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ENHANCED BIODEGRADATION OF POLYAROMATIC HYDROCARBONS IN MANUFACTURED GAS PLANT WASTES

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ABSTRACT

Scientists at the Institute of Gas Technology (IGT) have focused on enhancing destruction of polyaromatic hydrocarbons (PAHs) present as pollutants in manufactured gas plant (MGP) soils. The factor that bears the most restrictive influence on successful biological PAH degradation is low pollutant transfer from soil into an aqueous environment where biotreatment processes can take place. Physical and chemical enhancements were used in conjunction with biological processes. Physical enhancements overcame the mass transfer problem and made possible the biological destruction of aromatic hydrocarbons. One- to three-ring aromatic hydrocarbons were readily biodegraded in liquid, soil slurry, and -- to a lesser degree -- composted soil systems. Four- to six-ring PAHs remained persistent but were effectively destroyed when chemical co-treatments were used. Combined biological/chemical/physical processes are currently being tested to achieve the most extensive PAH degradation possible for MGP soils.

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INTRODUCTION

Previous work suggests that binding of polyaromatic hydrocarbons (PAHs) to soil particles may limit their biodegradation by restricting availability of PAHs to microorganisms.(2,3,5) Thus, the feature of manufactured gas plant (MGP) soils that governs the rate and extent to which PAH biodegradation will be achieved is pollutant mass transfer from the soil or bulk tar phase to the aqueous solution where soil microorganisms thrive. The studies presented here describe ways these mass transfer limitations have been overcome to achieve effective organic pollutant degradation. Generally, biodegradation of two- and three-ring PAHs occurs more readily than biodegradation of four- to six-ring PAHs. Particular emphasis has been placed on enhancement techniques that are effective for reducing levels of these latter, persistent PAHs.

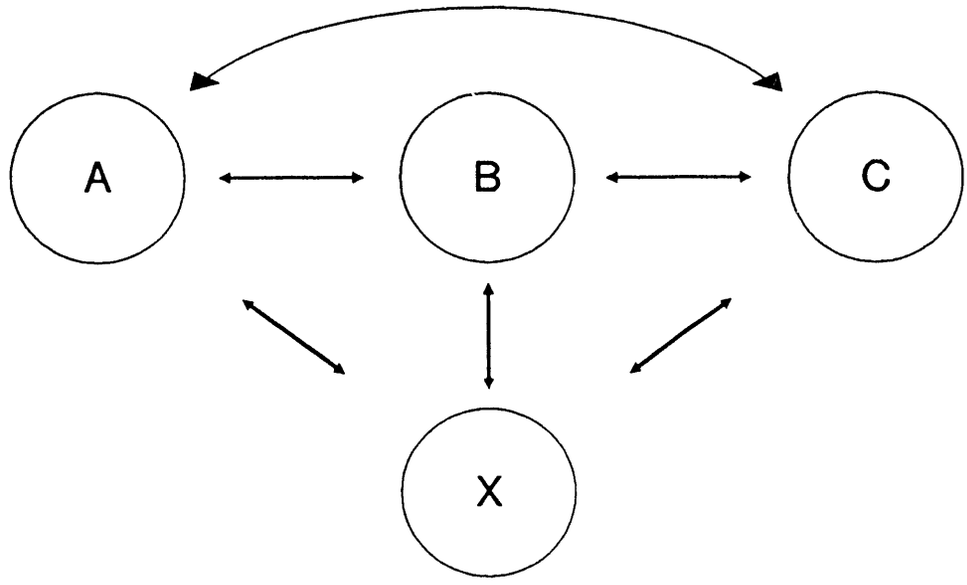
BACKGROUND

A model describing soil particle-PAH interactions that may govern PAH bioavailability is depicted in Figure 1. In this model, PAHs exist adsorbed to the soil particle, in the soil water (i.e., hygroscopic water bound to the soil, not capillary or gravitational water) and as constituents of any nonaqueous phase liquids (NAPL) (organic liquid phase) that might be present. All of these represent distinct components that are reservoirs of potentially biologically degradable PAHs. Figure 1 illustrates that PAHs might be exchanged among these various categories. However, for microbial degradation to occur, the pollutants must be exchanged from any of the soil associated components into the aqueous microenvironment where the microorganisms live. The hydrophobic character of PAHs may influence pollutant mass transfer and subsequent bioavailability somewhat. However, contaminant mass transfer from NAPL and fine soil agglomerates is probably the most rate-limiting determinant influencing PAH bioavailability.

MATERIALS AND METHODS

Analytical Methods

Extractions and Chromatography. All soils and liquids were extracted using standard EPA protocols. Soils used SW-846 Method 3540 and liquids used SW-846 Method 3510.(1) Either a 1:1 mixture of acetone and hexane or dichloromethane was used as the extraction solvent. Analytes were determined mass spectrometrically according to SW-846 Method 8270 (1) using a 15-meter-long DB-1 column (0.25 mm ID and 0.25 μm film) and a Perkin Elmer



A = PAHs Associated with Soil
(e.g., on Soil Particles, Within Soil Aggregate)

B = PAHs in Soil Water (e.g., Mobile/Immobile Water)

C = PAHs in Nonaqueous Phase Liquid, NAPL

X = PAHs Solubilized for Biodegradation

Figure 1. POSSIBLE SOIL-PAH INTERACTIONS GOVERNING PAH BIOAVAILABILITY

8320 gas chromatograph fitted with an ion trap detector (ITD-GC/MS). The injector temperature was held at 325°C, and the following temperature system was used: 40°C for 4 min followed by an increase to 300°C at a rate of 10°C/min; isothermal at 300°C for 1 min.

Soil Desorption Testing Using Various Solvents

A soil desorption procedure was developed and used to ascertain the extent to which various pollutants present in MGP soils would desorb in various solvent systems. Details of this desorption protocol have been described previously and will not be elaborated on here.(2,3) Briefly, however, the desorption of organic pollutants adsorbed to an MGP soil designated TGS-7(F) was evaluated using water, 100% ethanol, and 100% methanol as solvents. Desorption of one- to six-ring aromatic hydrocarbons from whole TGS-7(F) soil into these various solvents was determined using ITD-GC/MS. Experimental partition coefficients (Kp, L/kg) were determined for the suite of analytes and compared with aqueous Kp values described in the literature.(4)

Biodegradation of PAHs in Methanol Extracts

Because methanol had been used to evaluate enhancement of desorption with the TGS-7(F) soil, it was of interest to determine the extent of PAH biodegradation, if any, that would be achieved in liquid culture.

Experiments using extracts of contaminated soil were performed by Soxhlet extraction of 20-g samples of contaminated soil with 250 ml of methanol and then using 1 ml of this extract per 100 ml of basal salts medium (BSM) in shake flask experiments. The conditions tested were abiotic controls and bioaugmentation with PAH-degrading bacteria. PAH-degrading bacteria were added to these flasks only at the start of each experiment, which continued for a total incubation period of 6 weeks. Samples were analyzed by extraction (liquid-liquid) of the entire contents of each flask, concentrating the extract to 10 ml and analyzing for PAHs by ITD-GC/MS.

Biodegradation Treatment Endpoint Determination of PAHs Using Soil Slurries

An important consideration in the application of bioremediation for treatment of polluted MGP soils is a determination of the extent that pollutants are degraded under ideal conditions. This treatment endpoint can be determined by soil slurry testing; such a procedure has been described.(2,3) It should be emphasized that, although slurry treatment may be considered for MGP sites, the goal of soil slurry testing is limited to the determination of treatment endpoints as described in this paper.

The MGP soils subjected to soil slurry testing differ in soil particle and contaminant characteristics. Soils designated TGS-7(F) and TGS-9(C) were used in this investigation. The former was laden with 30,000 to 40,000 μg/g of soil of total PAHs and the latter contained about 10,000 μg/g soil of total PAHs. TGS-7(F) was a sandy soil, whereas TGS-9(C) contained 35% clay.

Soil slurry experiments were performed by placing 20 g of contaminated soil in 500-ml Erlenmeyer shake flasks containing 100 ml of the bacterial growth medium, BSM.(5) Contaminated soils were inoculated (bioaugmented) with PAH-degrading bacteria and incubated at ambient temperature (22° to 25°C). Bioaugmentation was performed weekly for the duration of the study. Fresh BSM was also added weekly to ensure an adequate nutrient supply for microbial activity. At the conclusion of each experiment, the soil portion of each flask was air-dried at room temperature, Soxhlet extracted with a 1:1 mixture of acetone and hexane, and analyzed by ITD-GC/MS.

Biodegradation of PAHs in Soil Microcosms

A study was begun to evaluate a variety of amendments intended to enhance the biodegradation of PAHs present in

TGS-7(F) soil, the details of which have been previously described.(5) This was an ongoing investigation designed to simulate the treatment endpoints that would be expected from a prepared bed land treatment scenario, as shown in Figure 2, using soil microcosms (soil pans). The various treatment conditions are summarized in Table 1.

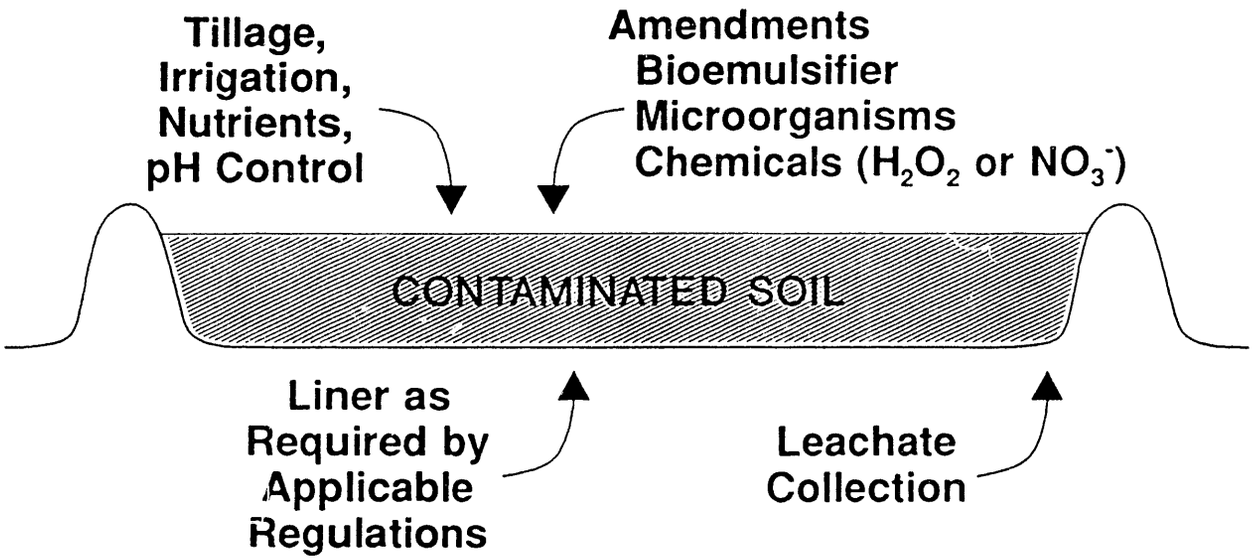


Figure 2. PREPARED-BED SYSTEM FOR BIOLOGICAL TREATMENT OF PAH-CONTAMINATED SOILS

Chemical Co-treatment Using Fenton's Reaction

A free radical reaction called Fenton's Reaction has been effective in reducing toxic and/or refractory organics in municipal wastewaters (6) and has been a component of our studies to enhance degradation of PAHs present in MGP wastes. To this end, the effectiveness of Fenton's reagent treatment of two contaminated soils [TGS-8(B) and TGS-7(F)] was evaluated by preparing a 10-mM solution of $FeSO_4 \cdot 7H_2O$. To quadruplicate reaction vessels (300-ml stainless steel centrifuge bottles), 130 grams of each MGP soil were mixed with 190 ml of 10-mM $FeSO_4 \cdot 7H_2O$. Next, 80 ml of 30% H_2O_2 were added (5 to 20 ml/h) while the reaction vessels were gently agitated. This treatment was repeated on each of 4 consecutive days. Prior to the addition of fresh reagents after the first day, soils were separated from supernatant liquid by centrifugation. Fresh reagents were then added to the soils. Soxhlet extracts were performed on 20 grams of each replicate as well as on untreated soil. These Soxhlet extracts were concentrated to 10 ml and analyzed by ITD-GC/MS.

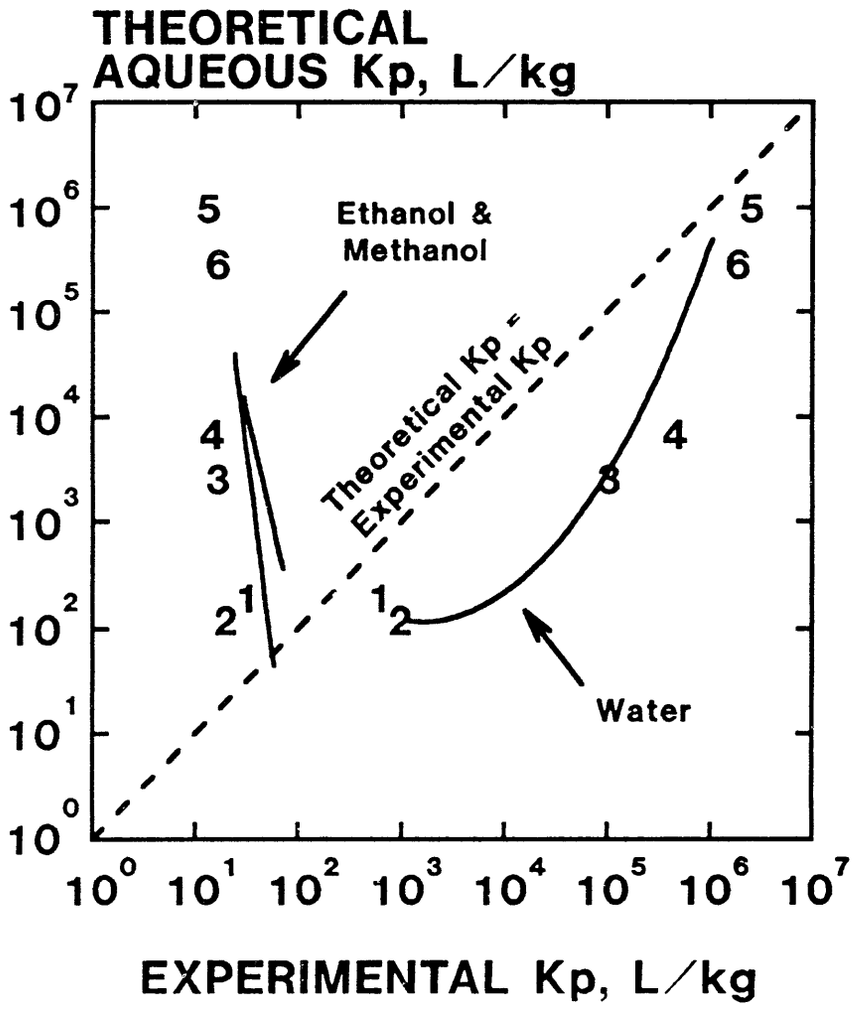
Table 1. TREATMENT CONDITIONS FOR SIMULATED LAND TREATMENT EXPERIMENTS USING TGS-7(F) CONTAMINATED SOIL IN SOIL MICROCOSMS

Treatment Code	Treatment Conditions
A	TGS-7(F) soil mixed 1:1 with uncontaminated fill soil obtained from the waste site
B	Treatment A supplemented with nutrients N and P
C	TGS-7(F) soil mixed 1:1 with cattle manure and supplemented with nutrients N and P
D	Treatment C + Bioemulsifier added on a twice-weekly basis
E	Treatment C + IGT Culture enriched from pure PAH compounds, coal tar, and TGS soil extracts added on a twice-weekly basis
F	Treatment C + IGT-SITE Culture enriched from TGS-7(F) site soil added on a twice-weekly basis
G	Treatment C + IGT and IGT-SITE Cultures mixed together and added on a twice-weekly basis
H	Treatment G + Bioemulsifier added on a twice-weekly basis
I	Treatment H; Soil sonicated at the beginning of the experiment with supplements added on a twice-weekly basis thereafter

RESULTS AND DISCUSSION

Soil Desorption Testing Using Various Solvents

The results of experiments intended to evaluate the desorption of aromatic hydrocarbons from TGS-7(F) soil using water, methanol, and ethanol are depicted in Figure 3. The dashed line represents desorption of these pollutants with published -- hence, theoretical or expected -- aqueous partition coefficients. These theoretical partition coefficients are determined using reagent PAHs first adsorbed to a selected soil and then desorbed in an aqueous system. All of the aromatic hydrocarbons subjected to desorption with water as a solvent fall below the dashed line. This indicates that the TGS-7(F) pollutants are tightly bound to soil and not readily desorbed. In effect, many of the PAHs may be present adsorbed to soil particles or within soil aggregates (Compartment A, Figure 1). The TGS-7(F) soil also contained a high proportion of NAPL



Legend

1 = Ethyl Benzene

2 = Naphthalene

3 = Anthracene & Phenanthrene

4 = Fluoranthrene & Pyrene

5 = Benzo(a)pyrene

6 = Benzo(g,h,i)perylene

Kp = Partition Coefficient of PAH Mass Transfer from Soil into Solvent

NOTE: Incresing Kp values reflect tighter binding of PAH s to soil particles

Figure 3. DESORPTION OF PAHs FROM TGS-7(F) SOIL USING WATER, ETHANOL, AND METHANOL AS SOLUBILIZING AGENTS

(Compartment C, Figure 1), which were not readily desorbed from the soil when water was used as a solvent.

Figure 3 shows that extensive desorption of soil-bound PAHs from TGS-7(F) soil occurred when either ethanol or methanol was used as a desorption solvent, compared with the theoretical aqueous partition coefficients. It should be noted that aqueous Kp values were used in this figure to compare experimentally derived partitioning with the expected (theoretical) partitioning of pollutants.

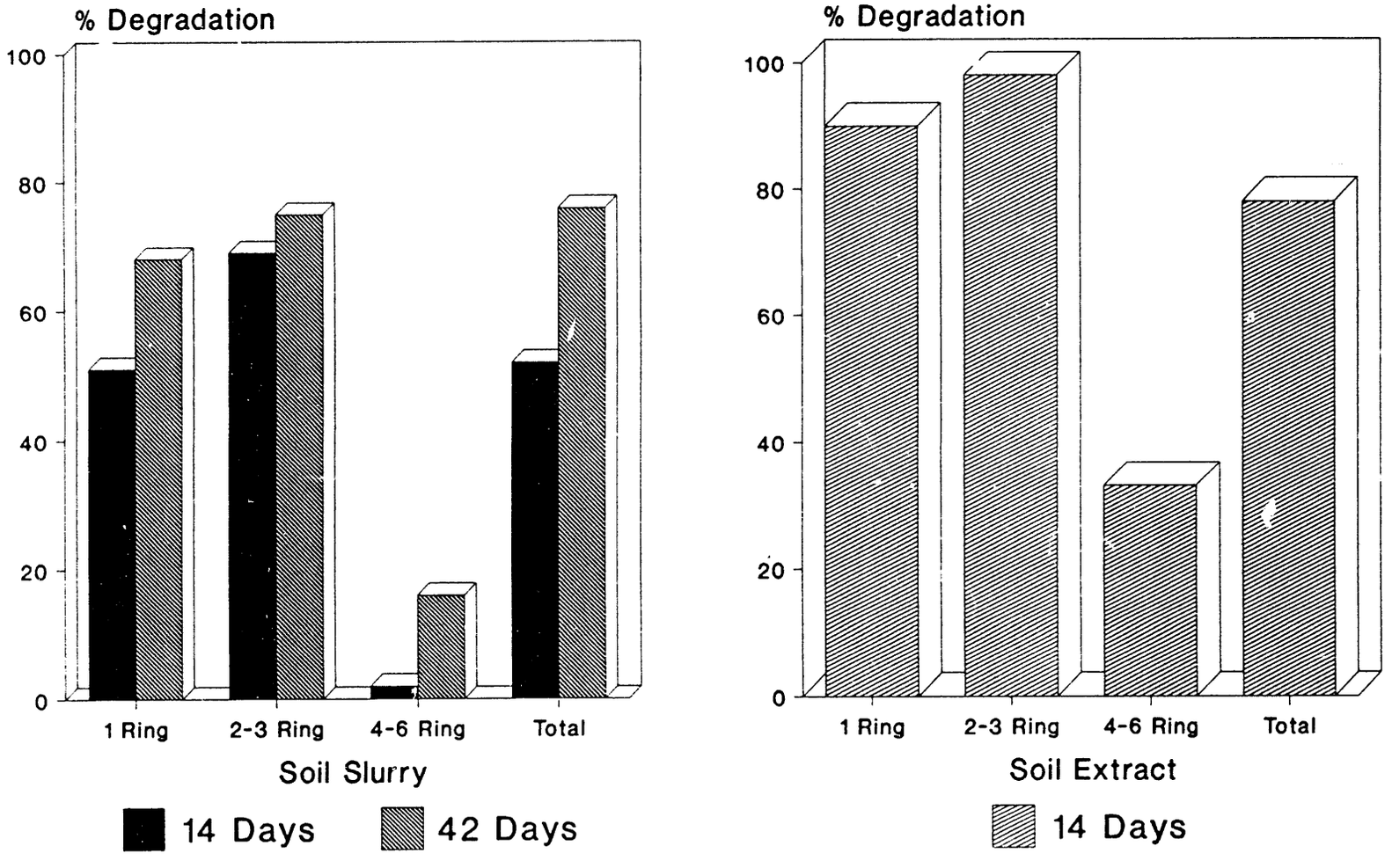
Enhanced desorption of aromatic hydrocarbons is achieved with either ethanol or methanol. Other investigations performed by IGT have determined that methanol and ethanol are equally effective in extracting PAHs from TGS-7(F) soil and are comparable with the extraction attainable using 1:1 acetone/ hexane mixtures, an EPA-approved solvent (data not presented). The finding that ethanol and methanol are effective in desorbing aromatic hydrocarbons from TGS-7(F) is also desirable because both are biologically compatible when delivered to biological systems at appropriate loading rates, as discussed below.

When one considers these results in the context of the soil-PAH interaction model presented in Figure 1, all compartments of the model would be affected by methanol or ethanol used to enhance pollutant desorption. Desorption of PAHs attached to soil particles (Compartment A, Figure 1) would be enhanced by ethanol or methanol treatment. Both ethanol and methanol are miscible with water and would be expected to facilitate elution of soil/ water-associated PAHs (Compartment B, Figure 1) into the aqueous environment of the soil microorganisms (Compartment X, Figure 1). Similarly, where a NAPL exists, either of these solvents would help facilitate the solubilization of PAHs and NAPL (Compartment C, Figure 1) for biodegradation. It is plausible that organics that comprise the NAPL might also serve as co-metabolic carbon and energy substrates and enhance PAH biodegradation.

All of the information regarding desorption testing of MGP soils has focused on overcoming the mass transfer of pollutants so they could be biodegraded. The data that follow depict biodegradation of MGP PAHs in systems where mass transfer is overcome by methanol extraction on one extreme, to a more limited extent in soil slurry systems, and least extensively in a system developed to simulate land treatment of MGP soils. All of these studies address Compartment X of Figure 1.

Biodegradation of PAHs Present in Methanol Extracts

Data illustrating the biodegradation of PAHs in methanol extracts applied at 1% (v/v) loading rates are depicted in the righthand panel of Figure 4. Total PAH levels were reduced by nearly 80% after 2 weeks of incubation. The most extensive biodegradation occurred for one- to three-ring PAHs to between 90% and 97% of their starting levels in the extract. These



*Includes aerobic biodegradation and some volatilization.

Figure 4. COMPARISON OF PAH DEGRADATION BETWEEN TGS-7(F) SOIL SLURRIES (20% SOLIDS) AND METHANOL EXTRACTS (1% v/v)

findings were obtained in a non-optimized batch incubation system where the cells were added only once at the beginning of the study. An optimized continuous treatment system with cell recycle would be expected to achieve better results, probably in a shorter time period.

Four- to six-ring PAHs were not as extensively biodegraded; however, it is possible that their biodegradation could be improved by adding cosubstrates and manipulating other cultural conditions. In a similar study using methanol extracts derived from a soil dominated by four- to six-ring PAHs, present at one-tenth of the concentration of PAHs in TGS-7(F) methanol extract, greater than 95% of all PAHs (one- to six-ring) were biodegraded in a 2-week incubation period (data not shown). Either differences in loading rates or innate chemical characteristics account for less biodegradation of four- to six-ring PAHs in TGS-7(F) soil. This is the basis of ongoing investigations.

PAHs extracted from soil are effectively biodegraded, indicating that, once PAHs exist in a biologically available form (Compartment X, Figure 1), they can be degraded.

Biodegradation of PAHs in Soil Slurries

One goal was to determine if physical treatment through vigorous mixing would facilitate PAH desorption and enhance biodegradation of MGP contaminants. The results of soil slurry evaluation using TGS-7(F) soil amended with nutrients and inoculated with PAH-degrading bacteria on a twice-weekly basis are depicted in the left panel of Figure 4. Data summarizing biodegradation of various PAH classes after 2 weeks and 6 weeks of incubation reveal that most degradation that occurs takes place within 2 weeks. Although not as extensive as that observed for liquid culture biodegradation of methanol extracts, degradation of total PAHs by soil slurry treatment was 50% in 2 weeks and about 75% after 6 weeks of incubation. The most extensive biodegradation was evident for one- to three-ring PAHs, where about 60% removal was attained in 2 weeks and 70% after 6 weeks. Four- to six-ring PAHs were not rapidly biodegraded but showed improvement with time, presumably because the one- to three-ring PAHs were preferentially metabolized.

TGS-7(F) soil was predominated by sands and contained less than 5% clays.(3) Vigorous mixing under the slurry conditions was expected to be effective for this soil. It was important to determine if microbial amendment of a soil with a high proportion of fine soil particles would demonstrate effective PAH biodegradation. A soil slurry study was performed using another MGP soil, designated TGS-9(C). This soil differed from TGS-7(F) in that it contained nearly 35% clay. The results of a soil slurry experiment using TGS-9(C) are summarized in Figure 5. Even with the high proportion of clay, notable PAH degradation was evident. Total PAH levels decreased by more than 75%. Virtually all of that decline was in two- and three-ring PAHs, which

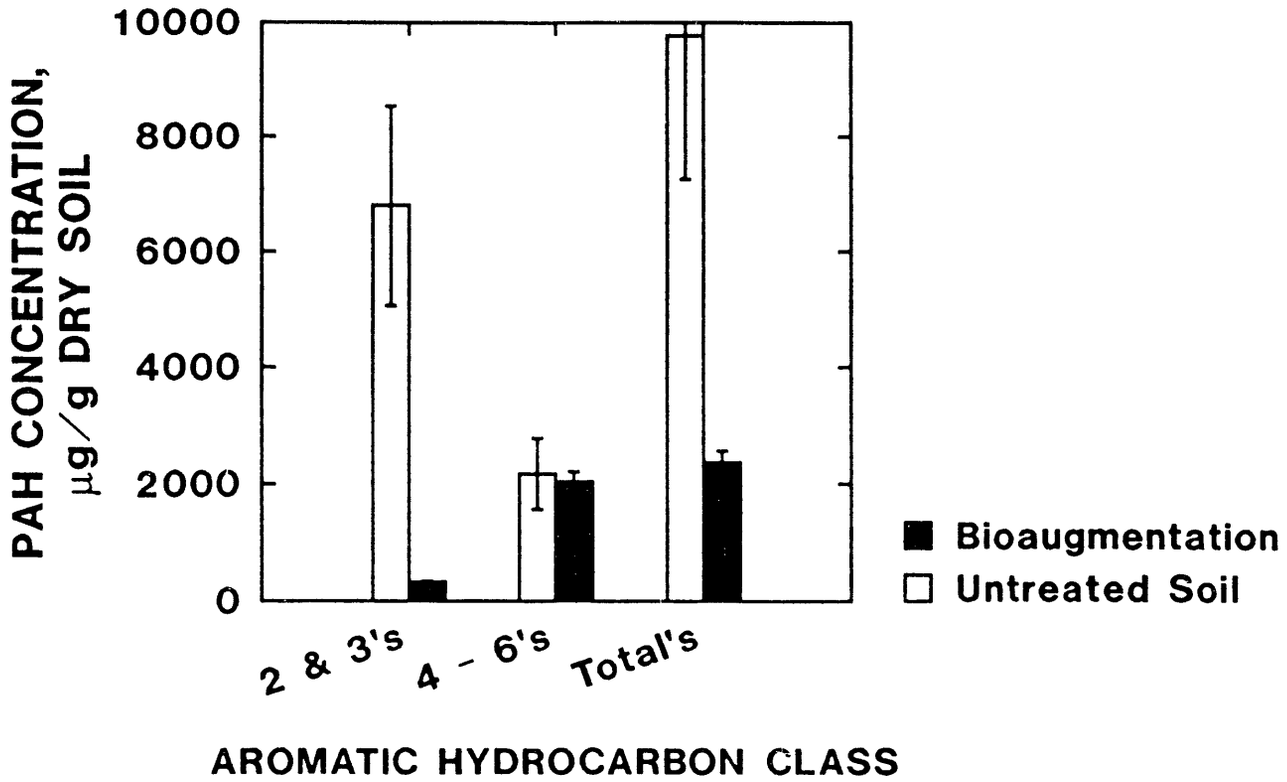


Figure 5. PAH BIODEGRADATION IN TGS-9(C) SOIL SLURRIES

decreased by over 95% from about 6800 µg/g to about 300 µg/g of soil. Four- to six-ring PAHs persisted and were not significantly biodegraded over the 6-week incubation period.

In spite of the high clay levels, biodegradation of PAHs was observed in the soil slurry system using TGS-9(C) soil. As with TGS-7(F), the drop in PAH levels was greatest for the two- and three-ring constituents compared with the four- to six-ring PAHs. It is believed that four- to six-ring PAHs are biodegradable but were not available for biodegradation due to mass transfer and solubility constraints. An ongoing investigation is addressing this issue in a soil slurry treatment system.

When soil slurry results for the sandy TGS-7(F) soil and the clay TGS-9(C) soil are compared, it is evident that considerable PAH biodegradation occurs when vigorous mixing is used to break up soil aggregates and overcome problems associated with mass transfer limitations. The extent to which PAH degradation occurs is not always clear. For TGS-7(F) soil, very little was gained by extending slurry biodegradation from 2 to 6 weeks, as indicated in Figure 4, except for four- to six-ring PAHs; for these compounds, only about 15% biodegradation was observed after 6 weeks. This observation was the basis for incubating TGS-9(C) soil for a longer period (6 weeks versus 4 weeks).

Biodegradation of PAHs in Soil Microcosms

Figure 6 shows a summary of an extensive soil microcosm experiment designed to evaluate the extent of biodegradation attainable in a land treatment system similar to that illustrated in Figure 2. As in the methanol extract and soil slurry experiments described above, various PAH classes, grouped by ring number, were evaluated. The most striking biodegradation was achieved for two- and three-ring PAHs. After 1 year of incubation with amendments made on a twice-weekly basis, all treatment groups achieved nearly the same endpoint in the range of 300 to 500 μg/g of soil from a starting concentration of about 15,000 μg/g. The most rapid degradation occurred in the first 2 months of treatment. Amendments that involved composting with manure and inoculation with bacteria enriched from the site soil (Treatments E to I, Figure 6) achieved the most rapid PAH reduction initially and the lowest levels ultimately. Two- and three-ring PAH biodegradation was enhanced by composting and amendment with competent microorganisms. Four- to six-ring PAHs were biodegraded, but not to the same degree as depicted in Figure 6 for two- and three-ring PAHs, as presented in Figure 7.

The most extensive biodegradation of the persistent four- to six-ring PAHs occurred early and stabilized such that a residual level of 3,000 to 4,000 μg/g total PAHs existed at the end of the study, as shown in Figure 7. This represents a decline of about 2,000 μg/g; it is not known why the four- to six-ring PAHs were not more extensively biodegraded. It is possible that they were not desorbed from soil into the aqueous environment where the soil microbes were active (Compartment K, Figure 1). Treatments were amended with PAH-degrading microorganisms (Treatments E to I) and nutrients added on a twice-weekly basis so the availability of competent microorganisms and necessary nutrients should not have been limiting biodegradation.

It is evident from this study that notable biodegradation of two- and three-ring PAHs and some biodegradation of four- to six-ring PAHs can be achieved in a land treatment system that involves some form of composting, nutrient amendment, and inoculation with PAH-degrading bacteria. The most extensive biodegradation occurred within 2 to 3 months, or about a growing season. After that period elapsed, the most persistent PAHs remained and may need to be subjected to other enhancements. The degradation of these pollutants through the use of chemical co-treatments is described in the following section.

Chemical Co-treatments Using Fenton's Reaction

To overcome problems in achieving degradation of persistent four- to six-ring PAHs, several experiments involving chemical co-treatment were performed. Some of this work is presented as a poster at this symposium, "Application of Fenton's Reagent as a Pretreatment Step in Biological Degradation of Aromatic Compounds,"

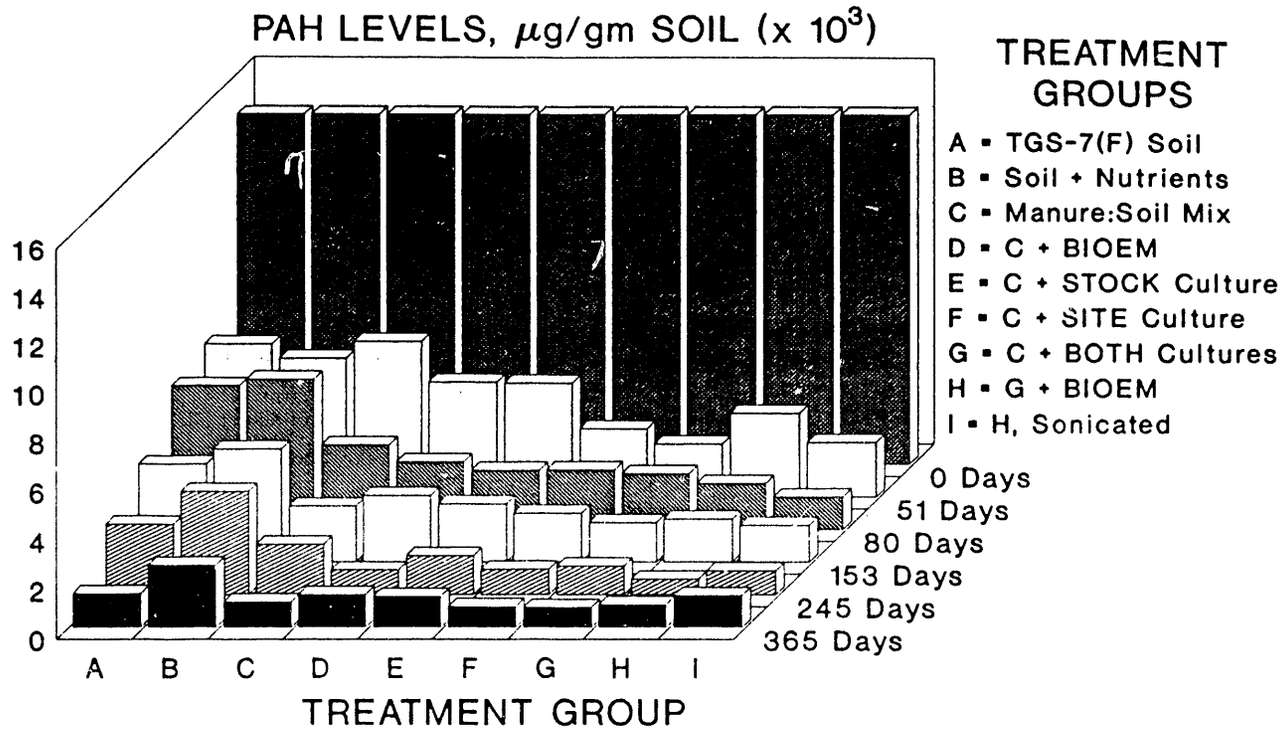


Figure 6. BIODEGRADATION OF TWO- AND THREE-RING PAHs IN SOIL PAN MICROCOSMS

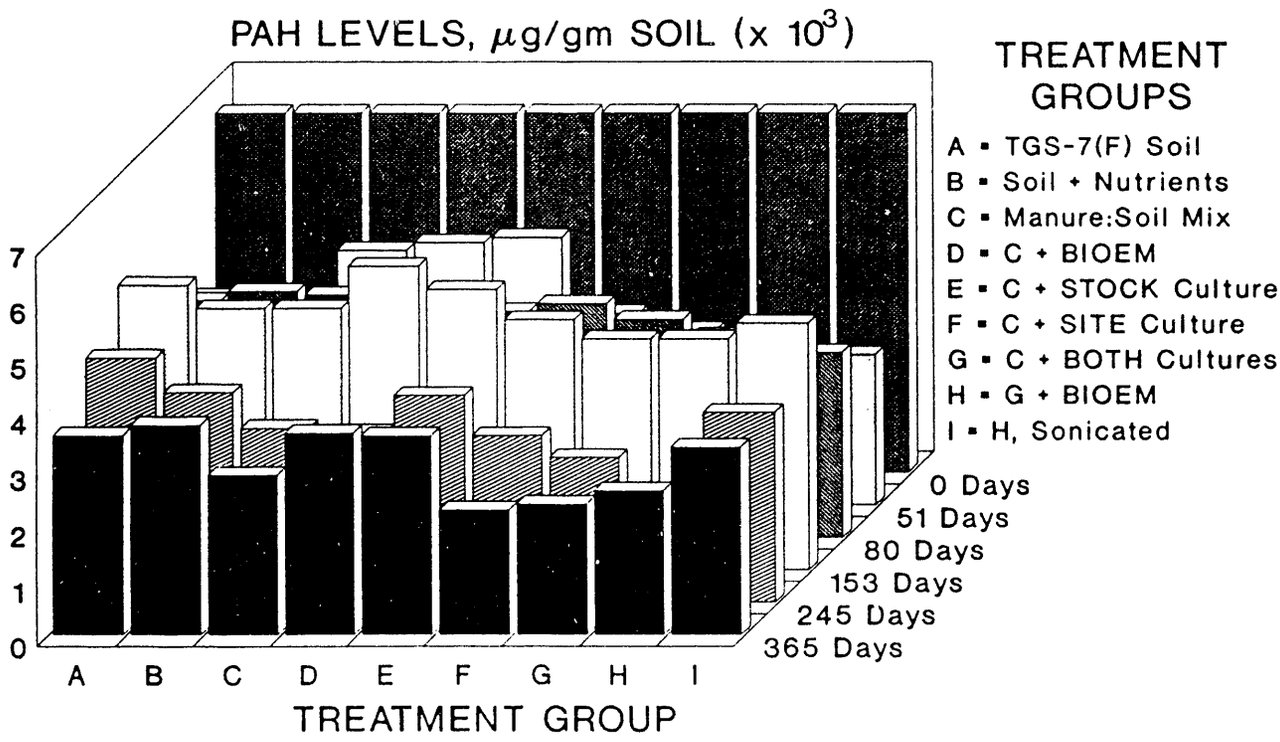


Figure 7. BIODEGRADATION OF FOUR- TO SIX-RING PAHs IN SOIL PAN MICROCOSMS

by Dr. R. L. Kelley, Dr. W. K. Gauger, and Mr. V. J. Srivastava of IGT. The studies described in the following paragraphs apply Fenton's Reaction to intact soil. Two soils were evaluated: TGS-8(B) and the TGS-7(F) soil derived from the soil microcosm studies just described. Application of Fenton's reagents (9% H_2O_2 + Fe^{++}) resulted in the removal of about 91% of all aromatic hydrocarbons in TGS-8(B) (one- to six-ring) (Figure 8, Table 2). Of the initial classes, about 98% of four- to six-ring PAHs were degraded (reduced from 17.83 μg/g to 0.37 μg/g dry soil); two- and three-ring PAHs were also degraded by 98% (reduced from 114.13 μg/g to 2.66 μg/g, dry soil); and one-ring aromatics were degraded by 69% (reduced from 41.47 μg/g to 13.06 μg/g, dry soil). It is important to note that the multi-ring aromatic hydrocarbons were degraded most extensively by Fenton's reagents. This phenomenon is predicted by molecular orbital theory (7) and has been verified consistently in IGT's laboratory studies.

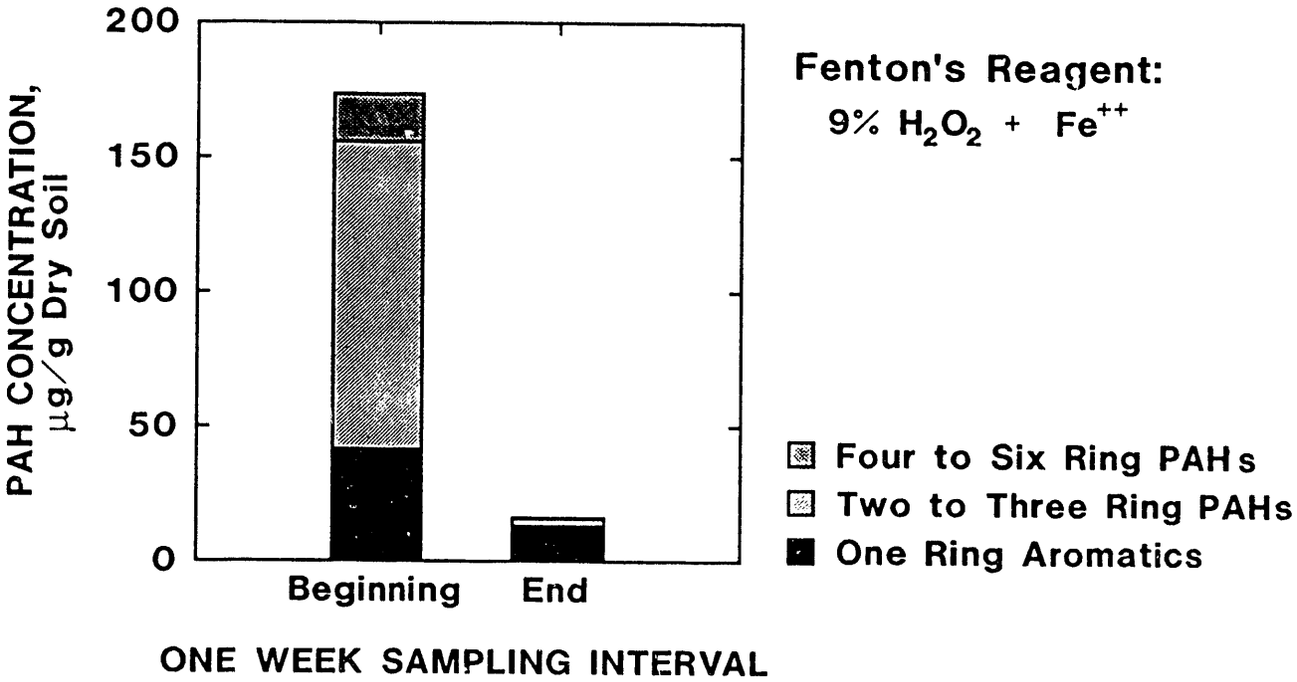


Figure 8. CHEMICAL TREATMENT OF TGS-8(B) SOIL USING FENTON'S REAGENT

Evidence of substantial reduction in two- to six-ring PAHs in the TGS-8(B) soil was highly encouraging. Soil pan studies described above revealed that four- to six-ring PAHs were persistent, even after 1 year of treatment in an ideal laboratory environment. We have theorized that chemical co-treatment using Fenton's reagents in conjunction with biological treatment would reduce the levels of four- to six-ring PAHs.

Soils derived from Treatments A and B (Figure 7 and Table 1) were pooled and subjected to Fenton's chemical treatment in the

Table 2. DEGRADATION OF PAHs PRESENT IN TGS-8(B) AND TGS-7(F) SOIL USING FENTON'S REAGENTS*

Soil	Treatment	One Ring	Two and Three Rings	Four to Six Rings	Total Aromatics
TGS-8(B)	Beginning, μg/g	41.47	114.13	17.83	173.44
	End, μg/g	13.06	2.66	0.37	16.09
	% Remaining	31.5	2.3	2.1	9.3
	% Degraded	68.5	97.7	97.9	90.7
TGS-7(F)**	Beginning, μg/g	168.43	3666.44	4750.70	8585.57
	End, μg/g	49.23	874.13	1328.61	2251.97
	% Remaining	29.2	23.8	28.0	26.2
	% Degraded	70.8	70.8	72.0	73.8

* 9% (v/v of slurry) H_2O_2 in presence of excess Fe^{++} added on each of 4 consecutive days.

** TGS-7(F) soil had previously been subjected to biodegradation by indigenous microorganisms for 1 year in soil microcosms.

same manner as TGS-8(B) soil. Of the remaining aromatic hydrocarbons present in the "spent" TGS-7(F) soil (8,400 μg/g dry soil), 71% to 76% of all aromatic classes were degraded by this chemical co-treatment process, as depicted in Table 2 and Figure 9. Single-ring aromatic hydrocarbons were reduced by about 71% (from 168.43 μg/g to 49.23 μg/g dry soil); one- and three-ring PAHs were degraded by over 76% (from 3660.44 μg/g to 874.13 μg/g dry soil); and four- to six-ring PAHs were degraded by 72% (from 4750.70 μg/g to 1328.61 μg/g dry soil). The residual total PAH levels have been reduced from nearly 40,000 μg/g of soil to about 2200 μg/g of soil using combined biological and chemical treatments to enhance PAH degradation. This represents nearly a 95% reduction in PAHs initially present in this soil.

In these investigations, the hydrogen peroxide treatment levels were relatively high (9%, v/v of slurry) and applied several times. Independent studies using radiochemical techniques have revealed that, at these H_2O_2 levels, PAHs are mineralized to carbon dioxide.(8) It would not be necessary to achieve mineralization using this type of treatment. Fenton's reaction involves the formation of free hydroxyl radicals, which, in turn, react with PAHs to form hydroxylated PAHs. The initial biochemical reactions that occur for biologically mediated PAH degradation involve the formation of hydroxylated PAHs. These initial hydroxylation steps are often rate-limiting. It should be emphasized that 2200 μg PAHs/g of soil need not be the final endpoint achieved by chemical co-treatment using Fenton's reagents. Another sequence of biological treatment might be effective in reducing these levels further.

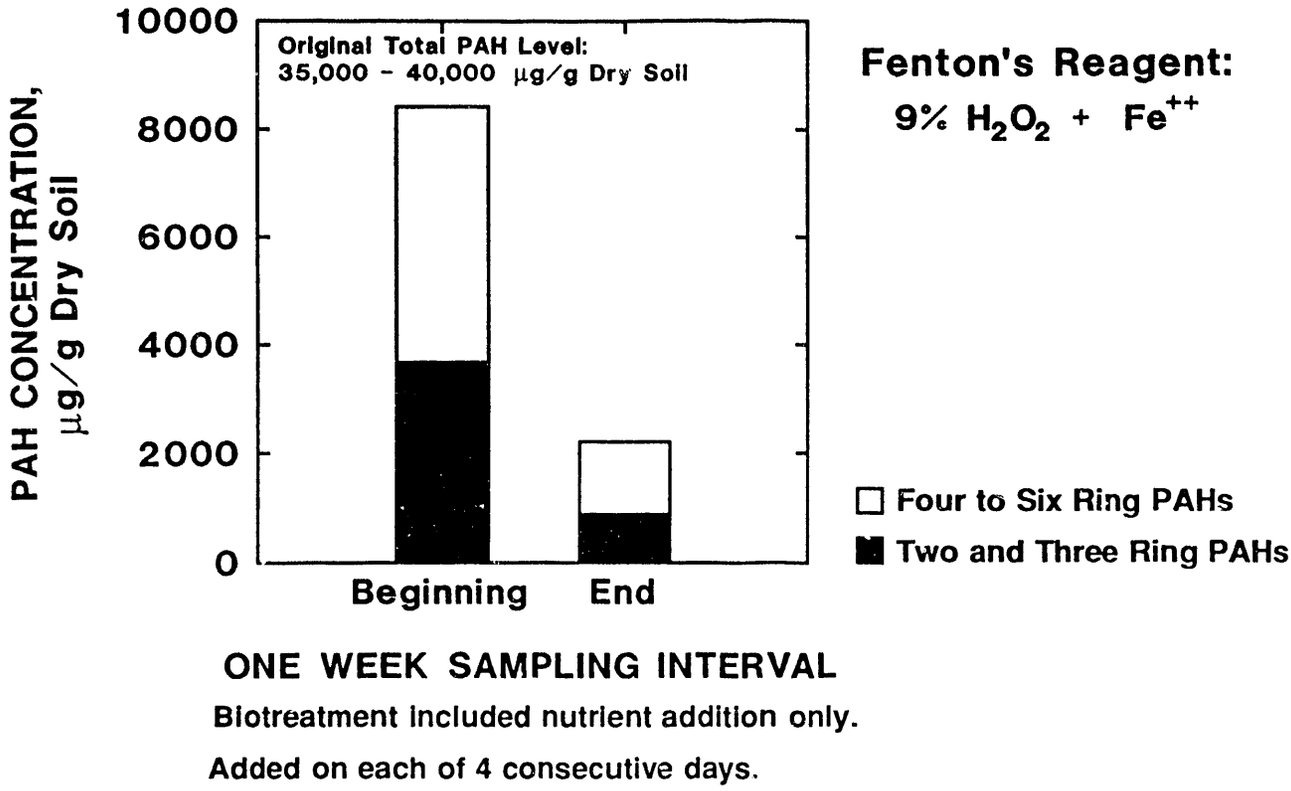


Figure 9. CHEMICAL TREATMENT OF PREVIOUSLY BIODEGRADED TGS-7(F) SOIL USING FENTON'S REAGENT

For the persistent (four- to six-ring) PAHs, chemical pre-treatment using Fenton's reagents applied at low (≤1%, v/v slurry) hydrogen peroxide levels followed by biological treatment may be a rational and economic approach to achieving the complete destruction of PAHs in MGP soils. This is currently being evaluated using several MGP soils.

SUMMARY

A variety of investigations have been undertaken to achieve enhanced biodegradation of PAHs in MGP soils. The greatest obstacle in achieving complete PAH destruction is limited mass transfer of soil-associated PAHs into the aqueous environment where competent soil microorganisms live. Physical processes (solubilizing agents and vigorous shaking) facilitate desorption of bound PAHs. When these are performed in conjunction with biological treatment, substantial PAH biodegradation can be attained. The most extensive biodegradation occurs when ethanol or methanol extracts of PAHs are subjected to treatment in a liquid system. Extensive (<90%) reduction of one- to six-ring aromatic hydrocarbons occurs rapidly compared with degradation of soil-associated PAHs.

When soils are slurried, moderate to high PAH reductions are attained. Although not as extensive nor as rapid as that ob-

tained with liquid extracts, this method achieves significant elimination of PAHs. Slurry treatments are most effective for one- to three-ring aromatic hydrocarbons; four- to six-ring PAHs are persistent.

In studies involving land treatment of MGP soils, we have observed the best biodegradation of one- to three-ring aromatic hydrocarbons in composted treatments. As observed for soil slurry treatments, four- to six-ring PAHs persist. Also, treatment endpoints were not as extensive in soils undergoing composting treatments as they were in soils subjected to either of the other treatment approaches (liquid extracts or soil slurries).

A major focus has been placed on enhancing the destruction of four- to six-ring PAHs. A promising approach involves chemical pre- or co-treatment with Fenton's reagents. This process appears to favor the destruction of multi-ring PAHs and can be used in conjunction with biological treatment.

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