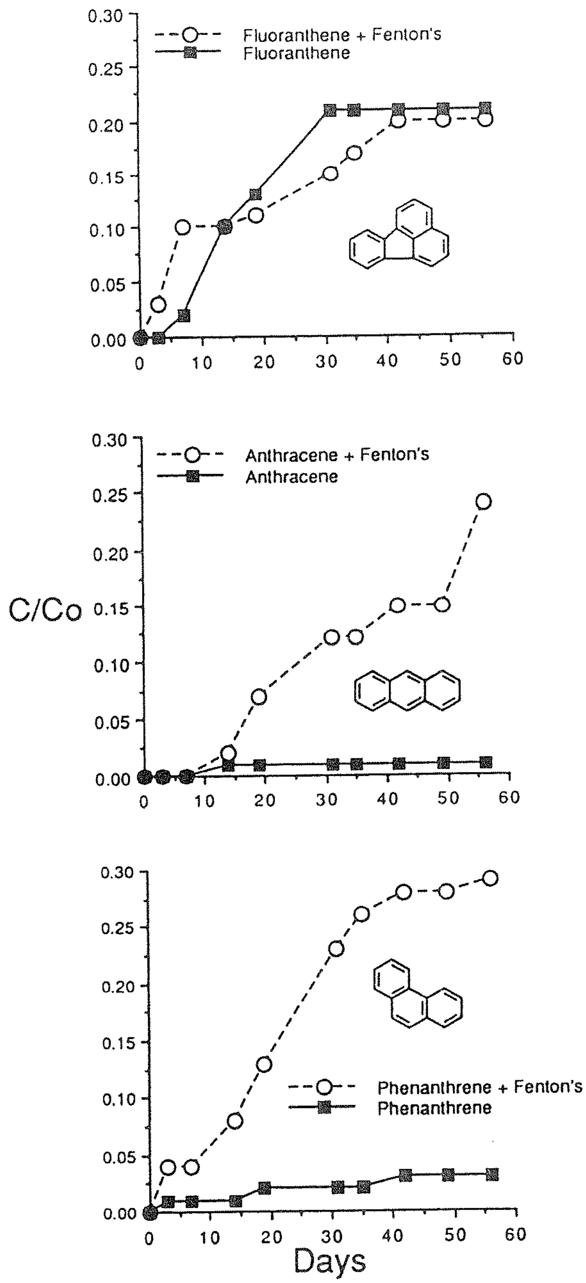


FIGURE 2. Mineralization of 3-ring PAHs determined by CO_2-C evolution rates in a spiked soil after treatment with and without Fenton's reagent (5 ml 2.8 *M* H_2O_2; 5 ml 0.1 *M* $FeSO_4$) incubated at 20°C for 56 d.

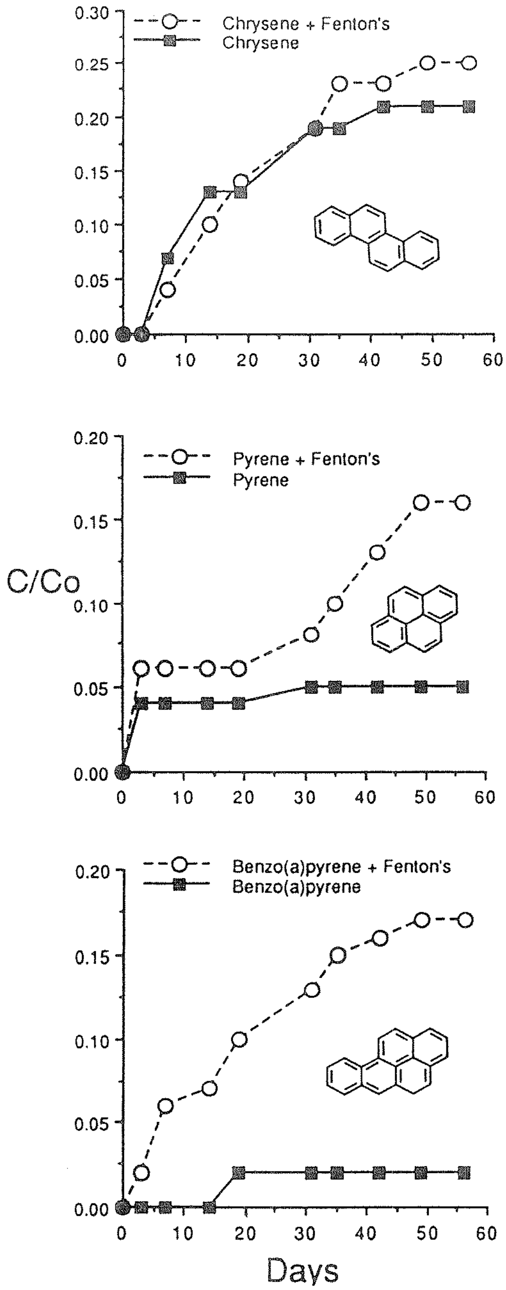


FIGURE 3. Mineralization of 4- and 5-ring PAHs determined by CO_2-C evolution rates in a spiked soil after treatment with and without Fenton's reagent (5 ml 2.8 *M* H_2O_2; 5 ml 0.1 *M* $FeSO_4$) incubated at 20°C for 56 d.

son, acenaphthene and fluorene were less readily mineralized, with reduced rates of CO_2-C released when compared with naphthalene (Table 2). With the application of Fenton's reagent as a pretreatment, mineralization of acenaphthene and fluorene were enhanced 1.2- and 2.7-fold, respectively, when compared with their respective nontreated controls. Chemical oxidation (Fenton's reagent) was not effective in enhancing the mineralization of fluoranthene; however, the advanced oxidative process did promote the breakdown of anthracene (24-fold) and phenanthrene (9.7-fold) over the nontreated controls (Figure 2, Table 2). Degradation of chrysene, pyrene, and benzo(*a*)pyrene were also enhanced after the addition of Fenton's reagent, with a 1.2-, 3.2-, and 8.5-fold increase in mineralization compared with the CO_2-C released without chemical oxidation (Figure 3, Table 2). Park *et al.* (1990) found very little decomposition of the four- or five-ring PAH compounds during 100 d of incubation. Overall, the use of Fenton's reagent as a pretreatment promoted the average mineralization of all nine spiked PAHs tested by 87% when compared with the controls.

Statistical relationships between PAH mineralization (excluding naphthalene, which is subject to volatilization) with and without Fenton's reagent after 56 d and

TABLE 2
Degradation of Polycyclic Aromatic Hydrocarbons in Soil as Measured by Recovery of CO_2-C After Incubation at 20°C ± 2°C for 56 d

	Recovery of CO_2C (%)	
Compound	**With Fenton's reagent**	**Without Fenton's reagent**
Naphthalene	62	53
Acenaphthene	20	17
Fluorene	35[a]	13
Phenanthrene	29[a]	3
Fluoranthene	20	20
Pyrene	16	5
Anthracene	24[a]	<1
Benzo(*a*)pyrene	17[a]	2
Chrysene	25	21
Average	28	15

Note: Thirty grams of soil (air-dry basis) were treated with 400 mg of the specified PAH, and CO_2 evolution was measured with a suspended alkali trap and acid titration. Appropriate controls treated with and without Fenton's reagent were subtracted from the PAH-treated soil.

[a] Significant ($p < 5\%$) when compared with the nontreated control treatment (LSD = 12.2).

TABLE 3
Correlation Coefficients Between the Chemical Properties of PAHs and Degradation of PAHs in Soil With and Without the Addition of Fenton's Reagent After Incubation for 56 d

	Correlation coefficient value (r)	
Chemical property	With Fenton's reagent	Without Fenton's reagent
Molecular weight	–0.69*	–0.59
Boiling point (°C)	–0.15	–0.14
Log K_{oc}	–0.32	–0.40
Log K_{ow}	–0.71*	–0.59
Water solubility (mg/l)	0.91***(0.24)[a]	0.79*(0.38)
Vapor pressure (mm)	0.90***(–0.14)	0.78*(0.33)
Specific density	–0.30	–0.34

Note: *,***: significant at the 5 and 0.1% levels, respectively.

[a] Values in parentheses indicate the r values for PAH degradation with naphthalene removed from the correlation matrix.

the chemical properties of the PAHs are reported in Table 3. The correlation coefficients (r-values) indicate that the molecular weight of PAHs and log K_{ow} (octanol-water partitioning coefficient) were significant factors influencing the degradation rates in the presence of Fenton's reagent. Water solubility and vapor pressure were also found to be significant factors for mineralization. Sheldon and Kochi (1981) had previously reported that the water solubility of persistent soil contaminants is an important characteristic limiting oxidation by Fenton's reagent.

When multiple regression analyses were conducted, molecular weight, log K_{oc} (accounting for organic matter partitioning), and water solubility of the PAHs accounted for 91% (R^2 significant at $p = 0.01$) of the variability in the measured Fenton's-PAH degradation rates when the data set included naphthalene. Removal of the naphthalene data indicated that K_{oc} (significant at $p = 0.05$) and molecular weight (significant at $p = 0.05$) were important variables but not water solubility after mineralization of the eight PAHs by the advanced oxidative process ($R^2 = 0.70$). The finding that log K_{ow} (via linear regression analysis) and K_{oc} (via multiple regression analysis) are significant factors in the degradation of PAHs by Fenton's reagent suggests that sorption of PAHs in soil limits their degradation rates. In support of this hypothesis, Karickhoff (1981) reported that adsorption or partitioning of an organic contaminant with soil organic matter is an important factor influencing degradation of the contaminant by Fenton's reagent.

Contaminants present in soil must be accessible to the generated aqueous phase $OH^{\cdot}$ in order for the hydroxylation reaction to occur. The level of H_2O_2 used to generate OH• in this study is detectable for up to 2 h in soil. Thus, compounds that are not in soil solution during this 2-h time frame probably will not encounter the generated OH•. Statistical analyses of PAH mineralization in this study suggested that the hydrophobic nature and partitioning of PAHs in soil contributes to the limited mineralization rates. Kile and Chiou (1989) found that the water solubilities of DDT and 1,2,3-trichlorobenzene in soil were greatly enhanced by the use of surfactants. Jafvert (1991) reported that SDS at concentrations as low as 10 m*M* and contact times as short as 3 h solubilized the majority of PAHs that had been adsorbed to soil. SDS was used in this work to determine if a surfactant could increase the degradation rates of native PAHs exposed to Fenton's reagent. Mertz and Waters (1949) first reported that primary and secondary alcohols and aromatic compounds were susceptible to oxidation by Fenton's reagent. SDS was selected after evaluation of other surfactants such as Brij 35 and Triton X, based on limited competition as a substrate for the generated OH• radicals. The native PAHs and remaining concentrations as determined by HPLC analysis before and after treatment with Fenton's reagent vs. pretreatment with 5 ml of 10 m*M* SDS followed by Fenton's reagent are reported in Table 4. Phenanthrene, fluoranthene, pyrene, and chrysene were present from previous exposure to crude oil. After the addition of Fenton's reagent, the extractable PAH concentrations decreased within 7 d by 43.8, 38.2, 9.1, and 1.2% for phenanthrene, fluoranthene, pyrene, and chrysene, respectively. Pretreatment with 10 m*M* SDS plus Fenton's reagent reduced the extractable PAHs within 24 h by 75.6% (phenanthrene), 77.6% (fluoranthene), 39.0% (pyrene), and 1.2% (chrysene). Increasing the concentration (2×) of Fenton's reagent (level II; see Table 4) in the presence of SDS was even more effective, with

TABLE 4
Polycyclic Aromatic Hydrocarbons Extracted from Soil Before and After Treatment with Fenton's Reagent

Compound	Initial concentration	PAH recovery: Fenton's reagent[a]	PAH recovery: SDS plus Fenton's reagent[b] Level I	PAH recovery: SDS plus Fenton's reagent[b] Level II
	mg/kg soil			
Phenanthrene	160	90	39	26
Fluoranthene	340	210	76	57
Pyrene	110	100	67	50
Chrysene	840	830	830	571

[a] Twenty grams of soil (air-dry basis) were incubated for 7 d at 30°C after the addition of 6 ml H_2O (control) or 3 ml 2.8 *M* H_2O_2 (125 mg) plus 3 ml 0.1 *M* $FeSO_4$ (13 mg) (Fenton's reagent).
[b] Twenty grams of soil (air-dry basis) were pretreated with 5 ml 10 m*M* SDS (3 h) and exposed to Level I, H_2O_2 (125 mg) plus $FeSO_4$ (13 mg), or Level II, H_2O_2 (250 mg) plus $FeSO_4$ (26 mg), for 24 h.

83.8, 83.2, 54.5, and 32.0% removal of the PAH parent compounds, respectively. Increased levels of H_2O_2 (5%) and $FeSO_4$ (0.12 *M*) were required for the breakdown of spiked 2,4-dichlorophenoxyacetic acid and 2,4,5-[trichlorophenoxy]propanoic acid in soil (Martens and Frankenberger, 1994). In comparison, *p*-chlorophenoxyacetic acid was oxidatvely degraded at H_2O_2 additions of <2%. These differences may be attributed to the wide range in water solubility of the phenoxy herbicides. Water solubility may also explain the differences observed with Fenton's reaction on native PAHs. Chrysene is approximately 200× less soluble than phenanthrene, 45× less soluble than fluoranthene, and 23× less soluble than pyrene. It appears that the reaction rates with Fenton's reagent are directly proportional to the water solubility of the PAH in question.

Native chrysene and fluoranthene were present at elevated levels in this soil when compared with the other PAH compounds (Table 4). It is of interest to note that microbial activity in the nonFenton treatment was as effective for mineralization of the spiked chrysene and fluoranthene as the Fenton-treated soil (Table 2). Adaptation of microbial populations to chronic PAH exposure has been reported to result in increased PAH mineralization (Heitkamp and Cerniglia, 1987).

In conclusion, the addition of Fenton's reagent to soil contaminated with PAHs increased the mineralization rates (average of 87% for the nine PAHs) compared with no addition of Fenton's reagent upon 56 d of incubation. The use of a surfactant (SDS) in combination with Fenton's reagent greatly enhanced PAH degradation in soil. These results suggest that remediation of PAH-contaminated soil with a surfactant and advanced oxidative processes that generate $OH^{\bullet}$ may have applications for increased mineralization of PAHs in soil.

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