Effect of sequestration on PAH degradability with Fenton's reagent: roles of total organic carbon, humin, and soil porosity

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Abstract

The phenomenon of contaminant sequestration—and the physicochemical soil parameters which drive this process—has recently been studied by several authors with regard to microbial contaminant degradation. Very little work has been done to determine the effects of contaminant sequestration on the chemical treatability (oxidizability) of soil contaminants; the current study was conducted to address this data gap. A suite of six model soils, ranging in organic matter content from 2.32 to 24.28%, were extensively characterized. Measured parameters included: (1) levels of total organic carbon (TOC); (2) contents of humic acid (HA); fulvic acid (FA) and humin; and (3) total porosity and surface area. Each soil was then spiked with coal tar and, after varying periods of aging/sequestration, subjected to slurry-phase Fenton's reagent oxidation. Percent recoveries of 12 PAHs, ranging from 3 to 6 aromatic rings, were determined. Results indicated that the susceptibility of each PAH to chemical oxidation was a function of TOC in four of the soils (those with TOC greater than approximately 5%), but was strongly dependent on soil porosity for low-TOC soils. The importance of these two parameters changed with increasing sequestration time, with the relative contribution of porosity-mediated sequestration becoming more important over time. Porosity-mediated effects were more rapid and significant with lower-molecular-weight PAHs (e.g. those with three or four aromatic rings) than with higher-molecular-weight, more hydrophobic compounds. These observations are discussed in light of current physicochemical models of the contaminant sequestration process.
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1. Introduction

Fenton's reaction—the generation of hydroxyl radical through the Fe^{2+}-catalyzed homolytic cleavage of hydrogen peroxide—has been widely studied and applied for remediation of organic-contaminated soils and other solid matrices [1–7]. It has been shown that hydroxyl radicals generated through Fenton's reaction are capable of oxidative degradation of numerous important xenobiotic and pollutant compounds. These include fuel hydrocarbons [8–12], chlorinated aliphatic [13] and aromatic [2,14,15] hydrocarbons, pentachlorophenol [16], pesticides [17], nitrobenzenes and nitrophenols [18], trinitrotoluene [5], benzene, toluene and other monoaromatics [9,19], and PAHs [3,6,7,20].

Extensive literature in the fields of bioremediation and ecotoxicology has been developed showing that organic xenobiotic compounds which have been in contact with soil display reduced availability, and that the magnitude of this effect increases over time. This is true whether availability is defined and/or measured as microbial biodegradability [21–24], extractability using mild solvents and/or conditions [25], earthworm uptake [21], toxicity to insects [26], or phytotoxicity [27,28]. It was in the last of these contexts that the phenomenon of sequestration of organic chemicals (in this case herbicides) was first described. It was observed, for example, in the late 1950s and early 1960s that application in soils with high organic matter contents resulted in substantial reductions in the herbicidal efficacy of simazine ([29] and references therein) and numerous other herbicides [30], and that the magnitude of this effect was strongly correlated with the level of organic carbon in the soil. Recent models of sequestration relating to contaminant biodegradation recognize that the overall sequestration process most likely encompasses two individual mechanisms; namely, partitioning into or onto humic matter [31] and diffusion into three-dimensional micropores of soil particles themselves [32]. Weber et al. [33], Weber and Huang [34], Young and Weber [35], and Xing and Pignatello [36] have each proposed two-site models to describe the processes inherent in interactions between hydrophobic contaminants and soil particles, in which sequestration begins with partitioning of contaminant molecules into or onto humic acid (HA) and fulvic acid (FA) polymer layers at the surface of soil particles, followed by diffusion into micropores. The latter structures most likely occur in the humin core of the particles, and are rendered partially inaccessible to the bulk solution phase by the overlayer of polymeric humic acid and FA.

Data on the effect of sequestration on the susceptibility of contaminants to chemical oxidation and remediation are much less common. Some authors have demonstrated that sorbed molecules have significantly different reaction rates with $^{\bullet}OH$ [15], and that soil-bound contaminants are more resistant to oxidative attack during chemical treatments than contaminants in solution [1,4]. The effects of sorption on contaminant degradability can be minimized with high oxidant (H_2O_2) loads, which apparently result in generation of as-yet-unidentified species that are capable of oxidizing sorbed contaminants [12,37], even in the absence of significant desorption [12]. However, all of this work examined the behaviors of contaminants that had been sorbed either to a single silty loam soil [37] or to silica sand [12] for a single set time period. They did not, therefore, directly address the effects of the temporal sequestration process in soils of different physicochemical characteristics. The goals of the research described herein were two-fold. The

first was to determine the impact of increasing residence time of PAH contaminants on their susceptibility to remediation in slurry-phase Fenton's reaction systems. At the same time, it was hoped that conducting these experiments in a range of physicochemically distinct soils would provide a better understanding of those soil parameters that might be key to the successful application of Fenton's chemistry as a soil remediation process. Use of field-contaminated soils to discern the effects of different parameters would be difficult or impossible, as the sequestration process is time dependent, and is influenced by cycles of soil wetting and drying [38]. Therefore, without explicit knowledge of the soil/contaminant contact time—and precipitation events during this period—for each environmental sample, it would be highly problematic to accurately glean the influence of soil properties themselves. Thus, all of the work described herein was done with artificially spiked soils which had previously been subjected to a range of physicochemical characterization.

2. Materials and methods

2.1. Soil characterization

Six model, non-contaminated soils were collected from vegetated areas in the northwestern Greater Chicago area. Particle size analyses were performed by the hydrometer method [39]. Total organic carbon (TOC) concentrations were determined by ashing soil samples at 440 °C, according to ASTM method D2974-87. Soil organic matter (SOM) was fractionated into HA, FA and humin as follows. An aliquot of 15 g of each soil material (only 2 g of soil #4 was needed due to its high TOC level) were stirred in 100 ml of 0.1 M NaOH for 24 h. Samples were centrifuged at $2000 \times g$ for 30 min, and the extraction was repeated. The combined supernatants from this extraction contained the HA and FA fractions, while the residue contained the humin. Reagent-grade water (100 ml) was added to each humin sample and acidified (pH $\leq$ 2) with concentrated HCl. This suspension was centrifuged, and the supernatant discarded. The humin was then rinsed with de-ionized water until the rinsate contained no Cl^- (a negative test with $AgNO_3$); it was then dried at 60 °C. The HA/FA-containing supernatants were acidified (pH $\leq$ 2) and centrifuged. The resulting supernatants—the FA fractions—were individually loaded onto an XAD-8 column, which was washed with reagent water to remove salt. FA was eluted with 0.1 M NaOH, converted to the acid form using a hydrogen-saturated cation exchange resin, and recovered by lyophilization. The humic acid residue was treated as described above for the humin fraction (acid- and water-rinsed), and dried at 60 °C. All solid samples (whole soil materials, HA and humin) were quantitated using a Shimadzu TOC-V/SSM-5000A analyzer; aqueous FA was quantitated using a Shimadzu model TOC-500.

High-resolution nitrogen adsorption–desorption isotherms were measured at 77.4 K using a Quantachrome Instruments Autosorb-1C. Before the measurements, the soil samples were outgassed at 120 °C for a period of ca. 24 h. Determination of the void volume was performed with helium using standard procedures. Low-pressure data were corrected on thermal transpiration effect according to standard procedures. Specific surface areas and

pore volumes of soils were assessed by the BET method applied in the region of relative pressures from $p/p_0 = 0.05$–0.3.

2.2. PAH degradation in Fenton's reaction

Samples (120 g) of each of the six model soils were spiked with coal tar to a final concentration of 1000 ppm. This resulted in the following average concentrations of the 12 PAH (3–6-ring) which were targets of this study: phenanthrene (33 ppm); anthracene (9); fluoranthene (25); pyrene (18); benz[a]anthracene (5.0); chrysene (7.4); benzo[b]fluoranthene (4.0); benzo[k]fluoranthene (1.9); benzo[a]pyrene (3.0); dibenz[a,h]anthracene (2.7); benzo[g,h,i]perylene (2.9); and indeno[c,d]pyrene (3.2). Spiking was done by dissolving coal tar in dichloromethane (ca. 100 ml), adding to the soil with vigorous mixing, and allowing the solvent to evaporate overnight in a fume hood. Spiked soil was then covered and stored in the dark at room temperature until use.

Following appropriate periods of contaminant aging (0, 40, and 80 days), soils were subjected to slurry-phase treatment with Fenton's reagent according to the following procedure. Five grams of soil was slurried in 25 ml of de-ionized H_2O, and adjusted to a pH of 3.0 (±0.2) with HCl. Each reaction was amended with 100 mg of $HgCl_2$ to inhibit possible microbial activity; $FeSO_4$ (final conc. = 10 mM) and H_2O_2 (final conc. = 1.0%) were added separately. Slurries were shaken at room temperature for 14 days, after which soils were recovered and analyzed for PAH content as described below. For each soil, data for each timepoint was collected from $n = 2$ full Fenton's reactions and $n = 2$ controls (H_2O_2 omitted).

2.3. Analytical methods

Soil samples were centrifuged (10 min at $5000 \times g$) in stainless-steel containers to separate solid and aqueous phases. Soil solids ($\sim$2 g) were mixed with anhydrous sodium sulfate (1:1), allowed to dry overnight, and ground to a fine powder using a coffee grinder. Sonication was done twice using 1:1 dichloromethane/acetone (20 ml) as the solvent. The two extracts for each sample were combined and vacuum filtered through glass-fiber filter discs, evaporated to dryness under a stream of N_2 in a Turbovap Evaporator (Zymark, Hopkinton, MA), and re-dissolved in 1 ml of acetonitrile (ACN). Ten microliters of this solution was analyzed by reverse-phase HPLC using a Supelcosil LC-PAH column (15 cm $\times$ 4.6 mm) and a Waters HPLC system coupled to a diode-array detector (Waters Model 996). The following gradient was used, with a flow rate of 1.5 ml min^{-1} throughout:

Time (min)	H_2O (%)	ACN (%)	Hold time (min)
0	60	40	0
25	0	100	2
33	60	40	0

Identities of individual PAHs were verified by comparisons of their retention times and absorbance spectra to the components of a PAH standard mix (Ultra Scientific, North Kingstown, RI), and quantified using five-point standard curves (all $r^2 > 0.988$).

Table 1
Physicochemical characteristics of the six model soils used in this work

	Soil					
	1	2	3	4	5	6
Particle size distribution						
Sand (%)[a]	25 (0)	64 (1)	71 (4)	73 (2)	41 (1)	52 (1)
Silt (%)[a]	47 (4)	25 (1)	18 (4)	11 (0)	33 (1)	26 (0)
Clay (%)[a]	28 (4)	11 (0)	11 (0)	16 (2)	26 (0)	22 (1)
Textural classification	Clay loam	Sandy loam	Sandy loam	Sandy loam	Loam	Sandy clay loam
Organic matter analyses						
TOC (%)[a]	2.32 (0.00)	5.78 (0.00)	11.2 (0.3)	24.28 (0.08)	3.58 (0.08)	9.1 (0.3)
FA (%)[a,b]	0.5 (0.0)	0.9 (0.0)	1.4 (0.0)	4.0 (0.1)	0.7 (0.0)	1.1 (0.1)
HA (%)[a,b]	6.0 (0.3)	12 (2)	19.5 (0.6)	13 (1)	6 (1)	19 (1)
Humin (%)[a,b]	94 (3)	87 (3)	79 (4)	83 (18)	93 (2)	80 (3)
Total pore volume (ml/g soil)[c]	0.082 (0.005)	0.056	0.024	0.017	0.060	0.042
Total surface area (m^2/g soil)[c]	30.30 (0.07)	24.49	4.93	3.04	23.21	15.39

[a] Averages of duplicate determinations, with standard deviations in parentheses.

[b] Values for fulvic acid (FA), humic acid (HA), and humin are expressed as percentage of the total organic carbon (TOC) in each soil.

[c] Pore volume and surface area measurements were duplicated on soil #1 only, in order to estimate reproducibility.

3. Results

3.1. Soil characteristics

Table 1 lists all data obtained from characterizations of the six model soils used herein. These soils were found to encompass a wide range of TOC levels, with soil #1 being the lowest (2.32%), and #4 the highest (24.28%). Furthermore, significant compositional differences were observed when the organic matter in the soils was fractionated into HA, FA, and humin. Fractionation data showed that soils #1 and #5 were dominated by humin, as their organic matter was markedly lower in summed HA and FA (6.5 and 7%, respectively) than the other four soils, which contained between 13% (soil #2) and 21% (soil #3) of these acids. The humic material in soil #4, when compared to the other five soils, was also highly enriched specifically in fulvic acid (4.0% of the TOC). Soil pore volumes and surface areas, measured by the BET method, also covered a wide range of values. In order to provide a check of the reproducibility of this analysis (without the expense of repeating all six samples), duplicate determinations were done for soil #1; as shown in Table 1, the reproducibility for both BET parameters was excellent, with standard errors of 6% (pore volume) and 0.2% (surface area).
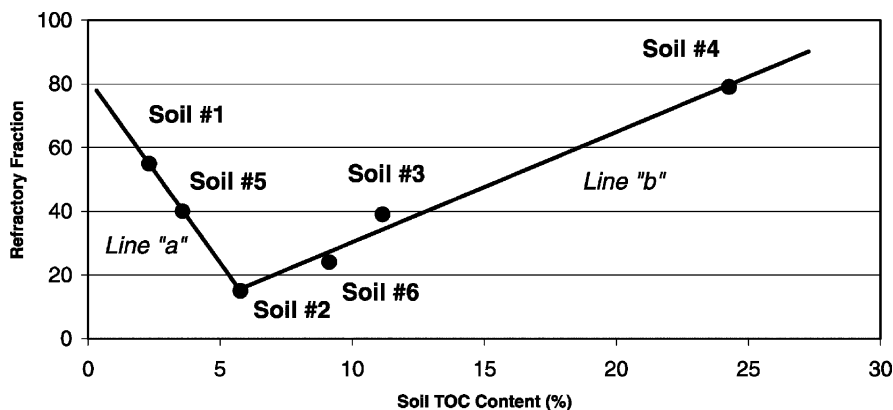
Fig. 1. Schematic generalized model for PAH-recovery behaviors observed in different soils. Line "a" encompasses the low-OC soils (soils #1 and #5), while line "b" contains the higher-OC soils (#6, #3, and #4). Soil #2, which consistently represents the apparent approximate inflection point between the two lines, is included in both "a" and "b" for the purpose of calculating r^2 values for the following figures.

3.2. PAH susceptibility to Fenton's reagent oxidation

The great majority of the data plots at each of the three sequestration timepoints displayed the same general pattern, shown schematically in Fig. 1. Soil #2, with 5.78% TOC, consistently showed the lowest amount of PAH remaining after treatment (i.e. the highest PAH degradation), and marked a clear transition point between two linear correlations that encompassed the remaining five soils. The actual data for PAH which is refractory to Fenton's reactions at each timepoint are presented in Fig. 2 (0 day sequestration), Fig. 3 (40 days), and Fig. 4 (80 days). All data are expressed as the percent of each individual coal tar PAH contaminant remaining relative to no-treatment control "reactions". This was done to guard against possible reductions in extraction efficiency, which might also be expected to occur during the sequestration process. In fact, this effect was found to be fairly small, as the average extractable concentrations of the 12 target PAHs in the no-treatment controls decreased by only 11 and 18%, respectively, after 40 and 80 days (Table 2).

In soils with TOC contents less than approximately 5% (i.e. soils #1 and #5), degradation efficiency was inversely correlated to TOC; in all cases, PAH was more refractory in soil #1 (2.32% TOC) than in soil #5 (3.58% TOC). Soils #1 and #5, in addition to having the lowest HA/FA contents (see above), also have the highest N_2-accessible pore volumes and surface areas. Furthermore, soil #1 has a higher value for each of these parameters than soil #5. The BET results are therefore consistent with the soil organic matter fractionations, both indicating that these two soils are dominated by humin, with very little humic and fulvic acids overlying this material. We propose that this renders the micropores in these two soils (and, to a lesser extent, soil #2) more available for the rapid "entrapment" of PAH molecules. This faster and/or more extensive migration of PAH into the humin pore spaces in these soils is the cause of their reduced susceptibility to chemical oxidation. Above the threshold of approximately 5% TOC, the relationship was the opposite of this—more contaminant

was resistant to treatment as soil TOC increased. This could be due to either or both of two factors, namely sorption of PAH onto SOM retarding its oxidation and the fact that the soils' organic matter consumes some portion of the oxidizing equivalents ($^{\bullet}$OH) generated through the Fenton's reagent treatment.
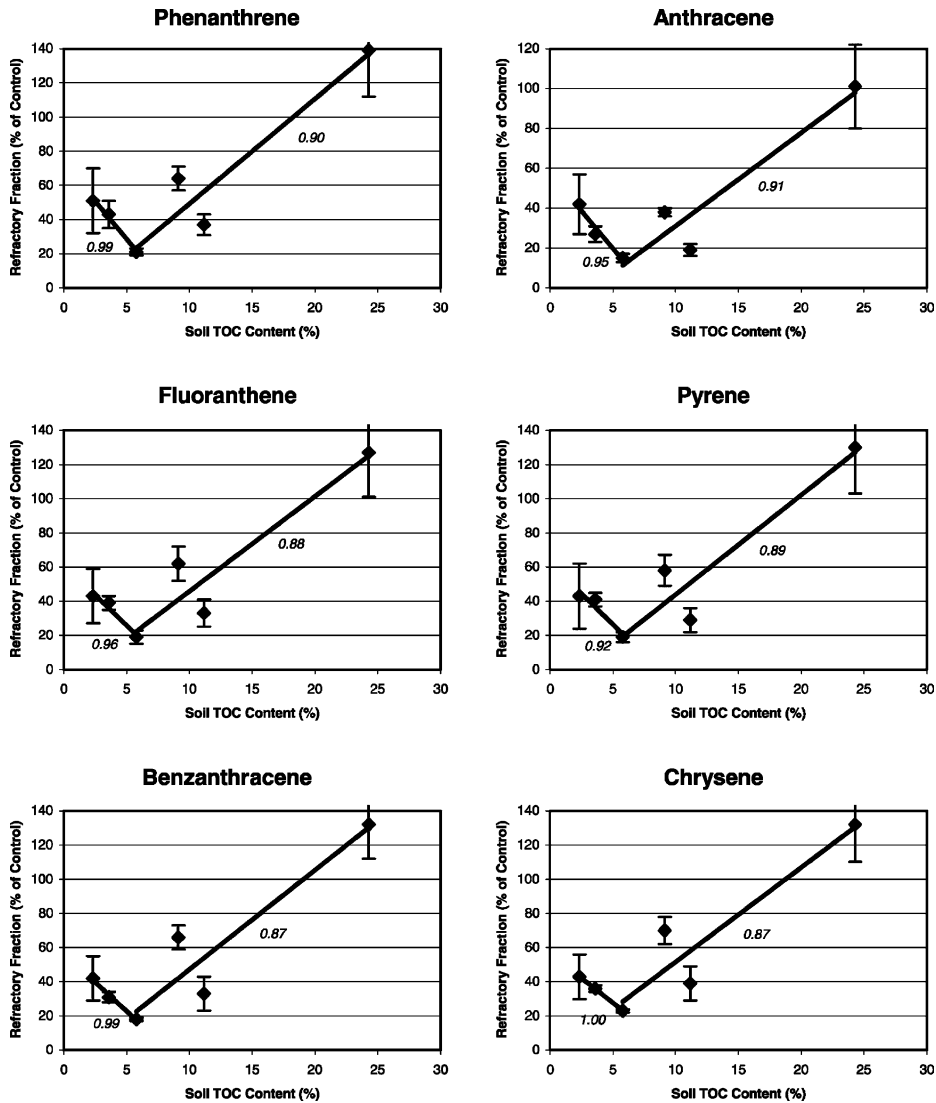

Fig. 2. Concentrations of 12 PAH (3–6-ring) remaining after slurry-phase Fenton's reactions (relative to H_2O_2-omitted controls) initiated immediately after introduction of coal tar to six model soils. Trendlines and r^2 values (italic text), determined using the mean recoveries averaged into each datapoint, are given in each panel for the portions of the data which conform well ($r^2 > 0.85$) to the linear relationships in Fig. 1 model.
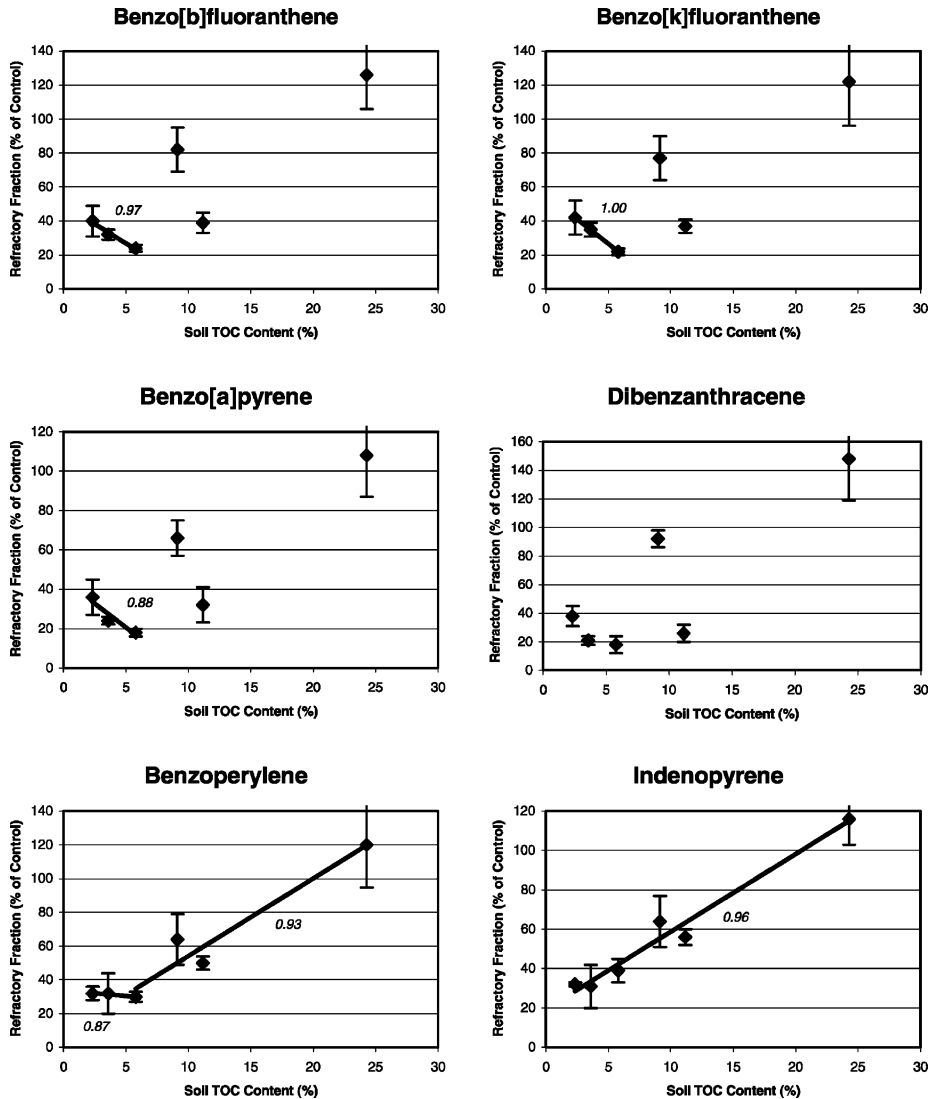
Benzo[b]fluoranthene

Benzo[k]fluoranthene

Benzo[a]pyrene

Dibenzanthracene

Benzoperylene

Indenopyrene

Fig. 2. (*Continued*).

Time-zero data showed that, for all six soils, the differences in "porosity-based" sequestration (in the soils with TOC values below approximately 5%) were relatively small, especially when compared to the magnitudes of the variations seen in the high-OC soils. Furthermore, these apparent porosity effects were dependent upon the molecular weights of the individual PAHs. This can be seen in Fig. 2; note that the slope of "line a", the portion of the curve which we attribute to porosity-mediated sequestration, is steepest with 3-ring compounds such as phenanthrene and anthracene, and lower with 4- and 5-ring com-

pounds. This result is consistent with the model that smaller PAH are more able to quickly diffuse into three-dimensional pores, and become refractory by this mechanism. In the cases of the most hydrophobic, highest-molecular-weight PAHs included—benzo[g,h,i]perylene and indeno[c,d]pyrene, porosity effects are nearly (or completely) negligible, and removal efficiency is directly proportional to TOC content across the full range of soils. Correlation coefficients were excellent in each of the two phases. The r^2 values for the "porosity-based" portions of the sequestration plots (line "a") averaged 0.93 (range 0.73–1) at time-zero,
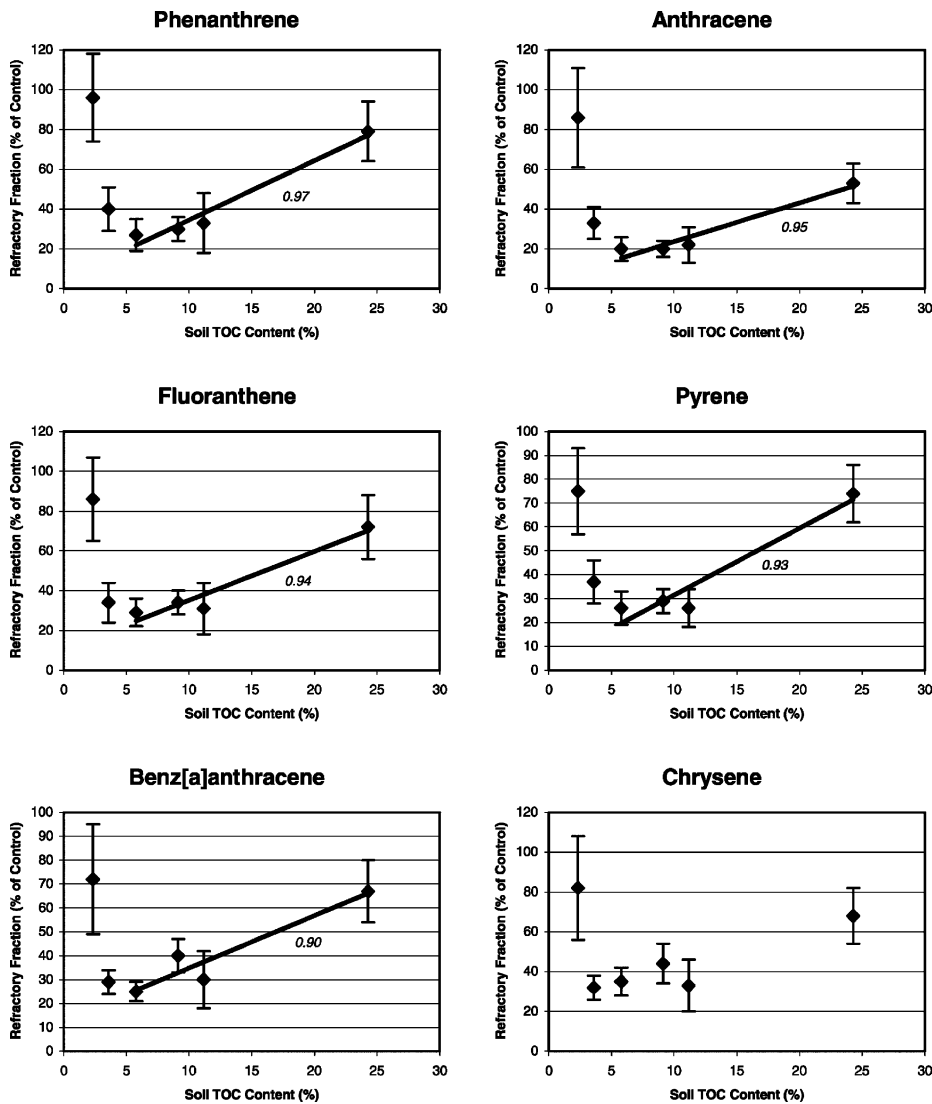
Fig. 3. PAH refractory to degradation in Fenton's reactions conducted after 40 days of contact time (sequestration) between soil and coal tar.
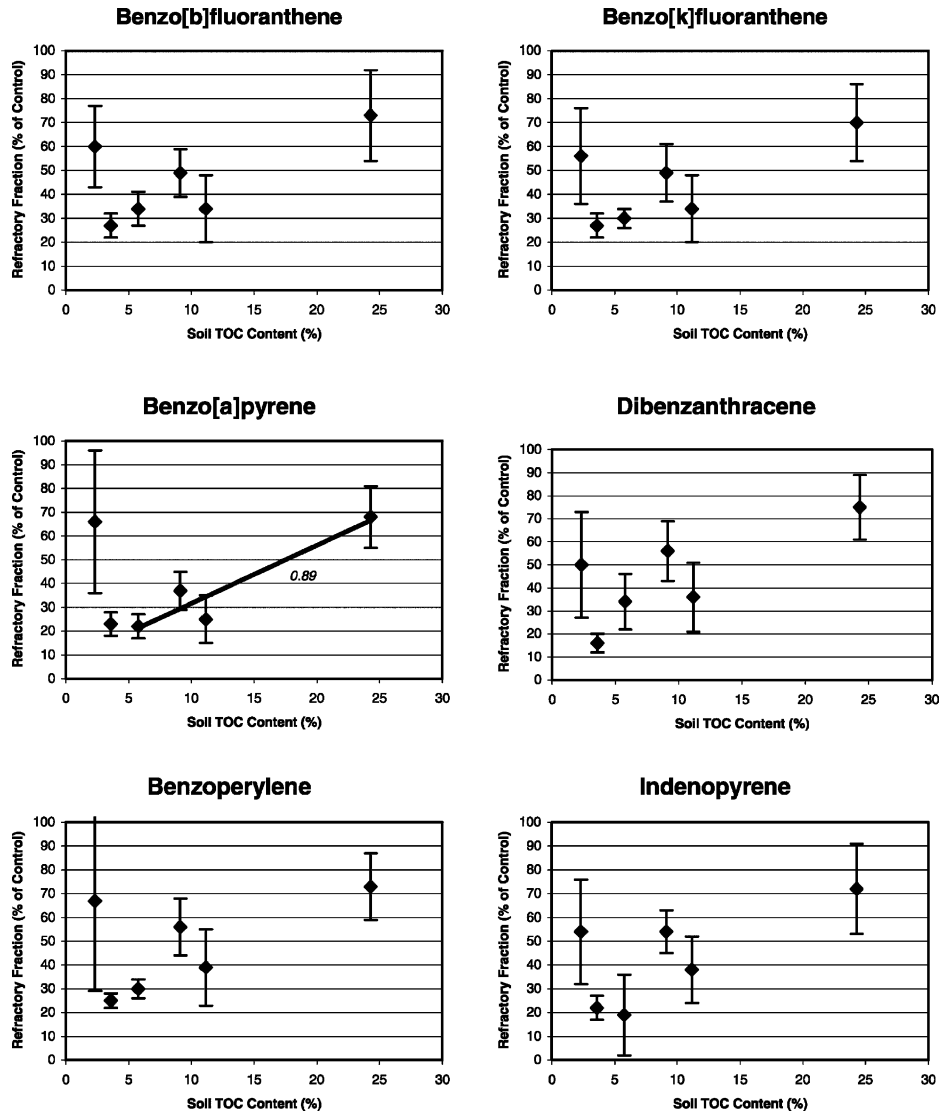
Fig. 3. (*Continued*).

while those for the "sorption/competition" phase (line "b") were between 0.75 and 0.96 (average = 0.85). In general, the most significant outlier in the sorption/competition-phase lines was soil #6 (9.13% TOC), in which essentially all of the PAHs were somewhat more refractory than expected, based on the remainder of the data points.

After 40 days of sequestration (Fig. 2), the apparent effect of porosity in the low-TOC soils had become much greater, as emphasized by the considerably higher levels of all PAHs remaining in soil #1 after treatment. This was also true for some of the lower-molecular-weight

species (e.g. phenanthrene, anthracene, and pyrene) in soil #5. It has been reported that entrapment within micropores (or "hole-filling") of contaminant molecules may become more important over time [36]. Our data support this, and suggest that fraction of contaminant which is "entrapped", and rendered refractory to oxidation by Fenton's reagent through this mechanism, is greater after 40 days of aging than at time-zero. Again, the magnitude of this effect (measured by steepness of the "line a" or "porosity" slope) was, in general,
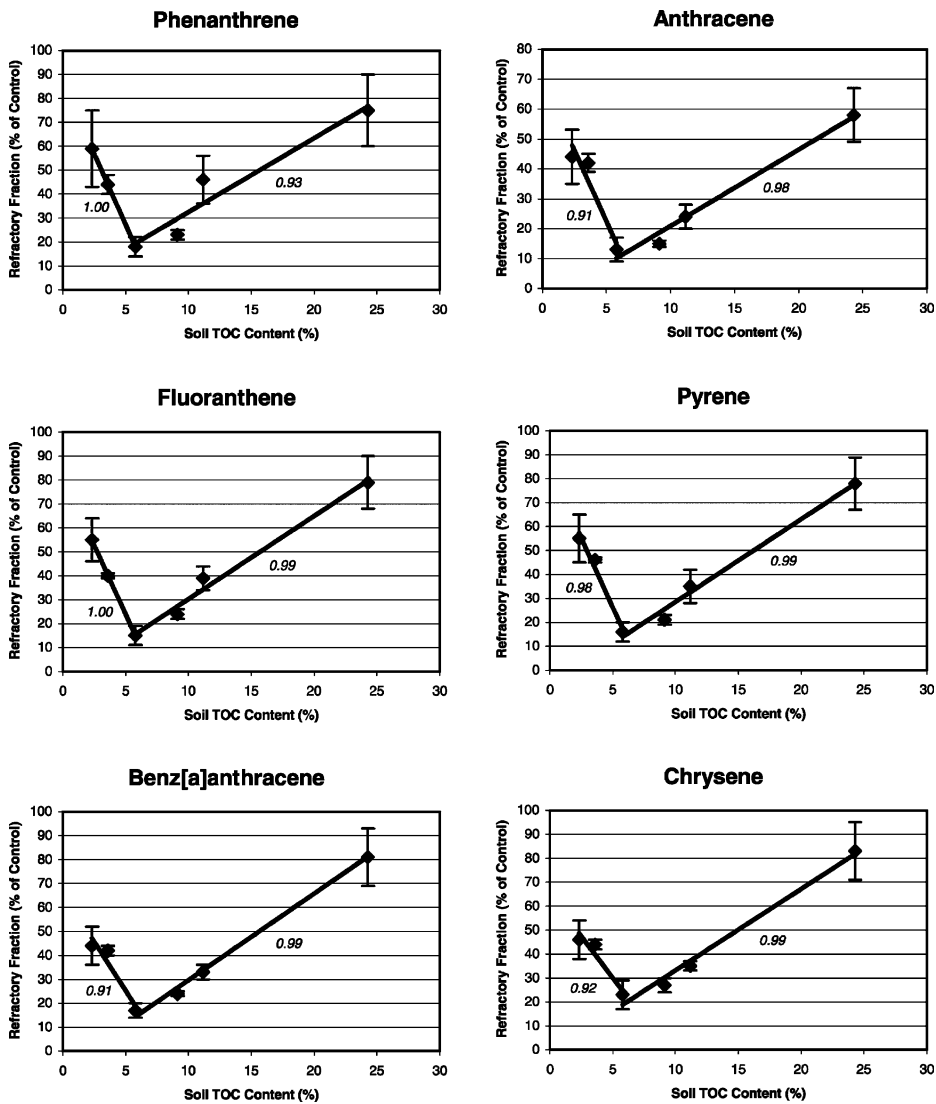

Fig. 4. PAH refractory to degradation in Fenton's reactions conducted after 80 days of contact time (sequestration) between soil and coal tar.
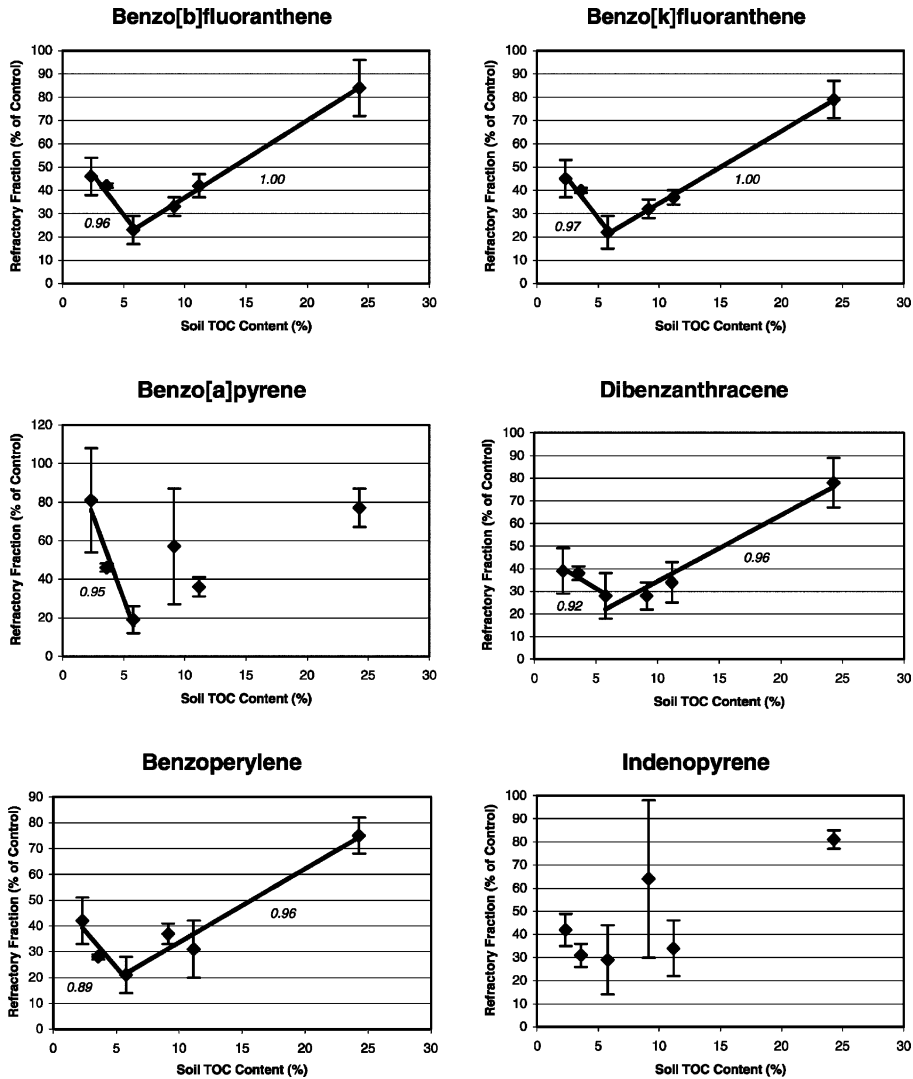
Fig. 4. (*Continued*).

larger for low-molecular-weight PAHs, although this pattern was not as uniform as in the time-zero data. This is also true in the "sorption/competition" phases of the various plots. In this case, correlation coefficients were lower than at time zero, although those for the compounds up to and including benz[*a*]anthracene still showed $r^2 \geq 0.9$. These r^2 values are indicative of the fact that the soil #6 results for these compounds are now much more in line with the regression line defined by the rest of the soils. In contrast, for the remainder of the compounds (those after benz[*a*]anthracene), soil #6 remains the primary outlier in the sorption/competition portion of the plot.

Table 2

Average percent decreases (across the six soils) in the amount of each PAH extractable from control (H_2O_2-omitted) reactions after 40 and 80 days

PAH analyte	Decrease in extractability (%)	
	40 days	80 days
Phenanthrene	16	14
Anthracene	24	31
Fluoranthene	19	19
Pyrene	22	20
Benz[*a*]anthracene	−1	11
Chrysene	6	14
Benzo[*b*]fluoranthene	7	19
Benzo[*k*]fluoranthene	−2	13
Benzo[*a*]pyrene	17	31
Dibenz[*a,h*]anthracene	6	2
Benzo[*g,h,i*]perylene	3	20
Indeno[*c,d*]pyrene	19	25
Average (all PAHs)	11	18

Data collected for contaminant degradability after 80 days of sequestration (Figs. 3 and 4) is very similar to that after 40 days of aging. One notable exception is that the amount of PAH refractory to treatment increased substantially in soil #5 (3.58% TOC) relative to the other soils. This would indicate that porosity-mediated effects are greater in this soil after 80 days than after 40 days; again, the magnitude of this effect seems to be higher in low-molecular-weight species such as phenanthrene and anthracene than in the highest-molecular-weight compounds (e.g. benzo[*g,h,i*]perylene and indeno[*c,d*]pyrene). Correlations were again very strong for all of the data: r^2 values for lines "a" and "b" both averaged 0.93 ($n = 12$ PAHs).

4. Discussion

Early models which were advanced to describe the process of contaminant sequestration in soils proposed partitioning into or onto humic matter on the surface of soil particles [31], or diffusion into three-dimensional micropores within the particles themselves [32]. More recent evidence indicates that, as might be expected with an extremely heterogeneous matrix, such as SOM, both of these mechanisms contribute to a "dual-mode" sequestration process [33–36]. These authors posit that soil contains two types of domain, both of which interact with contaminant molecules. The first of these consists of HA and FA bound or complexed at the surface of soil particles. This domain, which is highly porous, flexible, and lipophilic, has been described as "rubbery" [36] or "soft" [33] by previous authors. In fact, the HA/FA overlayer may actually provide, by virtue of its gel-like, colloidal nature, an "indistinct" surface to regions of SOM in which it is dominant [36]. This is in contrast to the rigid, inflexible, "hard" [33] or "glassy" [36] nature of humin, the organic matter which predominates within the cores of soil particles.

According to these models, the sequestration process consists both of dissolution of contaminant(s) into the "rubbery" HA/FA phase which coats the outer surface of soil particles and entrapment within the "glassy" humin phase's micropores. The latter of these has been referred to as an "internal surface" [40]. Most authors have concluded that interactions between soil and contaminants such as PAHs occur as a two-step process, with adsorption onto hydrophobic surface material taking place first, and partitioning into pores later [33–36,41]. In this model, entrapment within humin micropores will only be maximal after a contaminant has dissolved across the boundary layer of HA/FA [36]. For example, White et al. [42] examined phenanthrene bioavailability in native soil compared to bulk humin (soil with HA and FA extracted). The latter showed greatly retarded contaminant degradation relative to the former. However, the magnitude of this effect diminished as the length of the phenanthrene/native soil contact time increased, indicating that, given sufficient time, contaminant will enter the humin phase. One recent study which has advanced a conflicting view was based upon the distributions of both freshly spiked and aged phenanthrene across HA, FA, and humin fractions; because phenanthrene was always found in the humin fraction, these authors claimed that contaminant/humin interactions begin to occur (indeed, become dominant) immediately [43]. However, it is unclear that the solubilization of HA and FA during the extraction process did not result in transfer of phenanthrene to the humin fraction, producing the observed distribution as an artifact.

Our data support the former of these two models, as the apparent porosity-mediated effects on PAH susceptibility, which in this model would be due to entrapment in humin micropores, do not appear to be important for most compounds in the "time-zero" reactions. These effects first manifest themselves with low-molecular-weight PAHs; at all three timepoints examined, they are most extensive with these compounds. We propose that this reflects the differing kinetics of diffusion of low- and high-molecular-weight PAHs across the HA/FA boundary layer and into the humin core. It is well known that the affinity of PAHs for HA, relative to the solution phase, increases with the molecular weight of the PAH [44]; based on the present data, this seems to result in HMW PAHs taking longer to diffuse across the HA/FA domain and reach the humin phase. This, in turn, increases the duration of their susceptibility to chemical oxidation.

Soils and sediments that are dominated by hard humin carbon are, in general, those which have been subjected to a significant degree of diagenetic alteration [35,45]; for example, those derived from the erosion and weathering of shales and other sedimentary rocks. In contrast, soils and sediments which have not experienced diagenetic alteration are more likely to have organic matter fractions in which soft carbon predominates [35,45]. Our data indicate that porosity-mediated sequestration in humin-dominated soils can result in significant portions of the total contaminant load rapidly becoming refractory to chemical treatment, perhaps within a few weeks of initial contact. For example, porosity-mediated sequestration is already very evident in soil #1 (the most humin-dominated sample) within 40 days of spiking. Thus, it follows that contaminant releases into humin-rich soils and sediments, such as those listed above, will be more likely to prompt remediation as soon as possible after the spill. This will be particularly true if concentration-based endpoints are to be achieved in the cleanup process. In contrast, it appears that contaminants introduced into soft-carbon dominated soils may, in general, be expected to remain amenable to chemical oxidation for a longer period of time. The precise TOC value which serves as the "inflection

point" between the two soil types is probably dependent to some extent on the amount of oxidant added, as consumption of oxidizing equivalents by soil organic matter is expected to be one of the mechanisms impeding chemical oxidation of contaminants in high-TOC soils.

Acknowledgements

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