

In situ bioremediation of aquifers containing polyaromatic hydrocarbons*

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Abstract

In situ bioremediation has increasingly been proposed as a remediation option for a broad range of sites. A comparison of pump-and-treat processes to *in situ* bioremediation for a hypothetical polyaromatic hydrocarbon (PAH) contaminated aquifer is discussed with support from laboratory analyses. Influence of micro-processes such as desorption, dissolution, and diffusion on pollutant bioavailability and subsequent effectiveness of biodegradation at complex PAH-contaminated sites is considered. Low solubilities of four and five-ringed PAHs render them essentially impossible to remediate through pump-and-treat processes. Analyses indicate that following removal of more soluble PAHs in an *in situ* biodegradation process, the rate of degradation will be limited by the rate of dissolution such that oxygen transport requirements will decrease as the process continues.

Introduction

One of the dominant themes in the aquifer remediation literature of the past two years has been that the performance of pump-and-treat processes is limited by certain inherent factors associated with the dissolution, desorption and diffusion of contaminants [1-3]. During this same period, *in situ* bioremediation has increasingly been proposed as a remediation option for a broad range of sites, including those with soil permeabilities and contaminants which have not generally been considered amenable to this process [4].

In situ bioremediation treats both soils and groundwater contaminated with organic constituents by enhancing the natural biodegradation of the contaminants within the saturated zone. The process typically relies on indigenous bacteria which use the contaminants as a source of carbon and energy, converting the contaminants to carbon dioxide and water [5]. *In situ* bioremedia-

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tion involves installing a groundwater injection and extraction system to transport dissolved oxygen and water-soluble nutrients through the contaminated area. Selection of the best injection/recovery design depends upon the distribution of contaminants, the location of groundwater, the hydraulic conductivity of the soil and physical limitations of the site.

The vast majority of *in situ* bioremediation field experience has been associated with sites containing motor fuels (gasoline, diesel, jet fuel) where volatile aromatic hydrocarbons are the primary constituents of concern. However, *in situ* bioremediation is increasingly being considered for sites containing coal tars, heavy petroleum distillates, or residues from manufactured gas, petrochemical and refining operations where polyaromatic hydrocarbons (PAHs) are the primary constituents of concern. This paper will examine the rationale for considering an *in situ* bioremediation process at sites containing these constituents. It will then explore potential differences between remediation of volatile aromatic hydrocarbons and remediation of PAHs that may be significant when evaluating and/or designing clean-up processes. Finally, a series of laboratory biodegradation studies that evaluate the accessibility of PAHs to *in situ* treatment will be discussed.

Physical, chemical and microbial properties of PAHs

By definition, polyaromatic hydrocarbons are chemicals containing only hydrogen and carbon atoms, with two or more aromatic rings. They are, in a sense, the semi-volatile cousins of the volatile aromatic compounds (benzene, toluene, ethylbenzene and xylene) and, like the BTEX compounds, they are

TABLE 1

Important properties^a of representative aromatic hydrocarbons

Compound	Number of rings	Molecular formula	Solubility (mg/L)	K_{OC}	Log K_{OW}	R	Biodegradation half-life (days)
Benzene	1	C_6H_6	1780	85	2.1	5.25	5-10
Naphthalene	2	$C_{10}H_8$	30	2300	3.25	57	9-13
Anthracene	3	$C_{14}H_{10}$	0.045	1.8×10^4	4.45	886	<9-50
Phenanthrene	3	$C_{14}H_{10}$	1.0	1.8×10^4	4.46	908	<6-43
Benz[a]anthracene	4	$C_{18}H_{12}$	0.0057	1.38×10^6	5.6	6.9×10^4	63-231
Pyrene	4	$C_{16}H_{10}$	0.132	3.8×10^4	4.88	2.4×10^3	
Chrysene	4	$C_{18}H_{12}$	0.0018	2×10^5	5.61	1.3×10^4	41-116
Benzo[a]pyrene	5	$C_{20}H_{12}$	0.0012	5.5×10^6	6.06	2.7×10^5	

^a R is estimated for a soil with 35% porosity and an organic carbon content of 1%.

Solubilities and partitioning coefficients taken from Verschuere [15].

Biodegradation half-lives from API [16].

of significant environmental concern. The solubilities of PAHs in water decrease as their molecular weight increases. They are all considered to be biodegradable, but their rates of biodegradation appear to be limited by the rates of dissolution, which are related to their aqueous solubilities. Two and three-ring PAHs are generally considered to be readily biodegradable, while the biodegradation half-lives of four and five-ring PAHs can be on the order of months to years, depending upon both the treatment conditions and the contaminant matrix [6,7].

Table 1 summarizes the molecular formulae, solubilities, organic carbon partitioning coefficients (K_{oc}), the octanol-water partitioning coefficients (K_{ow}), retardation factors (R), and biodegradation half-lives for benzene and seven representative PAH compounds. The larger PAH compounds have very low solubilities in water; they are tightly bound to the organic constituents in soil; they biodegrade slowly, and they are also of sufficient potential environmental risk that targeted cleanup goals can be as low as 0.2 ppb in groundwater.

Analyzing pump-and-treat for a PAH-contaminated aquifer

A first approximation of the performance of a pump-and-treat process for organic constituents can be developed based on partitioning coefficients and the organic carbon content of the aquifer. The distribution of each of these compounds between the sorbed and the dissolved phases can be estimated from the octanol-water partitioning coefficient and organic carbon content of the soil. (This analysis does not distinguish between PAHs which are sorbed on soils and those present within occluded droplets within the soil matrix.) This distribution coefficient, K_d , is the ratio of the concentrations of the sorbed phase to the concentrations of the dissolved phase compound, and K_d can be multiplied by the density of soil and divided by the porosity of the aquifer to determine the relative mass of sorbed contaminant to dissolved contaminant per unit volume. This ratio will be referred to as K_a , the aquifer partitioning coefficient.

By combining the compound-specific information provided in Table 1 with the estimated values for the porosity and bulk density of the aquifer, the efficiency of a simple pump-and-treat system can be estimated. If we envision that all of the "contaminated" water from a particular volume of an aquifer is replaced by clean water, then the mass of PAH removed is equal to

$$1/(K_a + 1)$$

and the amount remaining is

$$1 - 1/(K_a + 1)$$

The fraction remaining after " N " pore volumes of flushing is equal to

$$[1 - 1/(K_a + 1)]^N$$

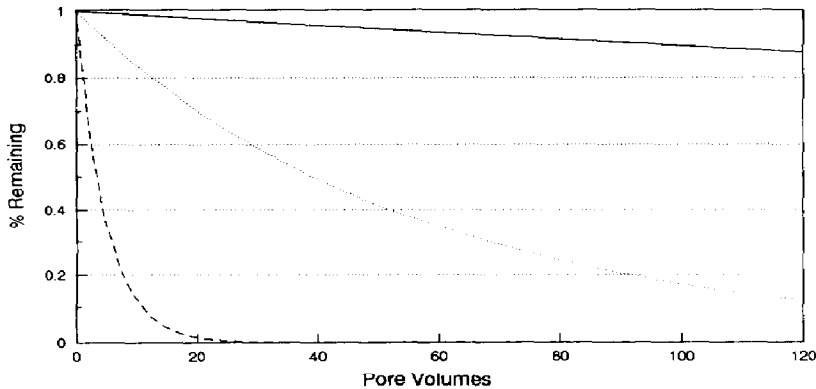


Fig. 1. Removal of aromatic hydrocarbons during pump-and-treat. (—) phenanthrene, (...) naphthalene, and (- - -) benzene. $F_{(oc)} = 1\%$ (organic carbon fraction).

The results of these calculations are summarized in Table 2.

Table 2 shows the fraction of each of the eight constituents remaining after an extended period of flushing at a site. As a point of reference, one pore volume of flushing is likely to require between one month and several years, depending upon the size of the treatment area and the rate of groundwater removal. The values calculated for benzene, naphthalene and phenanthrene are also displayed graphically in Fig. 1.

This analysis is obviously, overly simplistic. It ignores heterogeneities of the site, effective versus total porosity, flushing efficiencies, rates of dissolution

TABLE 2

Flushing efficiency of representative aromatic hydrocarbons

Compound	Fraction of contamination remaining after N pore volumes of flushing						
	1	10	20	40	60	90	120
Benzene	0.810	0.121	0.015	0.000	0.000	0.000	0.000
Naphthalene	0.982	0.838	0.702	0.493	0.346	0.203	0.120
Anthracene	0.999	0.989	0.978	0.956	0.934	0.903	0.873
Phenanthrene	0.999	0.989	0.978	0.957	0.936	0.906	0.876
Benz[a]anthracene	1.000	0.999	0.998	0.997	0.995	0.993	0.990
Pyrene	1.000	0.996	0.992	0.983	0.975	0.963	0.951
Chrysene	1.000	0.999	0.998	0.997	0.995	0.993	0.991
Benzo[a]pyrene	1.000	1.000	0.999	0.999	0.998	0.998	0.997
Average	0.974	0.866	0.833	0.798	0.773	0.745	0.725

*These calculations assume 35% porosity and an organic content of 1%.

and multiple other factors. But, it still provides a general analysis of the relative rates of extraction that can be expected for various constituents of a contaminated site. And for PAHs, the conclusion of this analysis is clear: pump-and-treat systems are very inefficient at removing PAHs from contaminated aquifers.

Analyzing *in situ* bioremediation for a PAH-contaminated aquifer

Oxygen transport has been identified as the rate limiting parameter for the *in situ* biodegradation of compounds at sites containing readily biodegradable compounds, including naphthalene and benzene [5,8]. The kinetics of microbial degradation in these systems are so much faster than the rate at which dissolved oxygen can be transported through a site, that rates of desorption, temperature effects and other factors which are significant in oxygen-rich environments, have proven to be of minor importance in designing *in situ* bioremediation projects. As a result, a first approximation of the rate of biodegradation achievable can be made by estimating the oxygen demand of the site and comparing this value with the rate at which oxygen can be supplied. This rate is, in turn, controlled by the rate of water movement through the site and the concentration of dissolved oxygen within the water.

The relative rate of *in situ* bioremediation under these conditions can now be compared with that of pump-and-treat by comparing the rate of oxygen supply to the rates of extraction. Table 3 presents a comparison of the two processes for a series of hypothetical aquifers containing various concentrations of PAHs. In each instance, the initial PAH concentration (1000, 250 or 100 mg/kg) is assumed to consist of equal amounts of each of the eight PAHs listed in Table 2. The performance estimates for *in situ* bioremediation are provided for three levels of dissolved oxygen; 10 ppm (water saturated with air), 40 ppm (water saturated with oxygen) and 150 ppm (water containing 300 ppm of hydrogen peroxide as an oxygen carrier). The calculations assume that three pounds of oxygen must be delivered to biodegrade one pound of PAH and that no other sources of oxygen demand are significant. The top portion of the table illustrates performance of the two processes expressed as mass removed per pore volume of treatment, while the bottom portion illustrates the percent of PAH that would remain after 10, 40 and 120 pore volumes of treatment. In Table 3A, the incremental performance of each process is shown, while in Table 3B the removal rates for *in situ* bioremediation are added to those estimated for pump-and-treat alone.

The implications of the type of analyses presented in Tables 2 and 3 are consistent with the results of more detailed analyses performed at actual sites.

- *In situ* bioremediation is most cost-effective when treating contaminants which have retardation factors greater than ten, where pump-and-treat is not very efficient.

- At sites containing contaminants with a wide range of solubilities, pump-and-treat may be the more efficient process initially and *in situ* bioremediation the more cost-effective at later stages of the project.
- A pump-and-treat process is often cost-effective (relative to *in situ* bioremediation), as long as the concentration of contaminants in the extracted water is greater than the concentration of contaminants that could be degraded by dissolved oxygen injected during an *in situ* bioremediation process.

Thus far, this paper has focused on the potential benefits associated with using *in situ* bioremediation for PAHs and has assumed that PAHs will respond to treatment in a manner similar to that in which volatile aromatic hydrocarbons respond. The next section of this paper explores the possibility

TABLE 3

A. Performance comparison of pump-and-treat versus *in situ* bioremediation^a

Initial PAH concentration (mg/kg)	Pump-and-treat PAH removed (in mg/kg) during various flushes				<i>In situ</i> bioremediation PAH removed (in mg/kg) based on the D.O. content of the injected water (ppm)		
	PV-1	PV-10	PV-20	PV-50	10	40	150
1000	26	5.8	2.3	1.3	0.8	3.2	12
250	6.5	1.45	0.58	0.33	0.8	3.2	12
100	2.6	0.58	0.23	0.13	0.8	3.2	12

B. Percent PAH remaining after various pore volumes of treatment^b

Initial PAH concentration (mg/Kg)	No. of PV	Pump-and-treat only	Concentration of D.O. in groundwater (ppm)		
			10	40	150
1000	10	86.6	85.8	83.4	74.6
	40	79.8	76.6	67.0	31.8
	120	72.5	62.9	34.1	0
250	10	86.6	83.4	73.8	38.6
	40	79.8	67.0	28.6	0
	120	72.5	34.1	21.3	0
100	10	86.6	78.6	54.6	0
	40	79.8	47.8	0	0
	120	72.5	0	0	0

^aCalculations assume that PAHs are comprised of equal quantities of the eight PAHs listed in Table 2 and no other source of oxygen demand is present. PV means pore volumes.

^bCalculations assume that PAH biodegradation is limited only by the transport of dissolved oxygen.

that PAH desorption/biodegradation, and not oxygen transport, becomes the rate limiting factor as the *in situ* bioremediation process progresses.

Total versus instantaneous oxygen demand

One fundamental assumption in the design of *in situ* bioremediation processes is that oxygen transport is the rate limiting step for the overall process. This model is used in designing the oxygen transport strategy including the injection and recovery system, the concentration of dissolved oxygen to be delivered, the type and frequency of monitoring and the predicted time frame of remediation. However, the rates of biological degradation within soil systems for the four and five ring PAHs, summarized in Table 1, are ten to twenty times slower than those for BTEX compounds and lighter PAHs. Similar results have been reported in slurry systems [7,9]. Biodegradation studies in Remediation Technologies, Inc.'s (RETEC's) laboratories and those of several academic institutions have also noted that these degradation rates vary widely and in some instances, compounds which are generally readily biodegradable are simply not "bioavailable" [9,10]. Collectively, the available information on PAH diffusion, dissolution and biodegradation suggest that dissolution and diffusion will control biodegradation and that biodegradation will control remediation at many PAH sites.

Recent research on the biodegradation of PAHs in soils from former manufactured gas facilities suggests that the soil matrix may control the extent of biodegradation achievable as well as the rate [11]. Four soils, designated B, F, G and J were selected for a series of biodegradation experiments.

These four soils were selected because their organic carbon contents ranged from less than 1% to over 50% (because of the presence of lampblack and other materials) and because the percentage of fine grained material ranged from 3% to 26%. Earlier studies had suggested that these two parameters might have a significant effect of the biodegradation process. Each soil was treated in two systems. The first was a simulated land treatment process, where the soils were amended with nutrients, kept moist and were mixed regularly to provide aeration and general mixing. The extent and rates of removal of PAH constituents during this "unsaturated" treatment for these four soils are summarized in Table 4. For comparison, a second set of biodegradation experiments were performed with the same soils, using a slurry phase treatment. This experiment was designated as "saturated" treatment. The rate and extent of PAH removal of these studies also appear in Table 4. As expected, the slurry treatment provided more rapid treatment than did the unsaturated treatment, but the ultimate concentrations of PAH achieved using the two methods is essentially the same for three of the four soils. However, Soil F, which contained 26% fines and 6.5% organic material, demonstrated 84% PAH removal in the slurry phase but no significant reduction in the less aggressive unsaturated treatment. The

TABLE 4

Summary of soil characteristics and modified first-order coefficients

Soil	Initial PAH concentration (mg/kg)	Fines content (%)	Carbon fraction (%)	First-order decay rate (day ⁻¹)		Reduction of PAHs (%)	
				Unsaturated	Saturated	Unsaturated	Saturated
B	160	3	0.6	0.054	0.24	93	96
F	190	26	6.5	- ^b	0.57	<20	84
G	20,000	7	16	0.024	0.19	78	74
J	29,000	27 ^a	58	0.041	0.24	42	46

^aIncludes lampblack fines.^bData was not fit to the mathematical model.

authors suggest that the presence of these fines allows the formation of aggregates which can retain significant quantities of organic constituents. Since these pores are smaller than bacteria, and many PAHs are very insoluble, these constituents remain unavailable for biodegradation in the absence of sufficient water (and perhaps mechanical energy) to disperse the aggregates.

If we extend the results of this study to an *in situ* bioremediation process where minimal mixing exists, it seems likely that the rate of PAH removal may be very low at sites containing lenses of fine grained soils. In these environments, the rate and extent of remediation will be limited by the rate of dissolution and diffusion of low soluble constituents from low permeability zones into those portions of the site where groundwater movement, oxygen exchange and microbial activity are occurring.

The distinction between an oxygen transport-limited and a diffusion-limited process is illustrated in Fig. 2. Scenario I represents the traditional assumption that oxygen transport is the rate limiting factor for *in situ* biodegradation. The plots shown in Scenario I demonstrate the effect of increasing the concentration of dissolved oxygen on the rate of *in situ* bioremediation. The three lines show the rates of remediation when a pore volume of water contains 2%, 10% or 20% of the total biological oxygen demand (BOD) of the area being treated. Under these conditions, the optimum design will deliver as much oxygen per unit volume of water as can be delivered without other detrimental effects (such as oxygen loss due to instability or degassing). Under these conditions, increasing the density of injection and recovery wells will result in increased oxygen transport and, subsequently, increased rates of remediation.

The Scenario II plot illustrates the rate of *in situ* bioremediation, if 20% of the contamination is "instantly degradable" and the remaining portion of the contamination desorbs at the rate of 1% per pore volume. Under these conditions, as soon as the instantaneous demand is satisfied (the readily degraded-constituents have been depleted) there is no advantage to supplying more dis-

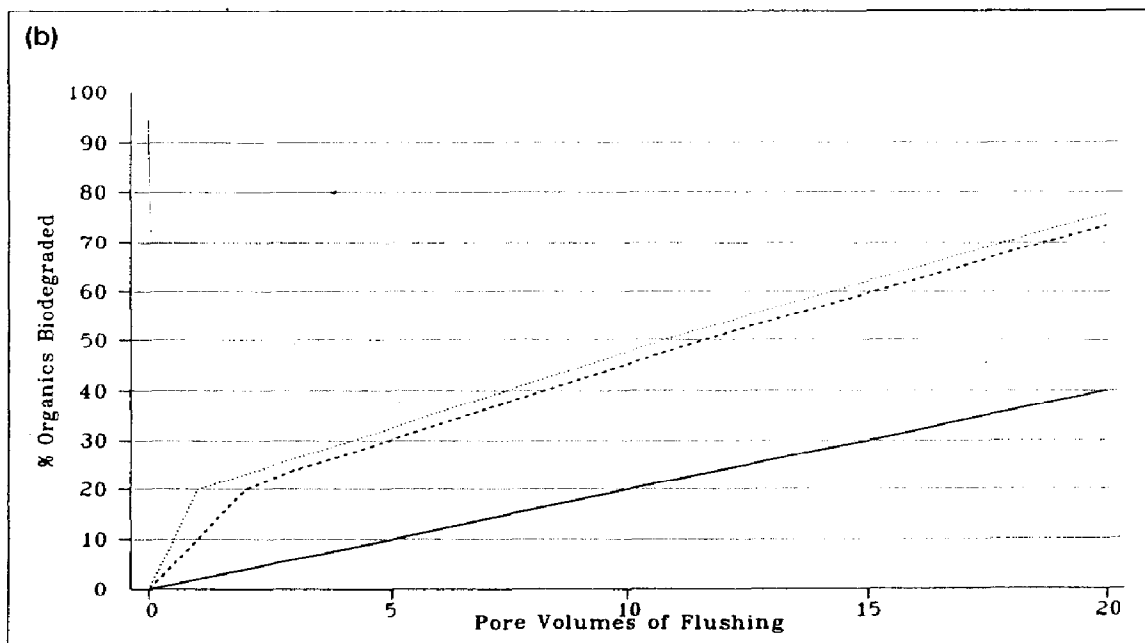
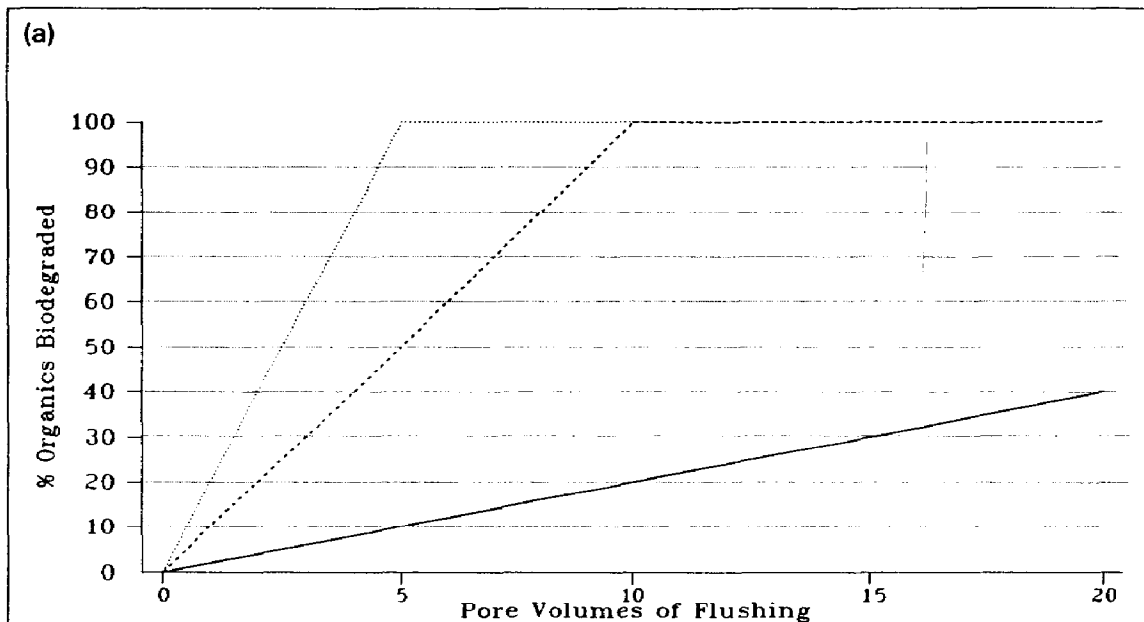


Fig. 2. Rate of bioremediation as a function of oxygen supply. (% BOD per PV). (a) Scenario I - All organics readily available, (b) Scenario II - 20% of organics readily available. (...) 2%, (- - -) 10%, and (—) 20% BOD per PV.

solved oxygen than is required to satisfy the continued oxygen demand created by freshly desorbed constituents.

Under the Scenario II conditions, after five pore volumes of flushing at the 10% level, continued oxygen delivery at the 5% level (meaning a concentration which delivers 5% of the total BOD of the site in one pore volume) provides the same level of remediation as the addition of four times that level.

Utilization of a "Scenario I" process for a "Scenario II" site can lead to serious design errors, including unrealistic predictions of remediation rates; addition of greater quantities of oxygen than can be used efficiently; possible termination of the process, when original oxygen breakthrough occurs while 80% of the total oxygen demand remains in the aquifer; and/or design of an aggressive injection/recovery system, when a system designed for a slower rate of oxygen delivery would produce comparable results.

***In situ* biodegradation under desorption-controlled kinetics**

In a pump-and-treat process, a PAH molecule which dissolves from the contaminant matrix is then likely to resorb and desorb multiple times before it is finally extracted to the surface. The relative time spent in the soluble and insoluble forms is reflected by the partitioning coefficient for that compound. In an *in situ* bioremediation process, the aquifer contains a viable population of PAH-degrading bacteria, plus the necessary oxygen and nutrients for microbial activity. Under this scenario, the PAH, once dissolved, may be biologically degraded, thus providing continued depletion of PAH constituents throughout the aquifer.

As the total mass of readily degradable contaminant is depleted and the rates of desorption of slowly desorbable constituents decrease, less and less oxygen will be needed in the treatment area to maintain an oxygen surplus. In many instances, hydraulic containment may not be warranted, as long as this oxygen surplus condition is maintained. Eventually, the dissolved oxygen supplied by the natural groundwater moving into the site will be adequate to maintain an oxygen surplus; and, continued oxygen delivery will no longer be beneficial, as the kinetics of remediation are independent of externally controlled forces.

Many micro-processes contribute to the effectiveness of biodegradation at complex PAH-contaminated sites. In particular, the time required to achieve targeted concentration goals is contingent upon the mechanisms of desorption, dissolution and diffusion. These same factors, along with the presence of other degradable constituents, are also likely to control the level of remediation that can be achieved. Soils containing two- and three-ring PAHs, which are soluble in the parts per million range, can be treated to very low levels because the rate and extent of desorption is sufficient to maintain viable bacterial activity. However, given the minimal solubility and strong sorption of higher molecular weight PAHs, whose maximum solubilities are only a few parts per trillion and

whose cleanup standards are very low, biological activity may not be great enough to support a viable microbial population, depending upon the availability of other carbon sources in the aquifer. After the more soluble PAHs have been removed, the rate of degradation will be limited to the rate of dissolution. At extremely slow rates of dissolution, the total mass of degradable carbon will be low and could drop below the critical level of carbon needed to maintain a viable population of PAH-degrading bacteria. However, there is no general agreement on what the effectiveness of *in situ* bioremediation will be.

Laboratory and field studies with groundwater from a wood treating site in Conroe, Texas suggested that biodegradation of PAHs could not reduce concentrations below 5-30 ppb for individual PAHs [8]. By contrast, dozens of treatability studies using slurries and trickling filters have shown soluble concentrations of PAH and volatile aromatic compounds can be reduced to below detection levels (1 ppb). Several carefully documented studies have also indicated biodegradation of various organic constituents to very low levels, though most of these compounds are more soluble than four-ringed PAHs [12,13]. More experimentation is required to understand those factors which control biodegradation at very low organic concentrations and to understand whether *in situ* bioremediation can achieve the extremely low concentrations being set for some remediation designs [14].

Laboratory studies

Ultimately, many of the questions raised in this paper can only be resolved after a combination of carefully controlled laboratory-scale experiments and field-scale experience. As a initial step in this process, RETEC has recently completed a series of studies using soils from a former wood treating facility .

Soil samples were collected from two different areas of the site. The first soil sample, designated "A", was collected near a former lagoon, which had received runoff from a wood treating operation for many years. The soils generally consisted of a mixture of silt, clay and fine sand. The in-place permeabilities of soils in this portion of the site are in the range of 10^{-3} cm/s. The soils obtained for the treatability study contained 11,706 ppm of PAHs prior to treatment.

The second soil sample, designated "B", was collected near a former pond located some distance from the lagoon. When the facility was in operation, heavy rainfall would cause the lagoon to overflow, thus contaminating the pond. Soils from the pond area were found to be clayey silts and silty clay, though in-place hydraulic conductivity was estimated at 2×10^{-4} cm/s, probably due to secondary permeability. The soils collected from this area contained 813 ppm total PAHs prior to treatment. A third soil, designated "C", was collected downgradient of the lagoon. This sample, though containing only 19 ppm of PAHs, was still sufficiently contaminated such that groundwater in contact with this soil was considered a potential threat to the environment.

Soils from all three areas were treated in a slurry reactor for 12 weeks to determine the maximum extent of remediation that could be achieved. Soils were analyzed for total and carcinogenic PAHs at the beginning and end of the treatment. In addition TCLP extractions were performed on the soils to determine how the mass of "extractable" PAHs (meaning extractable to leachate or groundwater) compared to the "total" PAHs detected (those extractable with an organic solvent). The results of these studies are summarized in the top portion of Table 5.

The concentration of total PAHs decreased by over 90% in reactors A and B and by about 60% in reactor C. Perhaps more significantly, the TCLP extractable fraction of the contamination was reduced by greater than 99.5% in the soils that were highly and moderately contaminated and TCLP extractable constituent levels were reduced to below detection limits in the slightly contaminated soil. This suggests that those constituents which are off the greatest risk to the environment, because of their migration potential, were almost completely removed during biological treatment.

Two of the soils, B and C were then placed into glass columns, through which water was transported at a rate of four pore volumes per day for 22 weeks. (A pore volume is the volume of water contained within the column). This water was amended with 40 ppm of dissolved oxygen as well as microbial nutrients. These results appear in the lower half of Table 5.

TABLE 5

Laboratory treatability studies with PAH-contaminated soils

Slurry study (12 weeks) (12 weeks)	Soil A		Soil B		Soil C	
	Soil (mg/kg)	TCLP extract (mg/L)	Soil (mg/kg)	TCLP extract (mg/L)	Soil (mg/kg)	TCLP extract (mg/L)
Initial total PAHs	11,706	5.473	813	2.683	18.93	0.00327
Initial carcinogenic PAH	665	<0.04	<50	<0.01	12.56	0.00008
Final total PAHs	707	0.028	4.59	0.00097	7.11	0.00047
Final carcinogenic PAHs	273	0.002	1.73	0.00004	3.35	ND
Reduction of total PAHs (%)	94	99.5	99.4	99.9	62	85
Reduction of carcinogenic PAHs (%)	59				73	
Soil column			Soil (mg/kg)	Effluent (mg/L)	Soil (mg/kg)	Effluent (mg/L)
Initial total PAHs			1174	0.0037	19	0.0083
Initial carcinogenic PAH			40			
Final total PAHs			350	0.000065	21	0.00048
Final carcinogenic PAHs			46			
Reduction of total PAHs (%)			70	98	0	94
Reduction of carcinogenic PAHs (%)			0			

For soil B, the PAH concentration in soil decreased from 1174 to 350 ppm (70%) while the level of contamination in the effluent decreased by 98%. In the column containing the slightly contaminated soil, C, there was no discernable change in soil concentration but the effluent concentrations decreased by 94%. A plot of effluent concentration versus time (Fig. 3) for these two column studies suggests a first-order decrease in concentration, both achieving concentrations of less than $1 \mu\text{g/L}$ total PAHs after extensive treatment (300-700 pore volumes).

Although no microbial inhibited controls were included in these studies, the

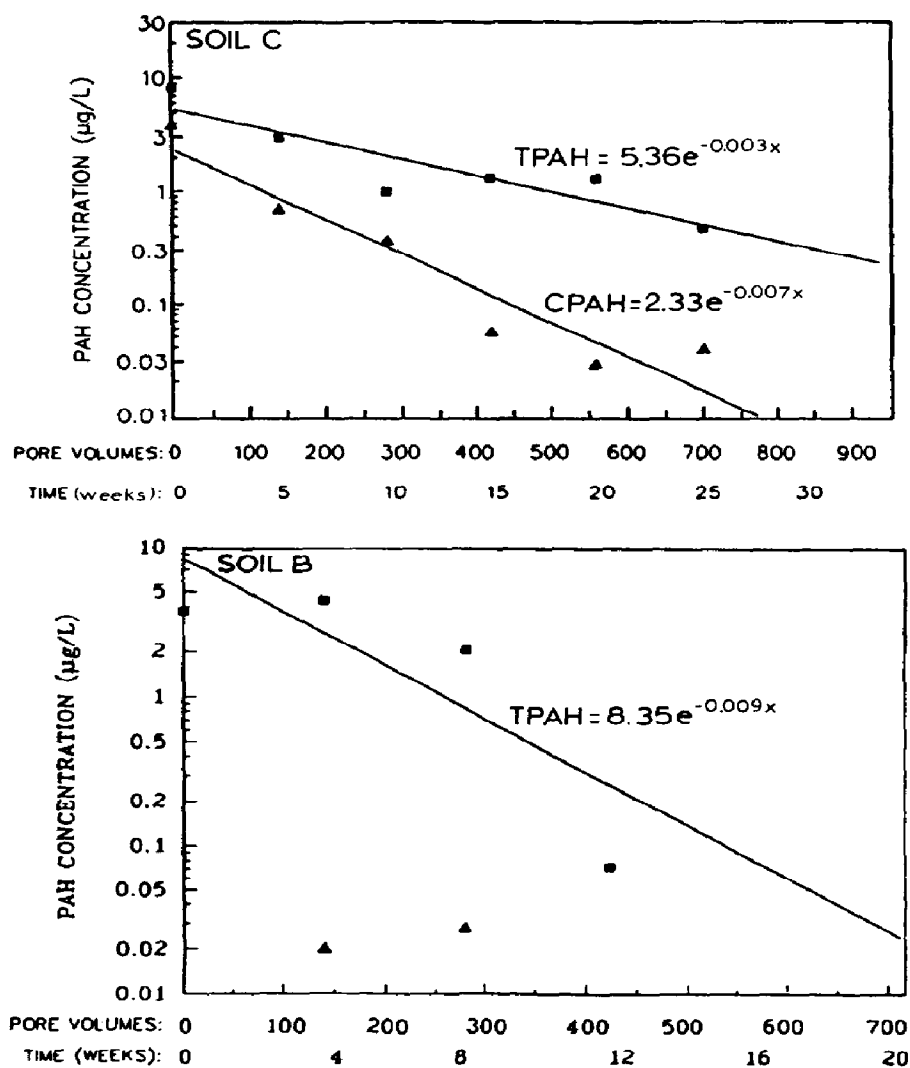


Fig. 3. PAH concentrations in effluents from columns of two creosote-contaminated soils. (■) Total PAH, and (▲) carcinogenic PAH.

concentrations of contaminants in the effluent were analyzed and were found to be insignificant relative to the changes observed. Mass balance calculations for Soil B indicate that less than 0.1% of the PAH removed can be attributed to direct loss in the effluent, suggesting that biodegradation was the primary remediation process. This information, in combination with microbial data, dissolved oxygen profiles and other indirect measurements, support the conclusion that the reductions resulted primarily from biological treatment rather than simple flushing.

Although the results presented represent a limited set of experiments, they provide an indication of both the feasibility and the complexity of *in situ* bioremediation processes for PAH contaminated sites.

Summary and conclusions

Essentially no remediation occurs for three-, four- and five-ringed PAHs in pump-and-treat processes.

The relative performance of pump-and-treat and *in situ* bioremediation can be estimated using simple mathematical models, but the validity of these models requires that partitioning between dissolved and sorbed constituents is fast relative to groundwater movement.

If desorption of PAHs is the rate-limiting step for the *in situ* bioremediation of an aquifer, the most cost-effective process will be that which provides slightly more dissolved oxygen than that required to satisfy the instantaneous oxygen demand of the site.

The rate of desorption and the extent of bioavailability of PAHs is site specific and not readily predictable.

Site specific treatability studies are recommended before predicting the kinetics or extent of biodegradation that can be achieved at PAH-contaminated sites.

Further research is required to understand the factors which control desorption and microbial degradation in soil systems containing low concentrations of PAHs.

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