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TREATMENT OF VACTOR SOLIDS

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Treatment of Vactor Solids

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Treatment of Vector Solids

Executive Summary

A pilot study was established in June 1996 to investigate an economical method for managing vector solids. In addition, a small sample of street sweepings was evaluated for biological treatment. Eleven piles of vector solids and street sweepings were established ranging in size from 1.25 yd³ to 5 yd³. All of the piles that were treated received a commercial fertilizer; the other significant variable was the frequency at which the piles were turned in order to provide aeration for microbial metabolism (once per week to once every four weeks). In addition, some specialty piles were established that received a surfactant (poly sodium vinyl sulfate) and peroxygens (calcium peroxide, sodium carbonate peroxyhydrate and hydrogen peroxide).

The piles were sampled over 400 days and analyzed for total petroleum hydrocarbons (TPH) and the marker polycyclic aromatic hydrocarbon (PAH) anthracene. The results showed that, no matter how much the piles were turned or what amendment was added, the TPH and PAH levels behaved the same as the control piles. In other words, the TPH and PAH concentrations declined exponentially over 400 days to acceptable levels. Although imprecise, periodic dissolved oxygen measurements from cores in the pile showed minimal oxygen, suggesting that all piles were oxygen limited. Even when the piles were turned once per week, they probably became oxygen limited because the oxygen that was entrained within the soil pores was likely exhausted by microbial metabolism within a few hours. The results show that a low maintenance program of keeping the solids moist but not turning the solids provide an effective and low cost means for their decontamination.

Introduction

The treatment and disposal of catchment basin solids represents a significant concern for the Washington State Department of Transportation and other agencies responsible for road maintenance. The material that passes through road drain grills must be periodically extracted to prevent clogging of these systems. Oils, greases, lubricants and gasoline and diesel fuels drip on the roadway and are washed down the drains. These hydrocarbons sorb onto soils and other solids and accumulate to such a concentration as to classify the material as a solid waste containing petroleum contamination, which reduces the opportunities for disposal. Current Total Petroleum Hydrocarbon (TPH) site clean up levels have been established by the Washington State Department of Ecology to be no more than 200 ppm. Vector solids (material extracted from roadway catchment basins) are characterized by TPH measurements in the 1000-2000 ppm range (Hoffman et al., 1982). Average analysis shows the hydrocarbons are present as ~95% aliphatic and 5% aromatics. The streets, roads and highways of Washington state generate over 50,000 cubic yards of vector solids each year. The average cost of transportation and disposal is \$90.00/yd³, creating a total financial burden in excess of four million dollars per year.

Problem Statement

The economical and safe disposal of vector waste solids is a significant concern among WSDOT maintenance personnel. Vector solids are a heterogeneous mixture of soils, debris, litter, and runoff waste materials that represent a significant disposal problem because of the presence of petroleum hydrocarbons.. Characterization studies performed by Hindin (1993) documented that vector solids contain high-molecular weight hydrocarbons from motor oils and hydraulic fluids including long chain alkanes and larger polycyclic aromatic hydrocarbons -- contaminants that are regulated by the Washington State Department of Ecology.

A telephone survey of state Departments of Transportation revealed that vector solids are most commonly stockpiled. They are also landfilled when state regulations will

allow. However, vector solids are not always accepted by sanitary landfills. As a result, these wastes tend to accumulate at maintenance stations, where personnel are constrained by the logistics and costs of vector solids disposal.

Bioremediation is a documented process for the treatment of hydrocarbons. However, the process is complicated by sorption, toxicity, and cold temperatures. Nonetheless, bioremediation holds the most promise for the treatment of vector waste solids.

One of the problems in the treatment of hydrocarbons is tracking the effectiveness of contaminant removal. The standard method of chemical analysis for hydrocarbons -- total petroleum hydrocarbons (e.g. WTPH-D) measures numerous other organic compounds such as humic and fulvic acids that leach out of leaves and wood. If a reliable means of tracking the contaminants is not available, documenting the clean-up of vector solids is nearly impossible.

Background Statement

Numerous treatment and remediation processes have been proposed to decontaminate vector solids. However, because of the complexity of the wastes and the matrix effects of the solids, the treatment processes used to date have not been highly successful. For example, recent studies in the bioremediation of vector sludges have focused on adding the solids to different organic matrices (e.g., biosolids, yard waste, sawdust) as a basis for enhancing biodegradation during composting. The results of these studies showed that 1) the hydrocarbons biodegraded very slowly in systems containing organic supplements, and 2) that naturally-occurring organic compounds associated with the biosolids and other organic matter were measured as hydrocarbons in the total petroleum hydrocarbon (TPH) analysis resulting in false positive errors.

Bioremediation of soils and solids has received widespread attention over the past 20 years. The process is based on adding nutrients (e.g., nitrogen, phosphorus, and oxygen) to the contaminated solids to promote the biodegradation of the waste materials (Alexander,

1985). Numerous modifications of bioremediation have been developed including slurry reactors, landfarming, and bioventing. Although bioremediation has been found to successfully decontaminate a number of compounds in soils and solids, it is sometimes limited by contaminant sorption and toxicity. Contaminants that are strongly sorbed to soils are not effectively biodegraded. However, if contaminant sorption is a problem, it is sometimes overcome by using surfactants (i.e., detergents) to remove the contaminants from the solids followed by bioremediation of the free material.

The microbial degradation of a number of hydrocarbons is well documented. As expected by their reduced nature, aliphatic and aromatic hydrocarbons biodegrade most efficiently under aerobic conditions. Alkanes proceed through dehydrogenase reactions that transformation to an alcohol, aldehyde, and a carboxylic acid. The final step in this process is β -oxidation, the same degradation mechanism used in the metabolism of natural fatty acids. A large number of bacterial species use aliphatic and aromatic hydrocarbons as their sole source of carbon and energy. Bioremediation rates of alkanes are related to their chain length; alkanes less than 10 carbons are more toxic to microorganisms as a result of their higher water solubility. Alternatively, biodegradation rates of long-chain alkanes ($> C_{10}$) are affected by water solubility and sorption. Aromatic compounds degrade by a dual dioxygenase-catalyzed hydroxylation mechanism in which oxygen is added to form a diol. The diol then proceeds through ring cleavage and the products enter standard metabolic pathways.

Polycyclic aromatic hydrocarbons follow similar pathways. However, biodegradation rates of PAH compounds larger than three rings are slowed by their need for specific enzymes to degrade these larger compounds. Therefore, the biodegradation of PAHs is a function of the ring size and the enzymatic complement of the microorganism. The general consensus is that two and three ring PAHs are readily biodegradable, whereas those containing four or more rings are exceedingly difficult, if not biorefractory. Furthermore, large-ring PAHs are highly hydrophobic and sorption also controls their rates of

biodegradation. Another factor that has been shown to influence the biodegradability of PAHs is the number and positions of substitution groups. Recent studies have documented that the addition of three methyl groups to a number of PAHs resulted in significantly-decreased rates of biodegradation.

Sorption, the accumulation of contaminants at surfaces, provides an inaccessibility mechanism analogous to the presence of a nonaqueous phase liquid (NAPL) phase. The primary sorbent in soils is organic matter, but in systems containing low organic carbon, clays or hydrous oxides are likely the primary sorbents. Sorption not only retards the rate of migration of hazardous contaminants and lowers the rate of phase transfer to the atmosphere, it can also significantly affect rates of abiotic and biotic transformations. The conceptual basis for the effect of sorption is that the bacteria that transform organic contaminants exist in the aqueous phase. If a contaminant partitions onto soil organic matter or a mineral surface, it is not in direct contact with the agents responsible for its transformation. However, soil and groundwater microorganisms that are actively metabolizing hydrocarbons produce natural surfactants which aid in desorbing the contaminants. These compounds are often based on complex hybrid structures of proteins, lipids, and carbohydrates, including rhamnolipids, phospholipids, and lipopolysaccharides. However, use of synthetic surfactants (e.g., Triton X-100) has been shown to greatly accelerate bioremediation rates.

Based on these principles, the focus of the proposed research was to evaluate bioremediation, a common treatment technology for the decontamination of vector solids.

Objectives

The project focused on the following objectives:

- 1) To investigate the process engineering that provides bioremediation rates suitable to WSDOT needs.
- 2) To accurately evaluate hydrocarbon levels during bioremediation using compound-specific analytical techniques.

Methodology

Eleven piles of vector solids were placed on a concrete pad on the Washington State University campus during June 1996. As shown in Table 1, the variables examined were turning (aeration) rates, fertilizers (augmentation of the matrix), pile size, and treatment with peroxygens and surfactants.

Table 1. Piles investigated in the bioremediation of vector solids.

Label	Size yd ³	Turning Frequency	Description
A	5	Weekly	Fertilizer and watered daily
B	5	Biweekly	Fertilizer and watered daily
C	5	Monthly	Fertilizer and watered daily
D	5	Control	Covered with tarps
E	5	Biweekly	Fertilizer and watered daily
F	8	Control	Covered with tarps
G1	1.25	Not turned	Fertilizer and watered daily Na ₂ CO ₃ added at onset
G2	1.25	Not turned	Fertilizer and watered daily CaO ₂ added at onset
H	2.5	Biweekly	Fertilizer and watered daily H ₂ O ₂ added at onset
I	2.5	Control	Covered with tarps
J	2.5	Biweekly	Fertilizer and watered daily 0.01% (w/w) poly sodium vinyl sulfate added at onset

Moisture content of 50% was maintained by watering for two hours each evening using a battery operated timer, 'Y' fittings to equalize pressure, and soaker hoses draped across the crests of the piles.

Every two weeks two samples were taken from each pile. The samples collected, per Washington State Department of Ecology recommendations (Ecology, 1991), from a

depth of at least eight inches at randomly selected locations. The samples were stored in 50 ml glass vials with Teflon coated septum and plastic screw caps. At the time of sampling a thermometer was inserted deep into the pile and the temperature was recorded.

Analysis

The vector solids samples were subsequently analyzed for moisture content, pH and TPH using capillary gas chromatography with a flame ionization detector (GC/FID).

Moisture content was determined by weighing 5 grams on a previously weighed plastic weigh boat. The sample was then placed in a Fisher Isotemp oven for 24 hours heated to 40°C and again weighed to the nearest 0.001 gram. The relative accuracy was determined by taking five weightings of the same sample and computing the standard deviation of the readings.

The pH was determined using a Fisher Accumet model #900 pH meter, with a Fisher pH probe (model #13-620-108). Approximately 5 grams of the sample was diluted with 20 mls of deionized water which was purified to 10^{14} ohms specific resistance.

The vector solids and street sweepings were extracted by weighing 5 grams (± 0.001 g) and placing it in a 50 ml glass vial with a screw cap and a Teflon coated septum. Approximately 5 ml of anhydrous Na_2SO_4 (Baker reagent grade, 12-60 mesh, 'Ultra-resi-analyzided'; 99-100%) was added prior to vigorous hand shaking to extract all available moisture. Twenty ml of methylene chloride (CH_2Cl_2 ; Baker, H.P.L.C. grade, 99%) was then added to the vial. The sample was vigorously agitated for 24 hours using a wrist shaker. Next, the sample was centrifuged for five minutes. The solvent was then decanted and filtered using a gravity funnel. The collected extract was then stored in a 2 ml target vial, which was filled to capacity to minimize possible volatilization.

The solvent used for the extraction was spiked with two internal standards -- Tertracosane ($\text{C}_{24}\text{H}_{50}$; Aldrich Chemical Co., 99%) and deuterated anthracene (Aldrich Chemical Co., 98+%). A 0.1 mg/kg was generated for each internal standard by

dissolving 0.500 grams (± 0.0002 g) in 500 mls in methylene chloride. By comparing the peak of the internal standards, which have of known concentrations and retention times, two quality control checks are made. Wandering retention times are indicators of GC/FID system performance fluctuations; secondly, the peak areas of known concentrations were compared with the calibration curves and double checked for consistency.

A Hewlett-Packard 5890A gas chromatograph and flame ionization detector were coupled with a model 7673A auto-sampler and a 7673 plotter/integrator. A two microliter injection was placed on a Supelco 3001 capillary column, (60 meters by 2 mm with a 0.2 mm i.d., phenylsilicate stationary phase). The carrier gas was nitrogen flowing at a rate of 6 ml/minute. The splitless injection was programmed to allow the sample to be place on the column for 0.7 minutes before the purge valve was opened. The purge valve remained open for the balance of the 75 minute run. The temperature ramping profiles are listed in Table 2.

Table 2. Temperature Ramping Profile

Initial Temp.	Rate	Final Temp.	Final Time
60°C	10°/min.	200°C	1.0 min.
200°C	2.0°/min.	250°C	1.0 min.
250°C	8.0°/min.	300°C	20.0 min.

The peak areas of the chromatograms were automatically integrated by a Hewlett Packard 7673 integrator/plotter. The solvent with internal standards chromatogram was manually subtracted from the data. The peak areas were then normalized and concentrations were determined by comparisons with the peak areas of the calibration standards. The calibration standards consisted of 67.5, 125, 250, and 500 mg/L Castrol

10/30 motor oil in methylene chloride. Many of the peaks have been labeled by running known substances which have the same retention times. The resulting normalized peak areas were subsequently entered into an Excel spread sheet. A typical chromatogram is shown in Figure 1.

Quality Assurance/Quality Control

The first step to insure accurate determination of the vector solid TPH was to gather two samples from each pile. By collecting the samples from random locations, at least eight inches below the surface, the enhanced oxygenation and lowered moisture content of the pile's surface was avoided by taking a sample representative of the majority of the pile.

Results and Discussion

Data obtained for TPH as a function of time for the 11 piles are shown in Figures 2 through 12. The data of Figure 2 show that TPH concentrations in the pile that was turned weekly and amended with fertilizer decreased to below 500 mg/kg in 180 days and to below detection after 400 days. In Figures 3 and 4, similar results were achieved; these piles also required 400 days for TPH levels to decrease to undetectable levels. The control pile (Pile D), which was not turned nor fertilized, showed TPH losses very similar to Piles A through C (Figures 2 through 4). The comparison of the data of Figures 2 through 4 to the control data of Figure 5 indicates that increased rates of aeration as well as fertilizer addition had no effect on the loss of TPH, and that the TPH degraded in the vector solids just as well without any fertilizer addition or turning of the piles. The lack of TPH degradation regardless of the degree of soil aeration may be related to how long the oxygen lasts in the solids after it is entrained there from turning. Most microbial metabolism takes

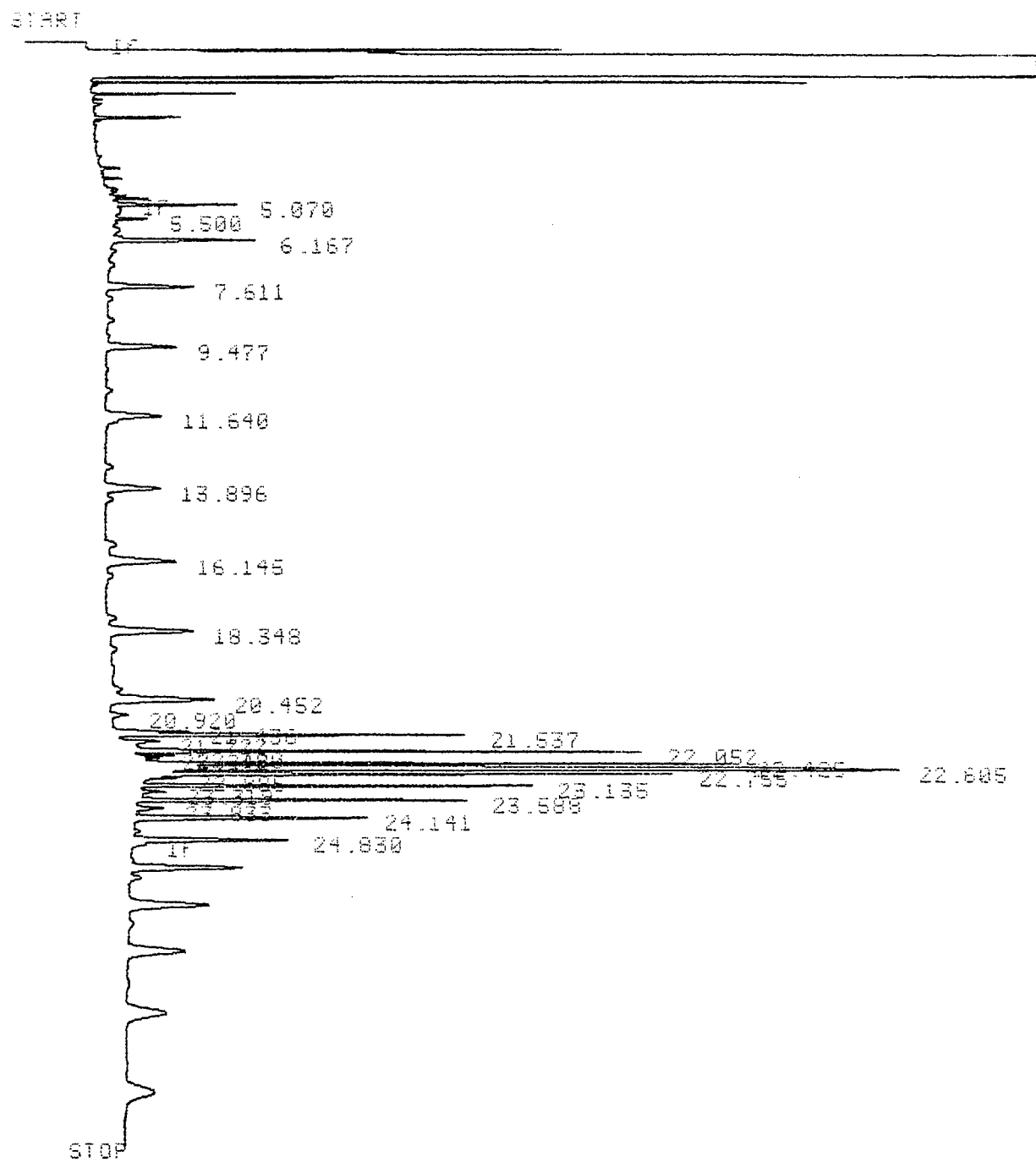


Figure 1. A typical TPH chromatogram.

**Pile "A" TPH (mg/Kg) Degredation vs. Time (Days)
-Aerated Weekly, Augmented with Fertilizer**

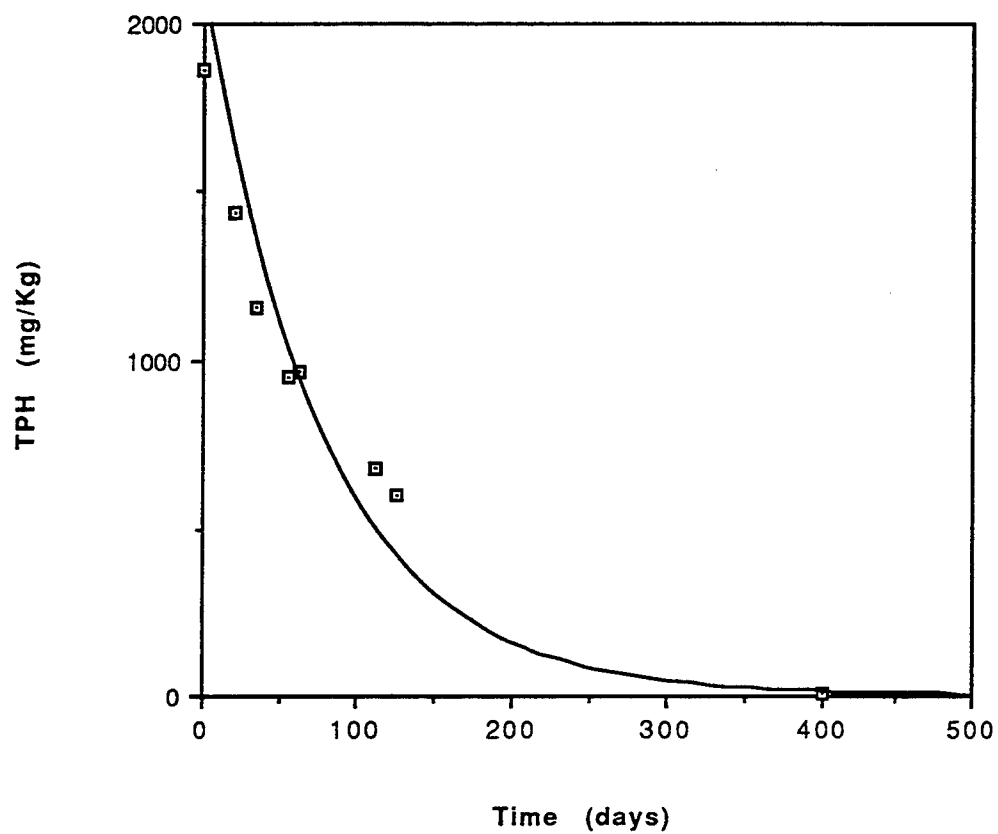


Figure 2. TPH degradation for Pile A (amended with fertilizer, aerated weekly).

Pile "B" TPH (mg/Kg) Degredation vs. Time (Days)
-Aerated Every Two Weeks, Augmented with Fertilizer

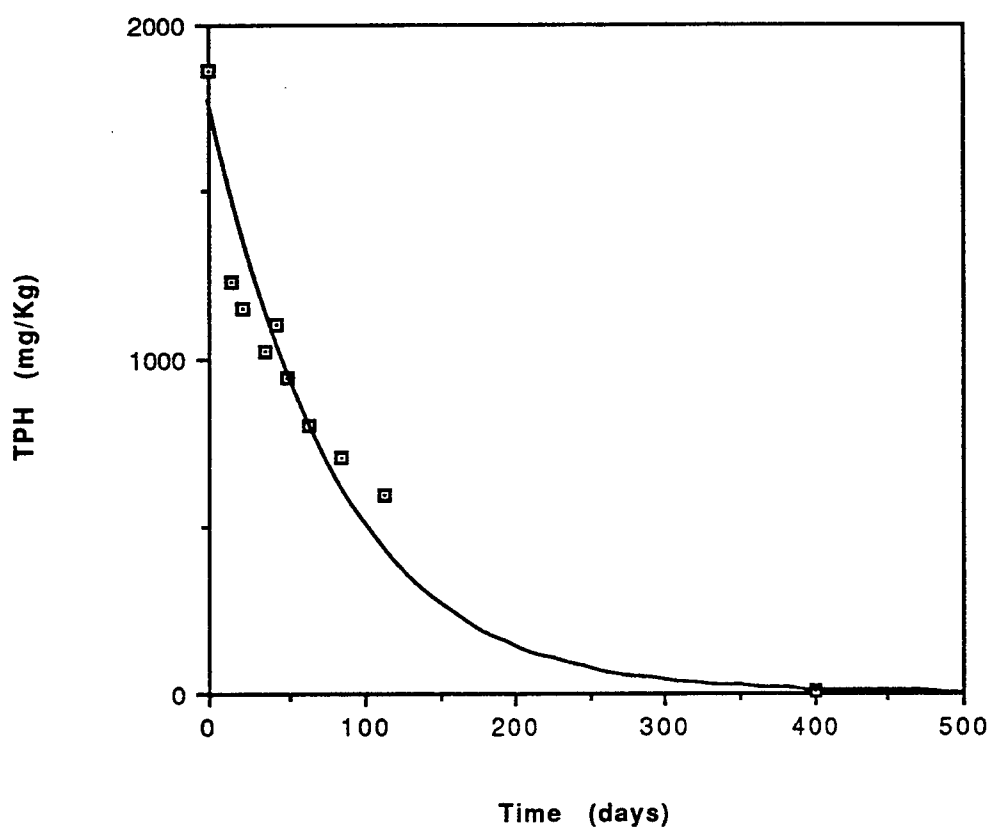


Figure 3. TPH degradation for Pile B (amended with fertilizer, aerated every two weeks).

Pile "C" TPH (mg/Kg) Degredation vs. Time (Days)
-Aerated Every Four Weeks, Augmented with Fertilizer

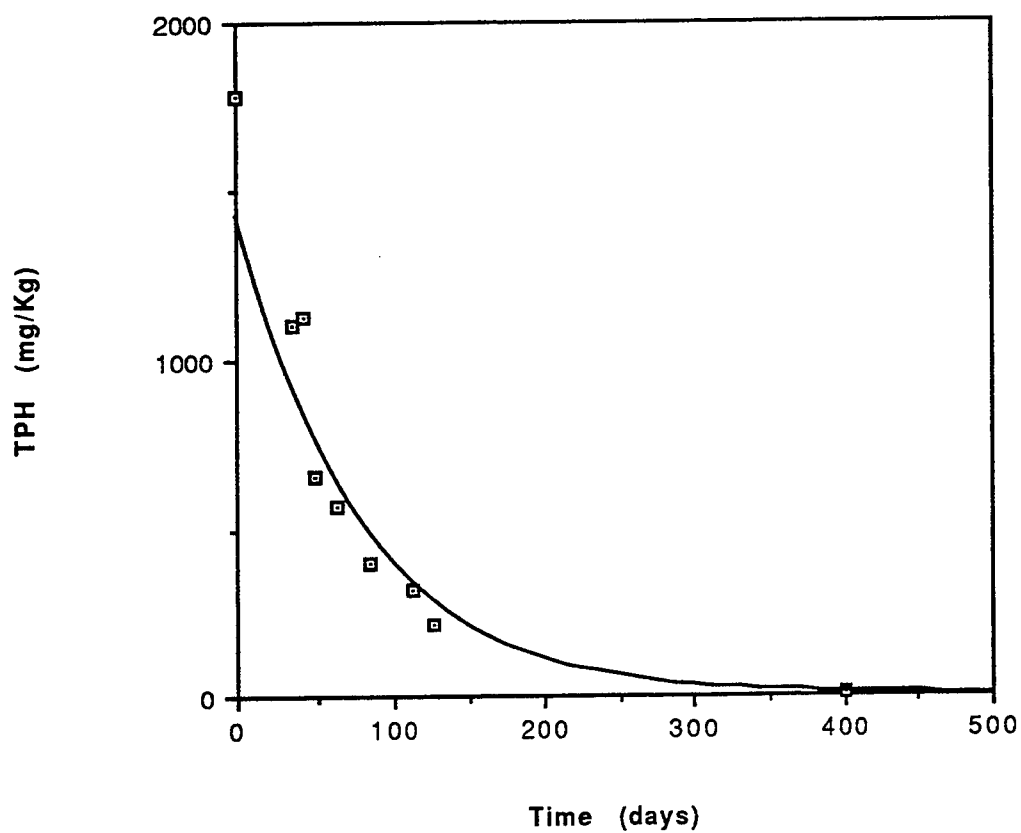


Figure 4. TPH degradation for Pile C (amended with fertilizer, aerated every four weeks).

Pile "D" TPH (mg/Kg) Degredation vs. Time (Days)
-Control; not Aerated or Fertilized

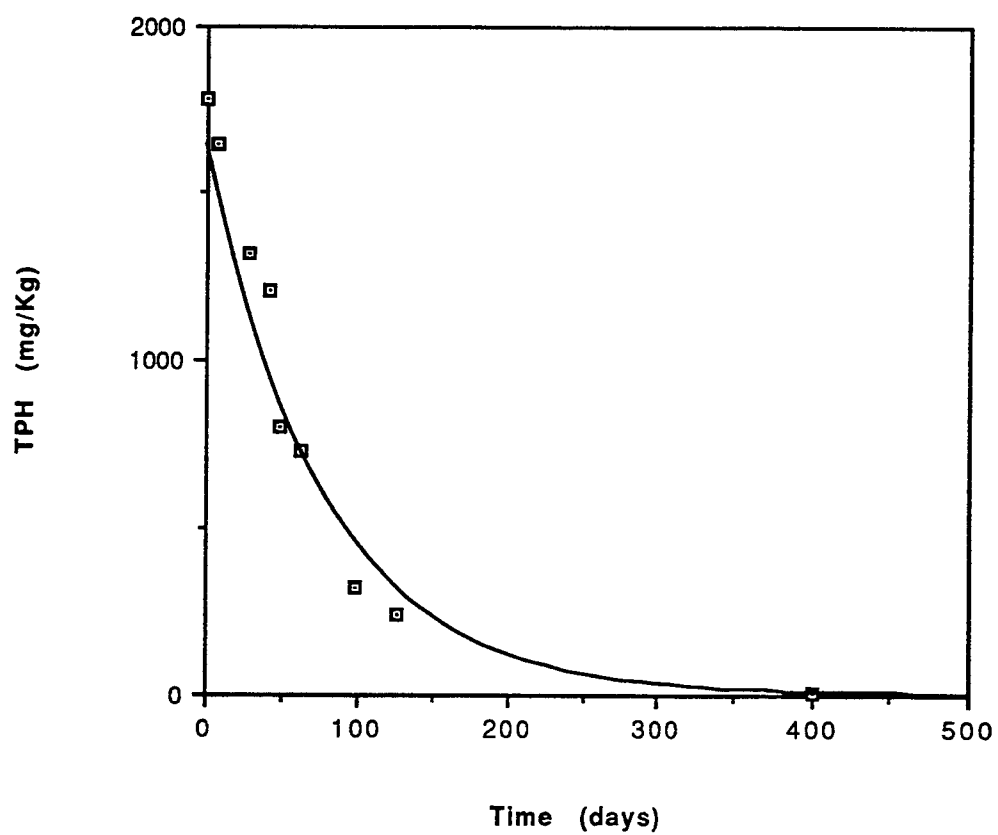


Figure 5. TPH degradation for Pile D (Control: no fertilizer addition; not aerated).

Pile "E" TPH (mg/Kg) Degredation vs. Time (Days)
-Aerated every Two Weeks, Augmented with Fertilizer

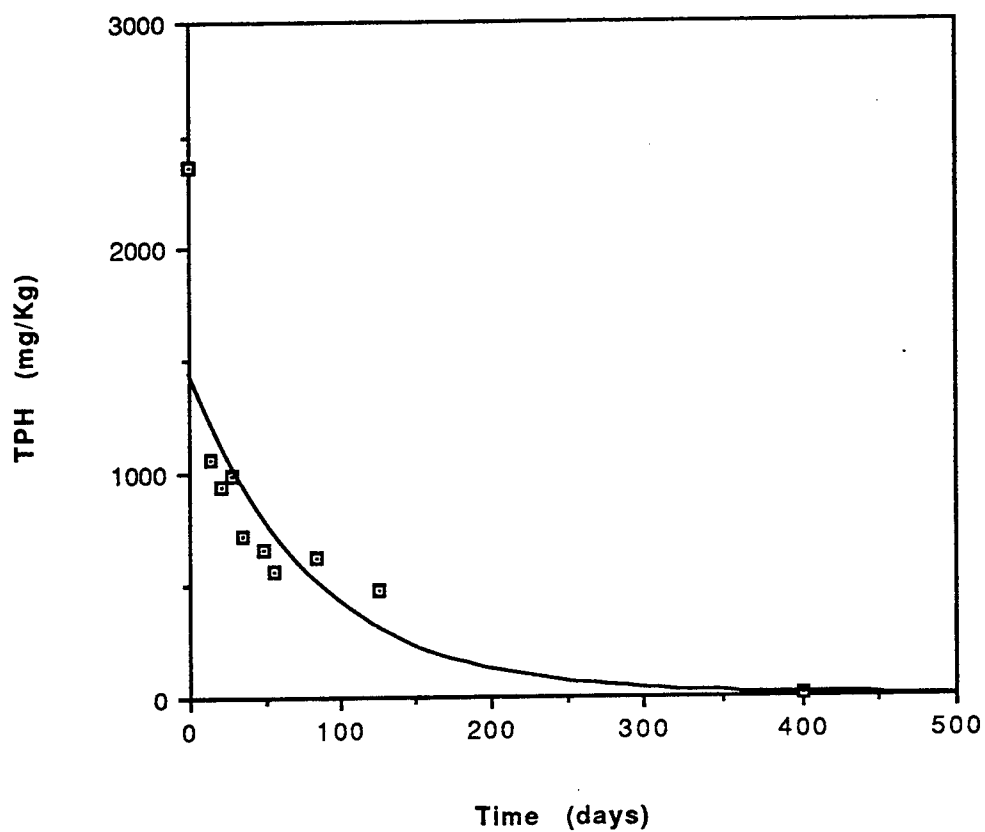


Figure 6. TPH degradation for Pile E containing street sweepings (Amended with fertilizer; aerated every two weeks).

**Pile "F" TPH (mg/Kg) Degredation vs. Time (Days)
-Control, never Aerated or Fertilized**

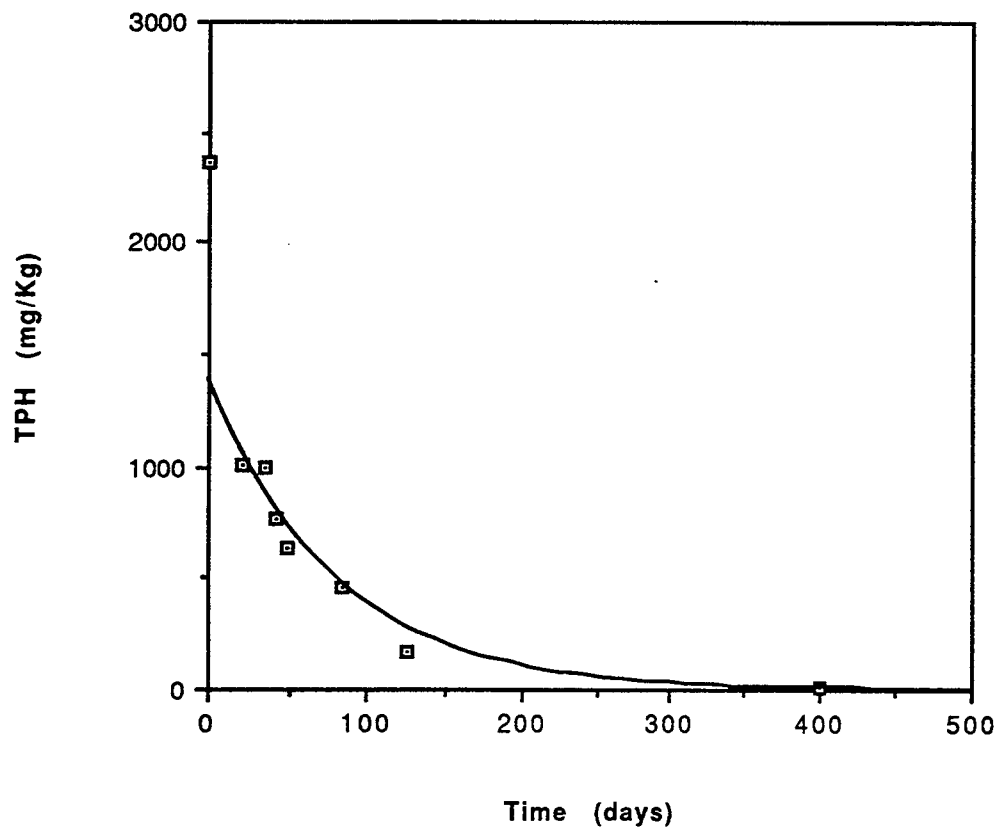


Figure 7. TPH degradation for Pile F containing street sweepings (Control: no fertilizer addition; not aerated).

Pile "G1" TPH (mg/Kg) Degredation vs. Time (Days)
-Never Areated
-Augmented with Sodium Carbonate Peroxyhydrate
(10 lbs/ cubic yard)

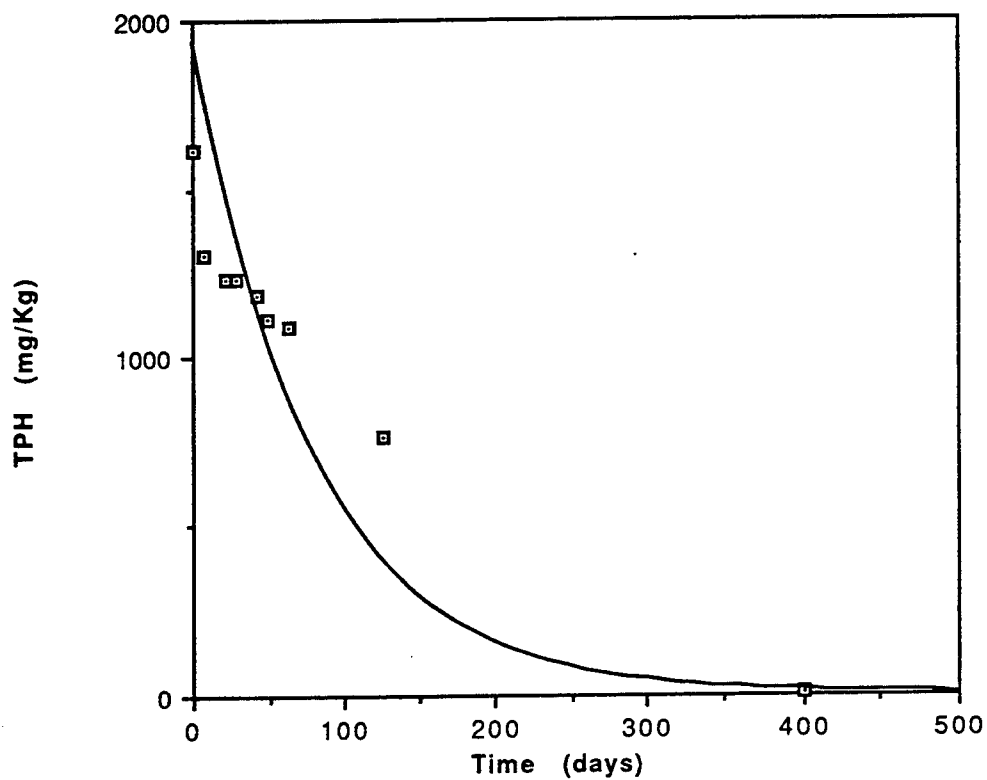


Figure 8. TPH degradation for Pile G1 (pretreated with sodium carbonate peroxyhydrate).

Pile "G2" TPH (mg/Kg) Degredation vs. Time (Days)
-Never Aerated
-Augmented with Calcium Peroxide
(10 lbs/ cubic yard)

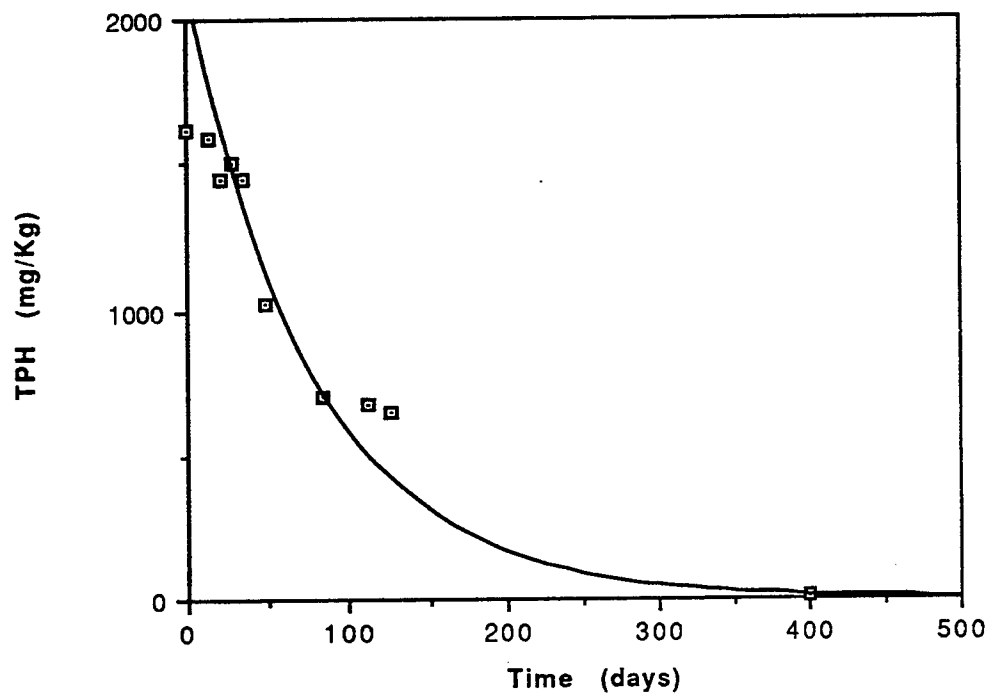


Figure 9. TPH degradation for Pile G2 (pretreated with calcium peroxide).

Pile "H" TPH (mg/Kg) Degredation vs. Time (Days)
- Aerated every Two Weeks
- Saturated with 2.0% Hydrogen Peroxide at onset

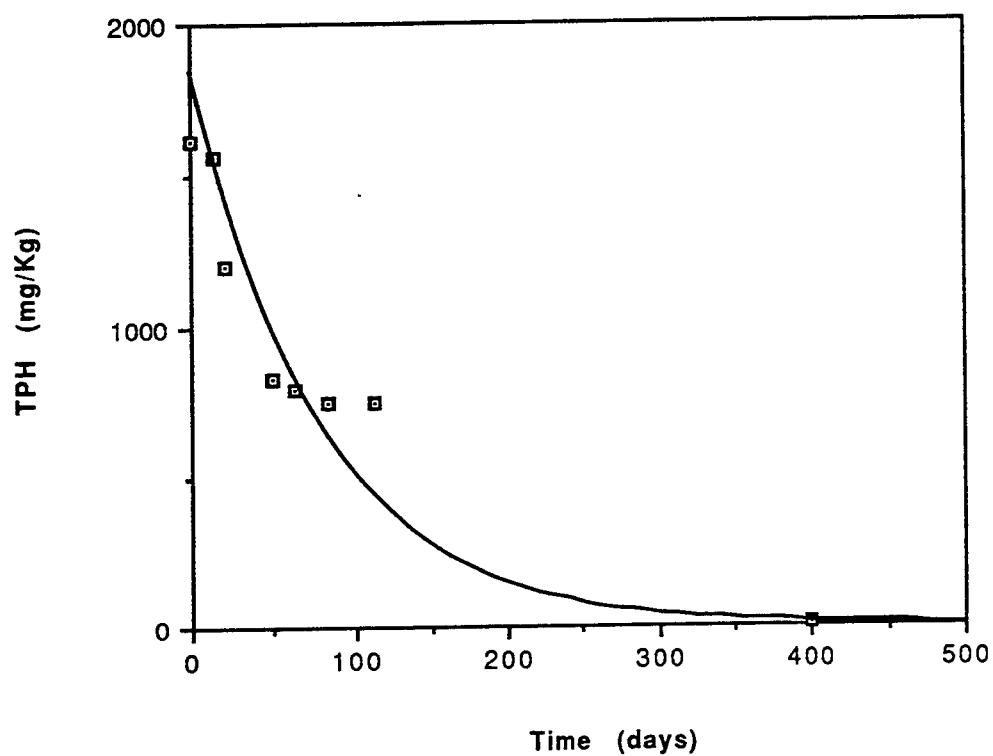


Figure 10. TPH degradation for Pile H (pretreated with 2% hydrogen peroxide).

Pile "I" TPH (mg/Kg) Degredation vs. Time (Days)
- Control; Never Aerated or Fertilized

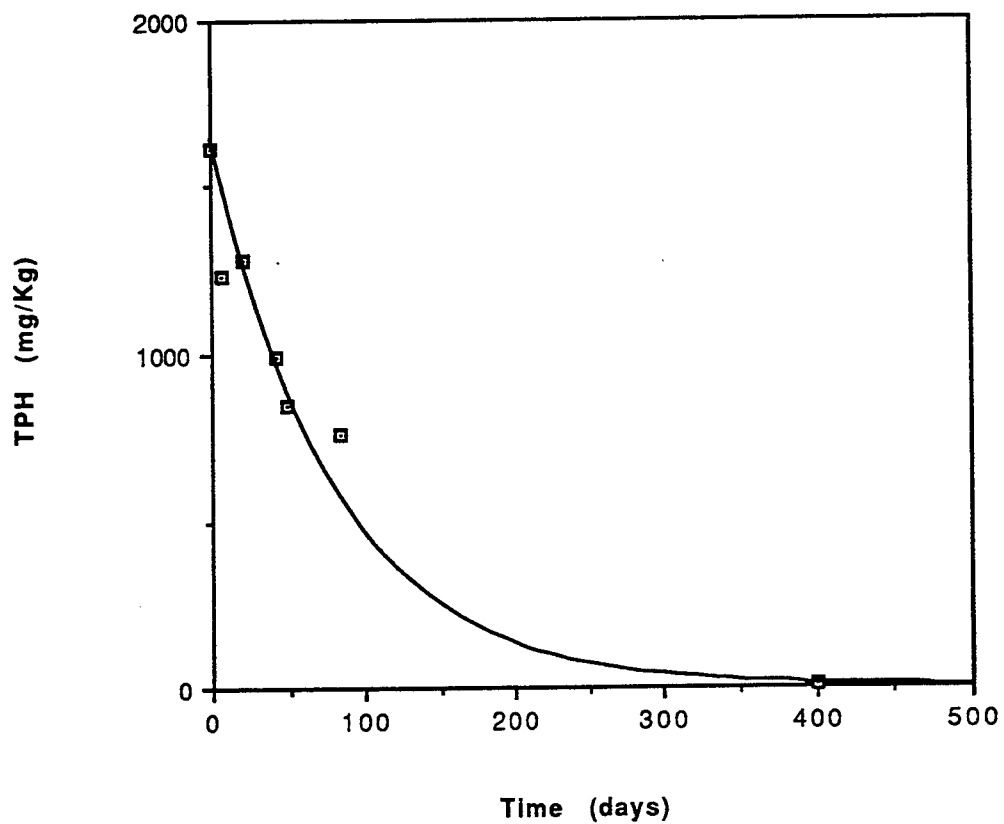


Figure 11. TPH degradation for Pile I (Control: no fertilizer added; not aerated).

Pile "J" TPH (mg/Kg) Degredation vs. Time (Days)
-Aerated Every Two Weeks
-Augmented with Poly Sodium Vinyl Sulfate
(0.01%. w/w)

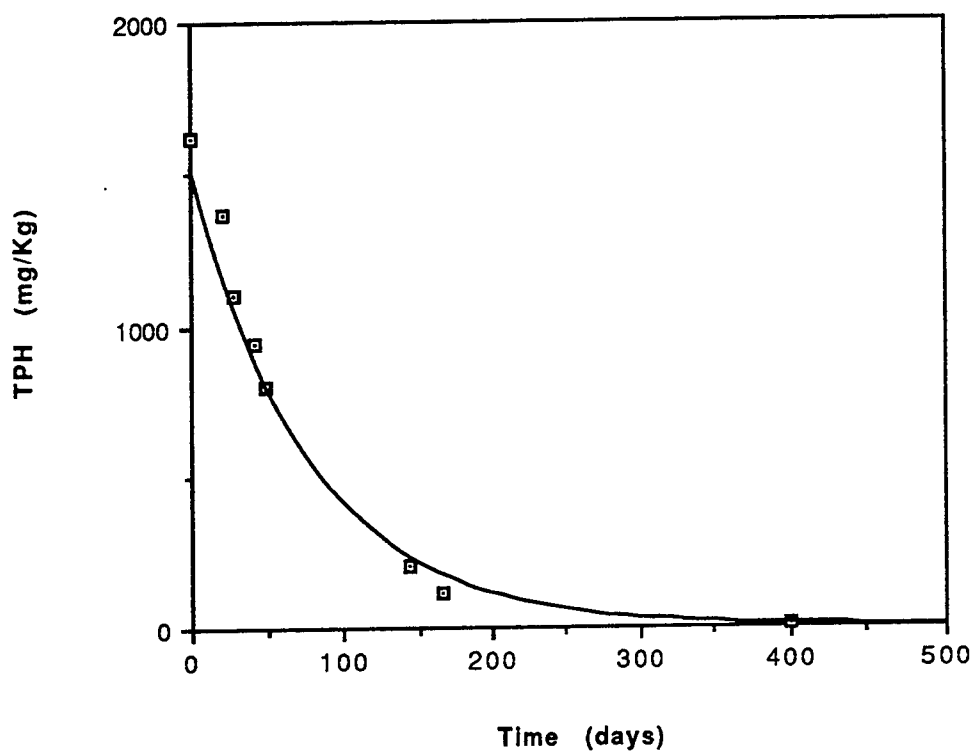


Figure 12. TPH degradation for Pile J (Amended with poly sodium vinyl sulfate).

up oxygen relatively rapidly, and most of the oxygen was likely depleted from the soil pores within a short period of time (e.g., within hours) after turning. Attempts were made to measure oxygen uptake rates within the piles by boring a hole 8 inches deep, inserting the dissolved oxygen probe, and reading dissolved oxygen concentrations over time. This procedure was not successful because a seal could not be formed over the probe to measure oxygen depletion. With oxygen limiting the biodegradation of the hydrocarbons in the solids, nutrients (fertilizer) levels were probably not important; in other words, whether fertilizer was added or not made no difference in TPH loss because the microbial degradation rates were so small. Nonetheless, the results of this segment of the study show that the frequency of turning the vector solids piles has no effect on treating the petroleum hydrocarbons.

The results of the street sweepings treatment are shown in Figures 6 and 7. The data of Figure 6 are for a 5 yd³ pile that was turned every two weeks. The results shown in Figure 7 are a control pile that received no turning or fertilizer. The results for the street sweepings are nearly identical to the results of vector solids piles. As with the vector solids, the time required for treatment of the TPH in the street sweepings are approximately 400 days. The data confirm that turning did not enhance the loss of petroleum hydrocarbons in the street sweepings and the vector solids.

Sampling was conducted through the fall of 1996. A severe winter from November 1996 through May 1997 prevented sampling because the piles were frozen. Total petroleum hydrocarbon concentrations in all of the piles was minimal after 400 days, and may have even been achieved before that time. Furthermore, TPH loss to minimal levels may occur more rapidly almost anywhere in the State of Washington, because Pullman is characterized by one of the coldest climates in the state. Vector solids may likely decline to background levels with four to six months on the west side of the state.

The results of three soil pretreatments -- sodium carbonate peroxyhydrate, calcium peroxide, and hydrogen peroxide, are shown in Figures 8, 9, and 10, respectively. The

intention of adding these chemicals to the piles on the day they were established was to partially break down the hydrocarbons and render them more available to the microorganisms. The results of Figures 8, 9, and 10 show that these pre-oxidants did not enhance the removal of the total petroleum hydrocarbons. The reason for their ineffectiveness may be related to the selection of improper conditions. The sodium carbonate peroxyhydroxide and calcium peroxide are high - pH peroxides that do not readily oxidize most contaminants. Although hydrogen peroxide is an effective oxidant, a small amount of catalyst, such as ferric sulfate, should have been disked into the vector solids prior to the addition of the hydrogen peroxide to enhance the pre-oxidation of the hydrocarbons. Although hydrogen peroxide by itself is a weak oxidant, catalyzed hydrogen peroxide is much more effective, and would have likely provided more effective results. The results of the control pile the same size as those that received the hydrogen peroxide formulations are shown in Figure 11. The control pile shows the same results as the piles that received the peroxide pretreatments. The TPH levels in the pile that received the surfactant poly sodium vinyl sulfate decreased more rapidly than the other piles, especially during the first few weeks of the study (Figure 12). A number of possible explanations may be possible for the rapid decline in TPH concentrations with the surfactant addition. Because the piles were likely oxygen limited, the desorbed TPH may have simply migrated out of the pile onto the concrete pad with the water that percolates through the pile to keep it moist. Alternatively, the hydrocarbons may have been biodegraded by anoxic or anaerobic processes after they were decanted. Of the two explanations, migration out of the pile with the added water is most likely.

The piles were sampled through Fall 1996 until they froze, at which time microbial activity ceased. The piles were sampled one last time in July 1997, and the results showed that TPH levels had decreased to below detectable levels. Throughout the study, pH was monitored by adding deionized water to a soil sample and measuring the pH with a pH

meter. The data were consistently within the pH range of 6.8 to 7.2, which is within the acceptable range for biological growth.

One of the goals of this study was to evaluate the biodegradation of specific compounds as treatment proceeds. However, the vector solids matrix is extremely complex and, as a result, they could not be analyzed by gas chromatography/mass spectrometry (GC/MS). Attempts were made to clean up the extracts using sorbents and other techniques; however, the extracts contained too many compounds and too many interferences to be effectively analyzed by GC/MS. Vector solids samples extracted in the environmental engineering laboratory were found to have too much background organic matter for GC/MS analysis and their analysis was not approved by the Murdock contract analysis laboratory at WSU.

Polycyclic aromatic hydrocarbons were analyzed by gas chromatography/flame ionization detection and matching of peaks based on retention times. Gas chromatography/mass spectrometry could not be used because the samples were too complex, containing numerous "ghost" peaks. The concentrations of the predominant marker PAH over the 400 day study, anthracene, is shown in Figures 13 through 23. As with the concentrations of TPH, 400 days were required for the PAH to decline to acceptable concentrations for most treatments. In a similar manner to the monitoring of TPH, the degradation of PAHs were not enhanced by the addition of fertilizer or by turning the piles. However, the addition of peroxygens, such as sodium carbonate peroxyhydrate, calcium peroxide, and hydrogen peroxide enhanced PAH degradation slightly. Polycyclic aromatic hydrocarbons react with hydroxyl radicals and other oxidants at extremely high rates (Watts, 1998) and are effectively removed from the sorbed state. Therefore, if accelerated PAH removal is desired, the vector solids may be pretreated with one of the peroxygens.

Another small vector solids plot, which was not technically a pilot-level pile, was a thin layer of solids placed on a road cut. Data collected over five months showed no

significant degradation of the TPH. Although PAHs were not measured on this layer, it follows that they would not have degraded if the TPH did not degrade (because the PAH fraction is a subset of the TPH chemicals). The moisture content of road side plot was less than the piles, which was obvious by visual inspection. It appears that the lack of moisture prevented the petroleum from desorbing and degrading.

As expected by their reduced nature, aliphatic and aromatic hydrocarbons biodegrade most efficiently under aerobic conditions. A large number of bacterial species uses aliphatic and aromatic hydrocarbons as their sole source of carbon and energy. Biodegradation rates of alkanes are related to their chain length; alkanes less than 10 carbons are more toxic to microorganisms as a result of their higher solubility. Alternatively, biodegradation rates of long-chain alkanes ($> C_{10}$) are affected by low water solubility and a correspondingly high degree of sorption. However, soil and groundwater microorganisms that are actively metabolizing hydrocarbons produce natural surfactants that aid in desorbing the contaminants. These compounds, which are often based on complex hybrid structures of proteins, lipids, and carbohydrates, include rhamnolipids, phospholipids, and lipopolysaccharides (Troy and Jerger, 1993).

As shown in Figure 24, alkanes proceed through dehydrogenase reactions with transformation to an alcohol, aldehyde, and a carboxylic acid. The final step in this pathway is β -oxidation, the same degradation mechanism used in the metabolism of natural fatty acids.

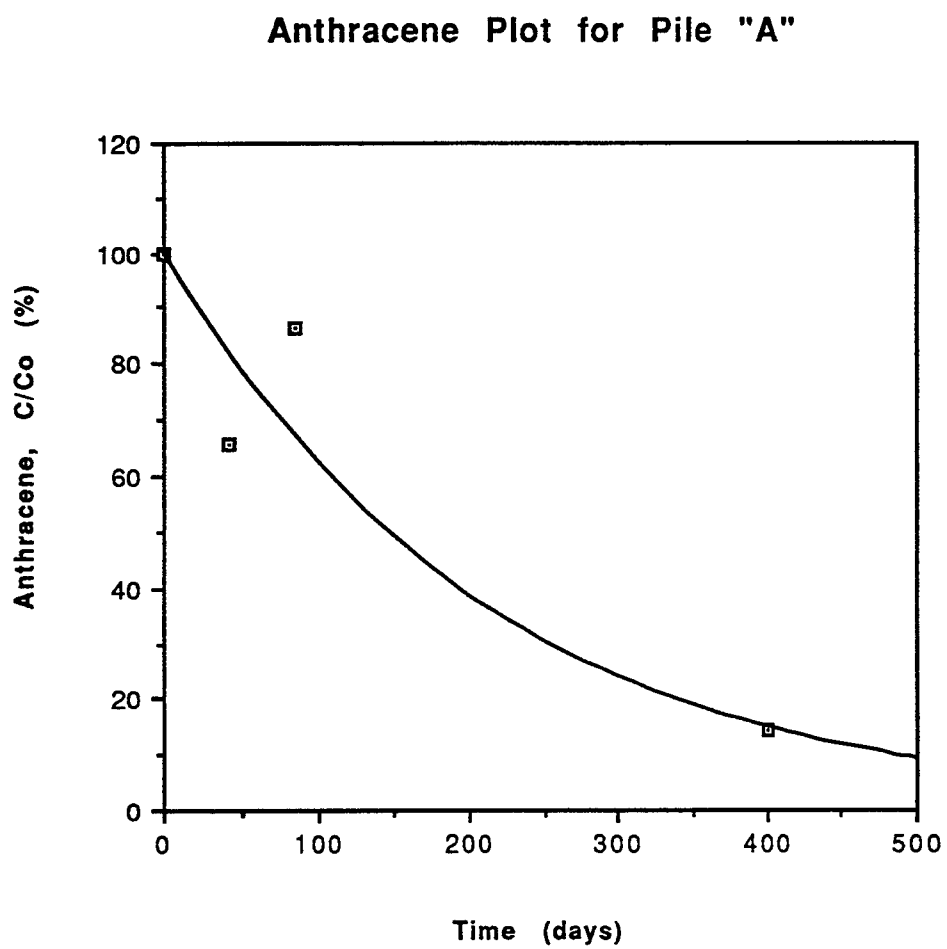


Figure 13. PAH degradation for Pile A (amended with fertilizer, aerated weekly).

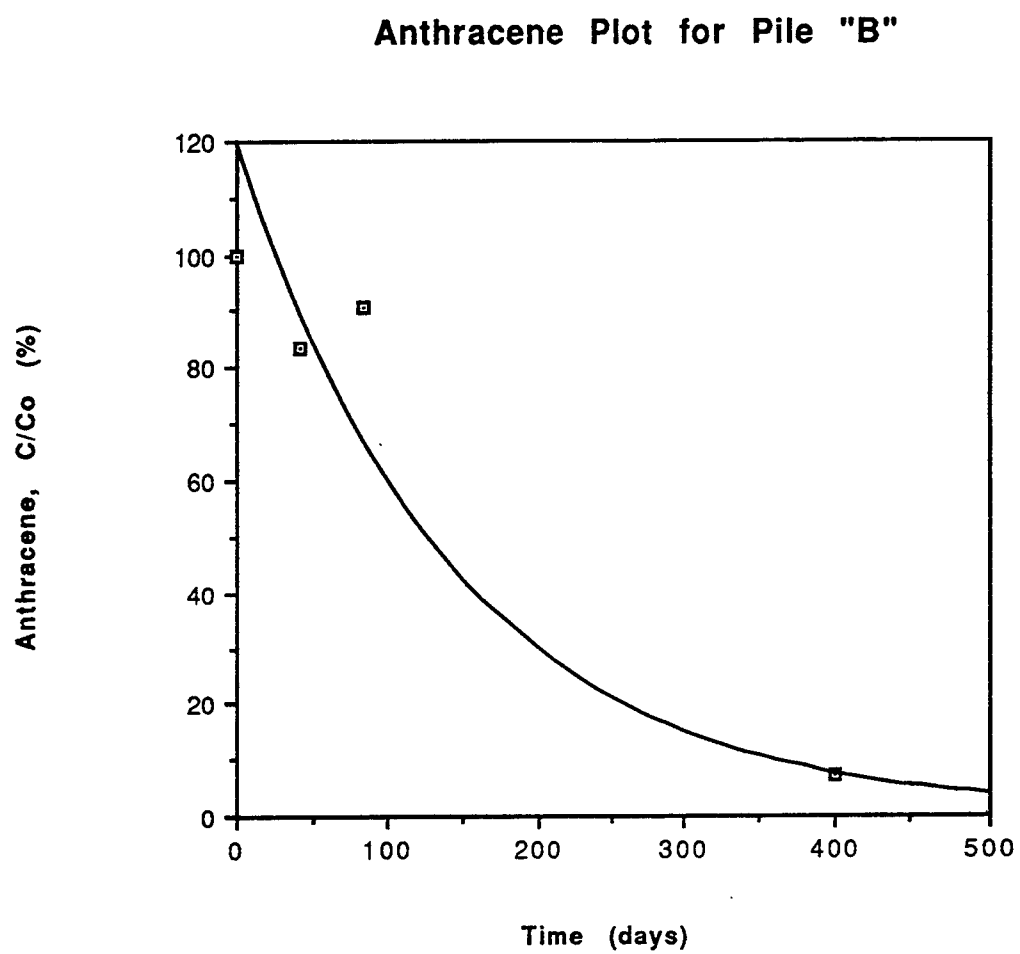


Figure 14. PAH degradation for Pile B (amended with fertilizer, aerated every two weeks).

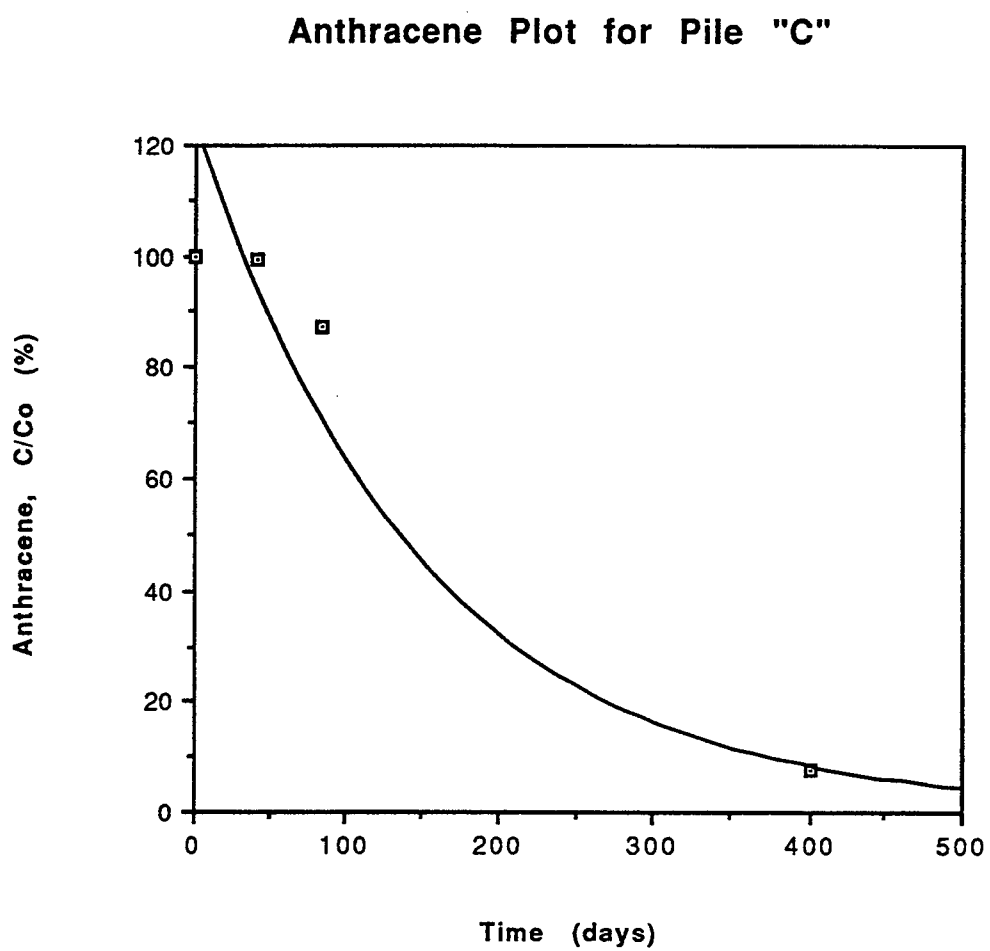


Figure 15. PAH degradation for Pile C (amended with fertilizer, aerated every four weeks).

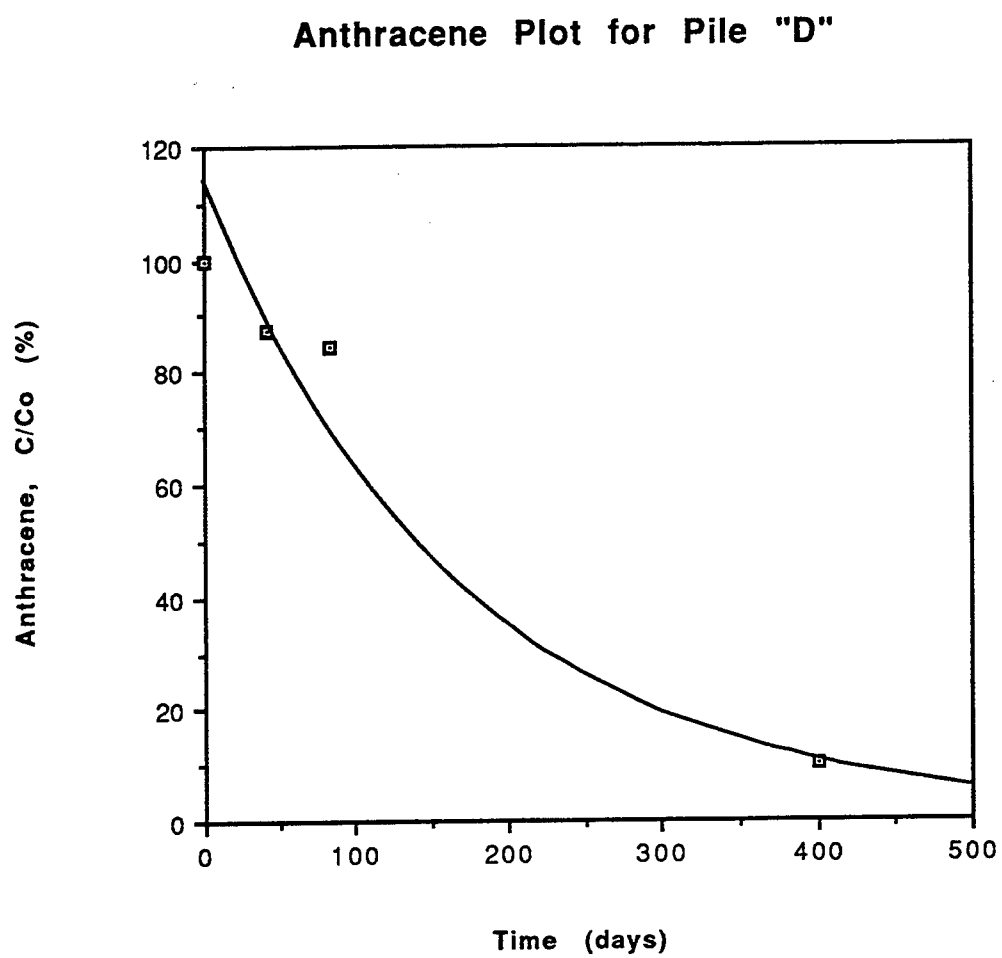


Figure 16. PAH degradation for Pile D (Control: no fertilizer addition; not aerated).

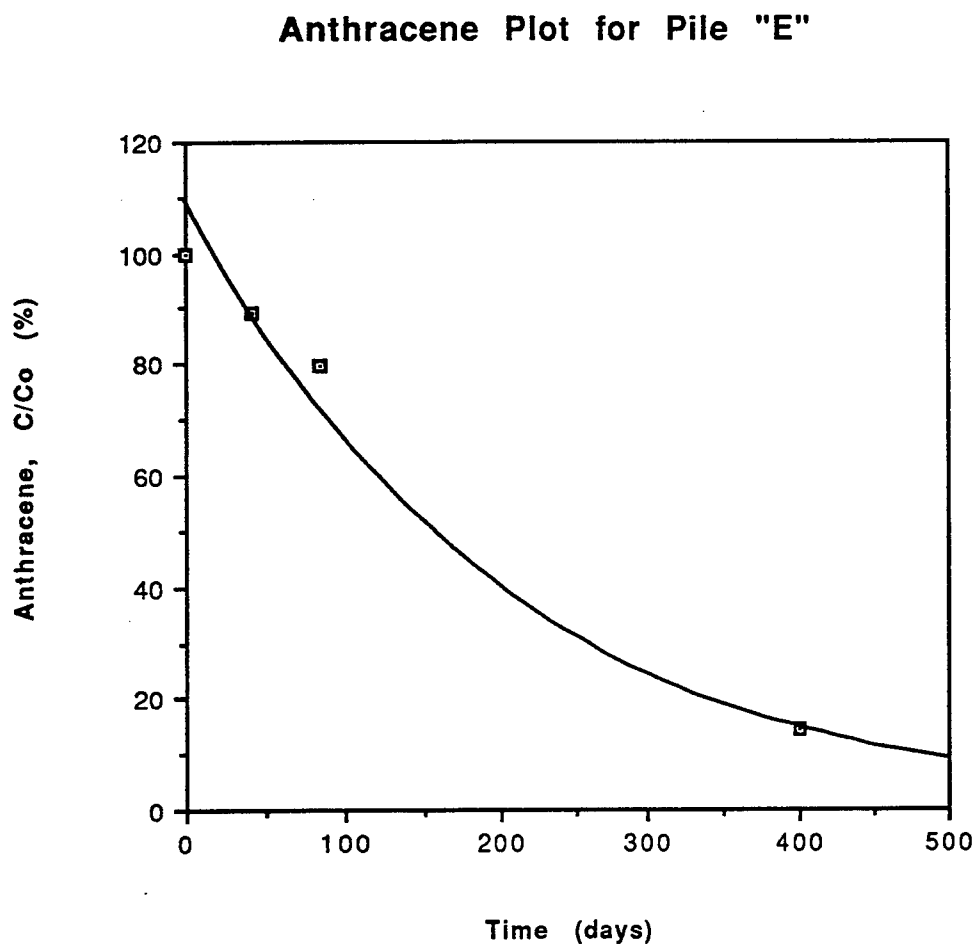


Figure 17. PAH degradation for Pile E containing street sweepings (Amended with fertilizer; aerated every two weeks).

Anthracene Plot for Pile "F"

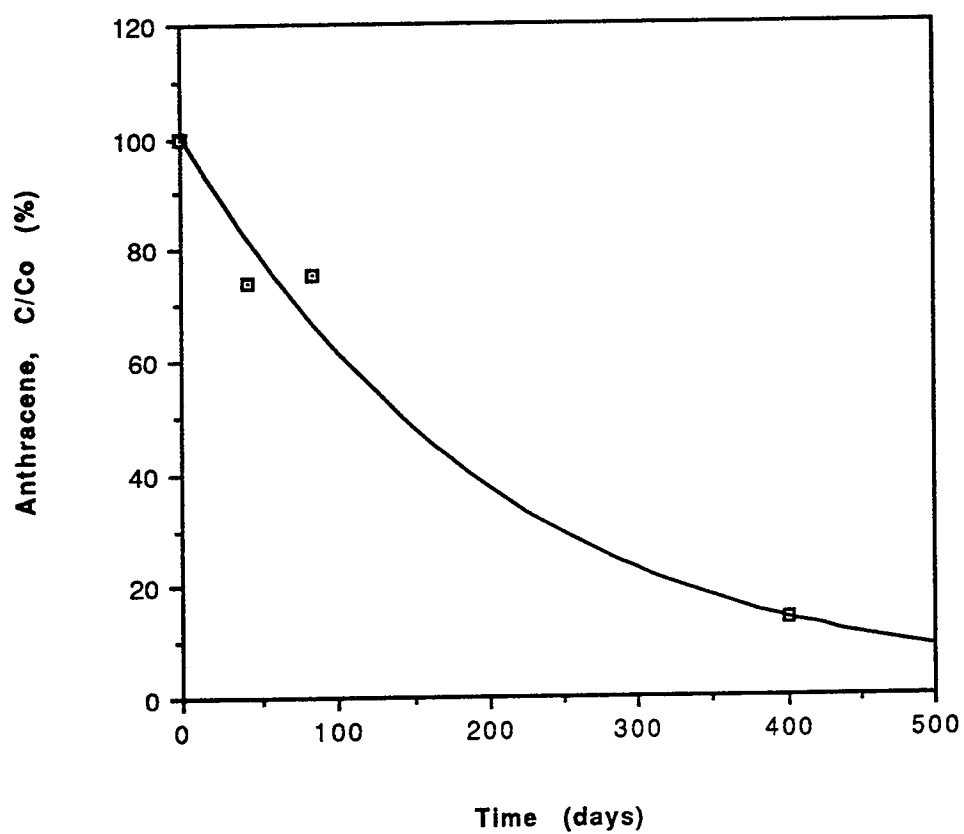


Figure 18. PAH degradation for Pile F containing street sweepings (Control: no fertilizer addition; not aerated).

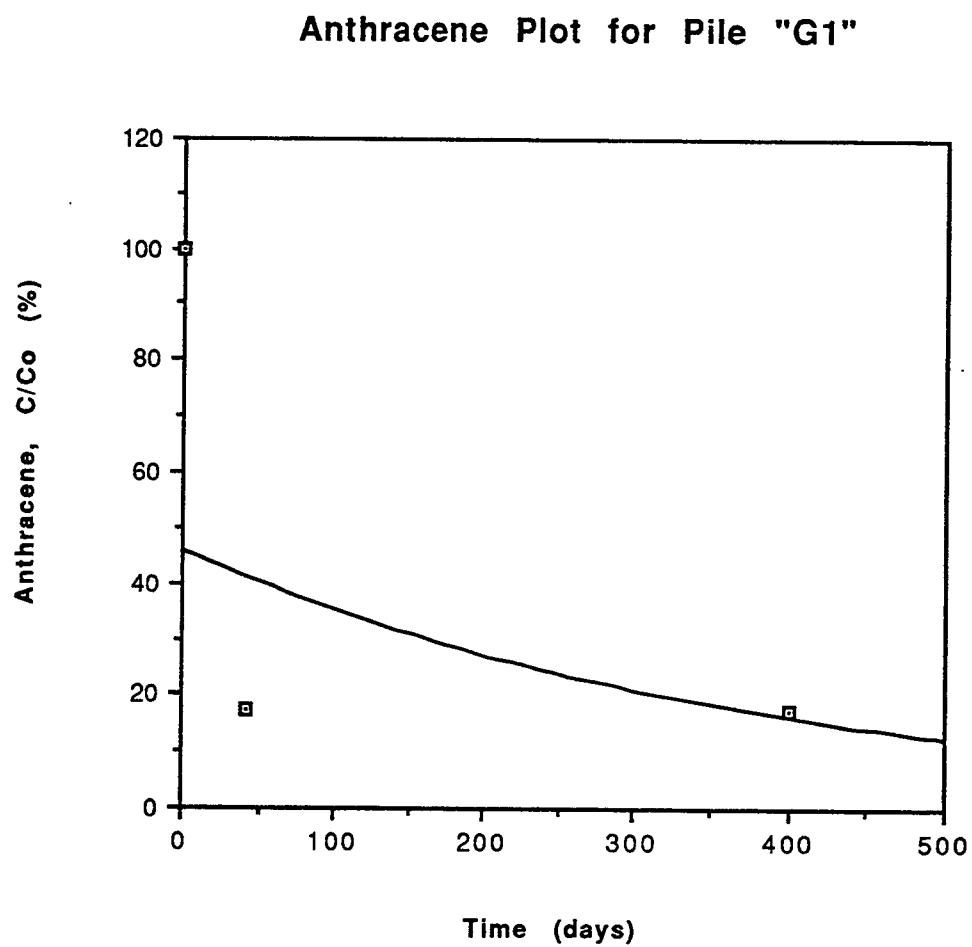


Figure 19. PAH degradation for Pile G1 (pretreated with sodium carbonate peroxyhydrate).

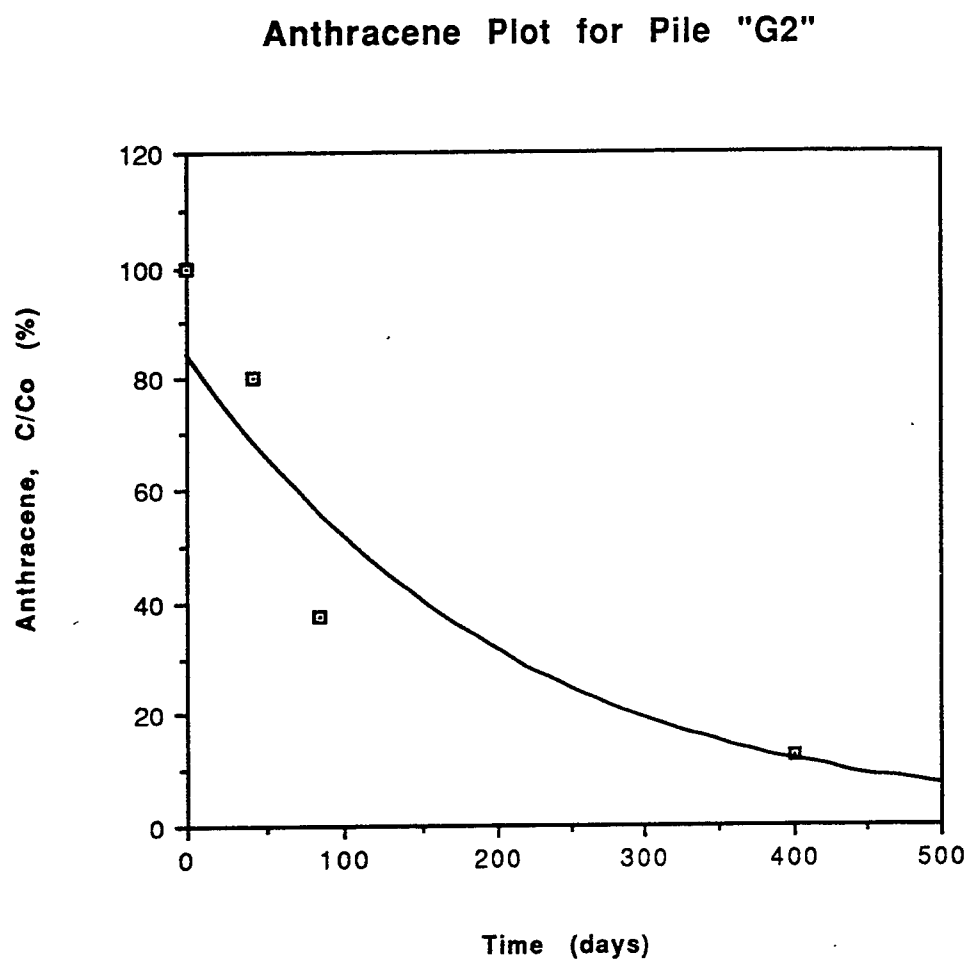


Figure 20. PAH degradation for Pile G2 (pretreated with calcium peroxide).

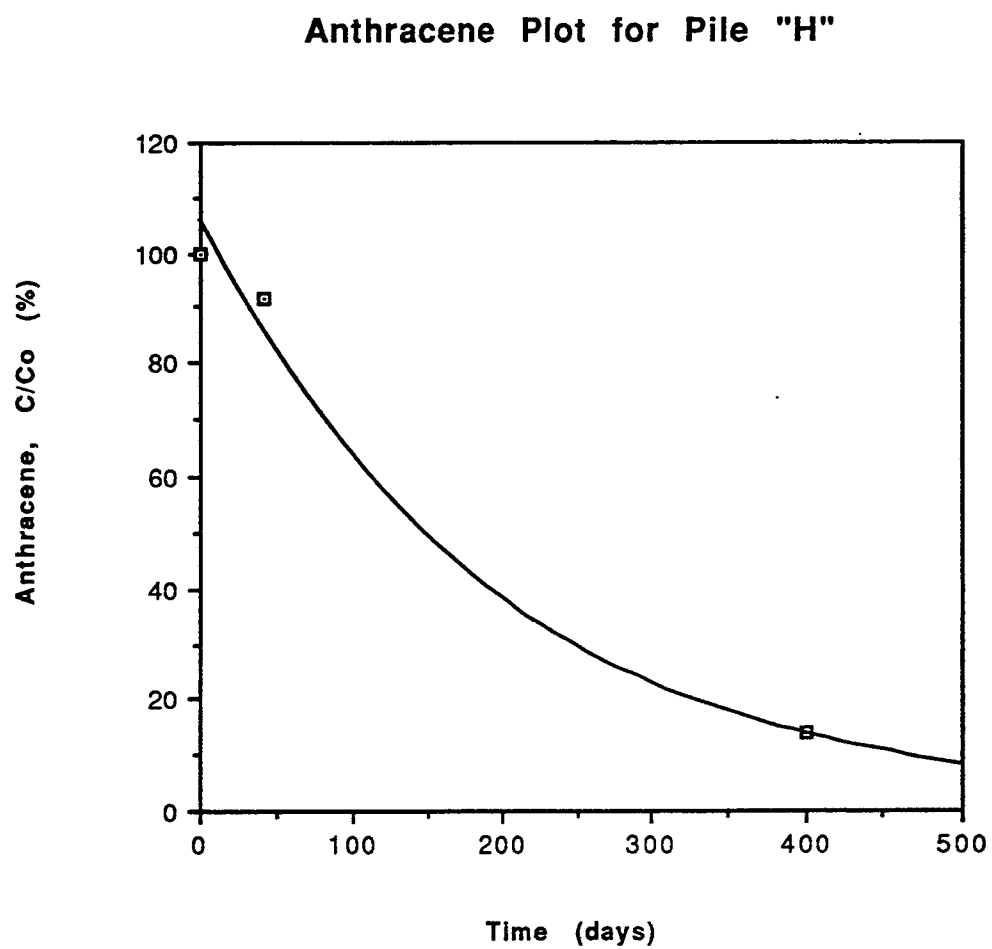


Figure 21. PAH degradation for Pile H (pretreated with 2% hydrogen peroxide).

Anthracene Plot for Pile "I"

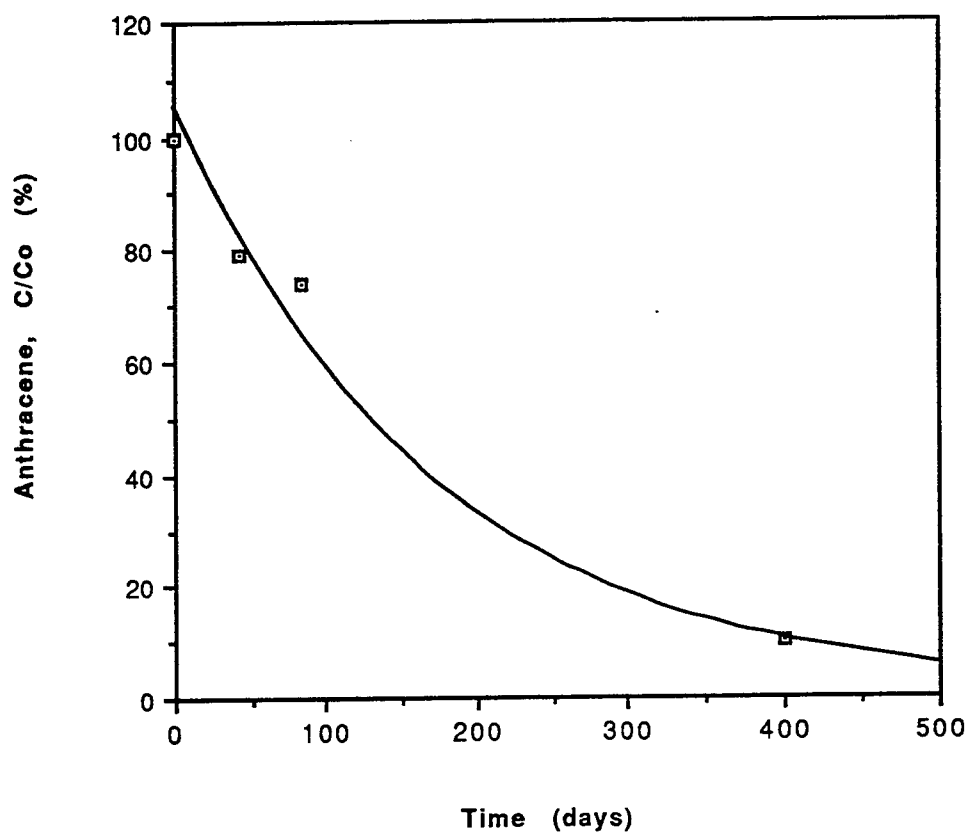


Figure 22. PAH degradation for Pile I (Control: no fertilizer added; not aerated).

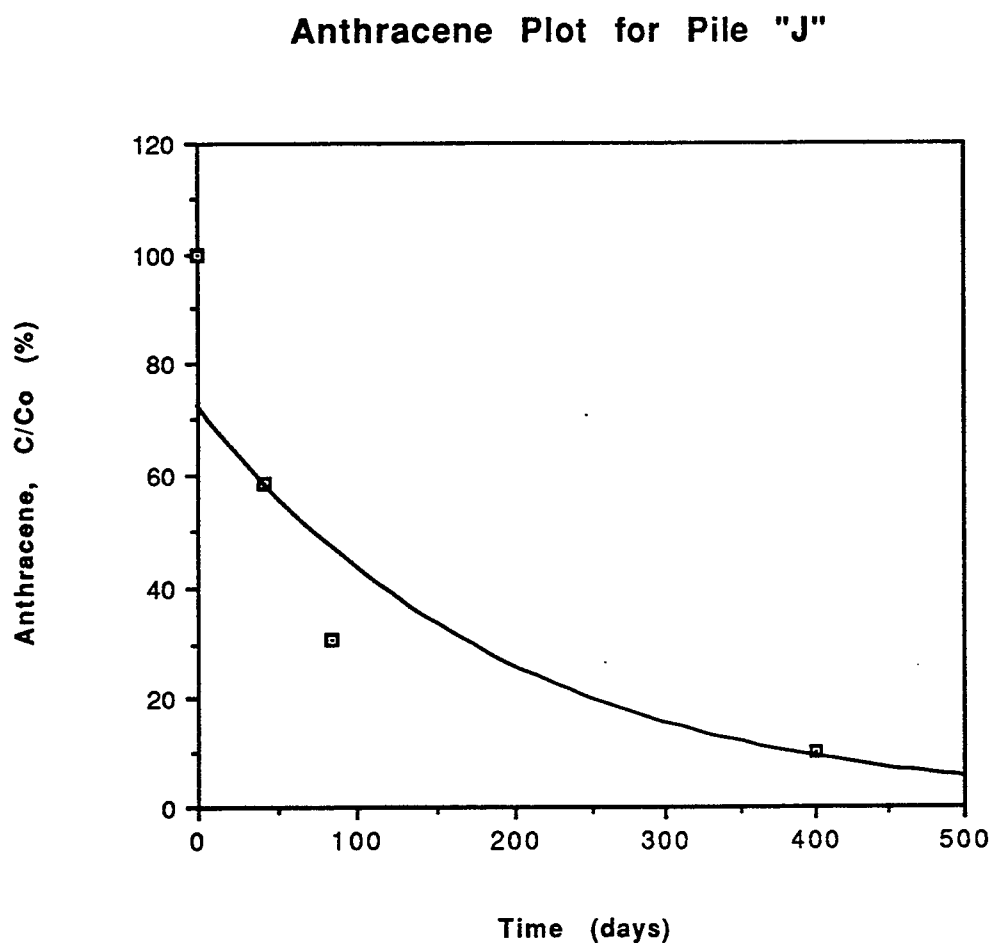


Figure 23. PAH degradation for Pile J (Amended with poly sodium vinyl sulfate).

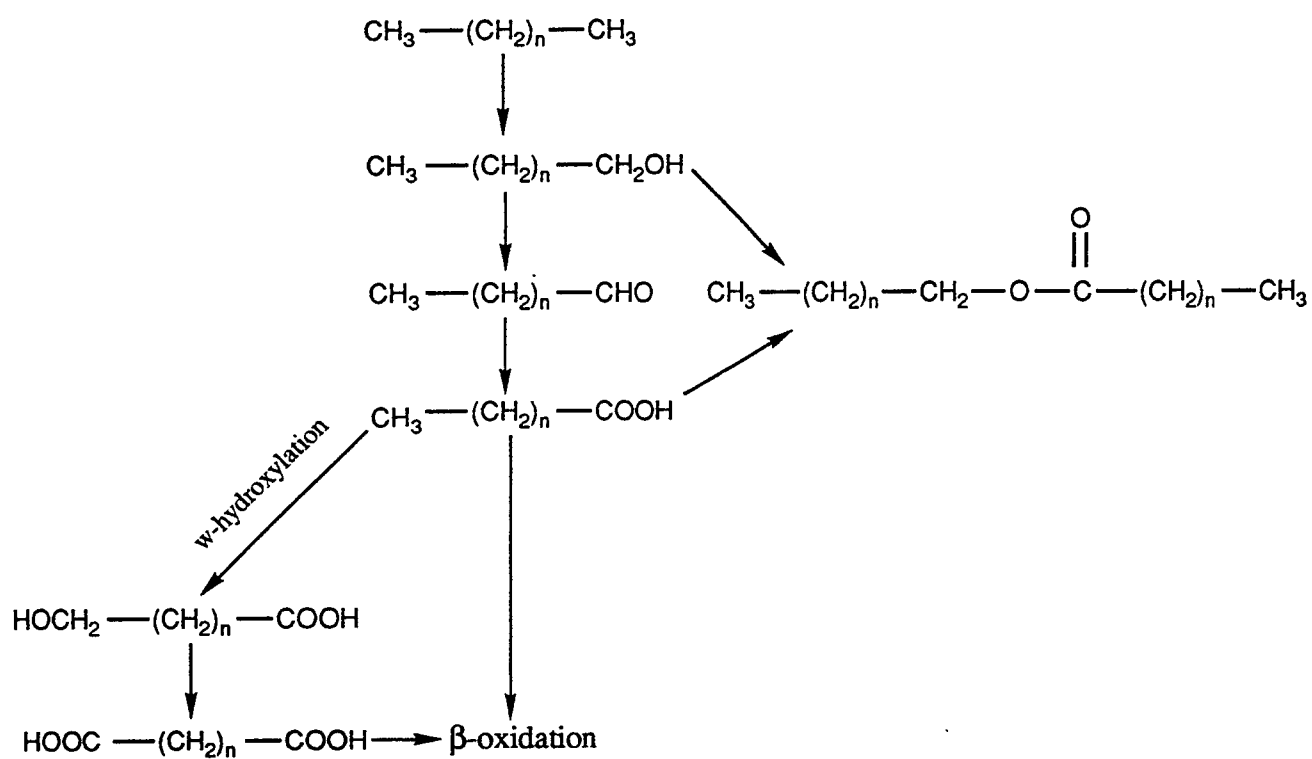


Figure 24. Pathway for the biodegradation of alkanes.

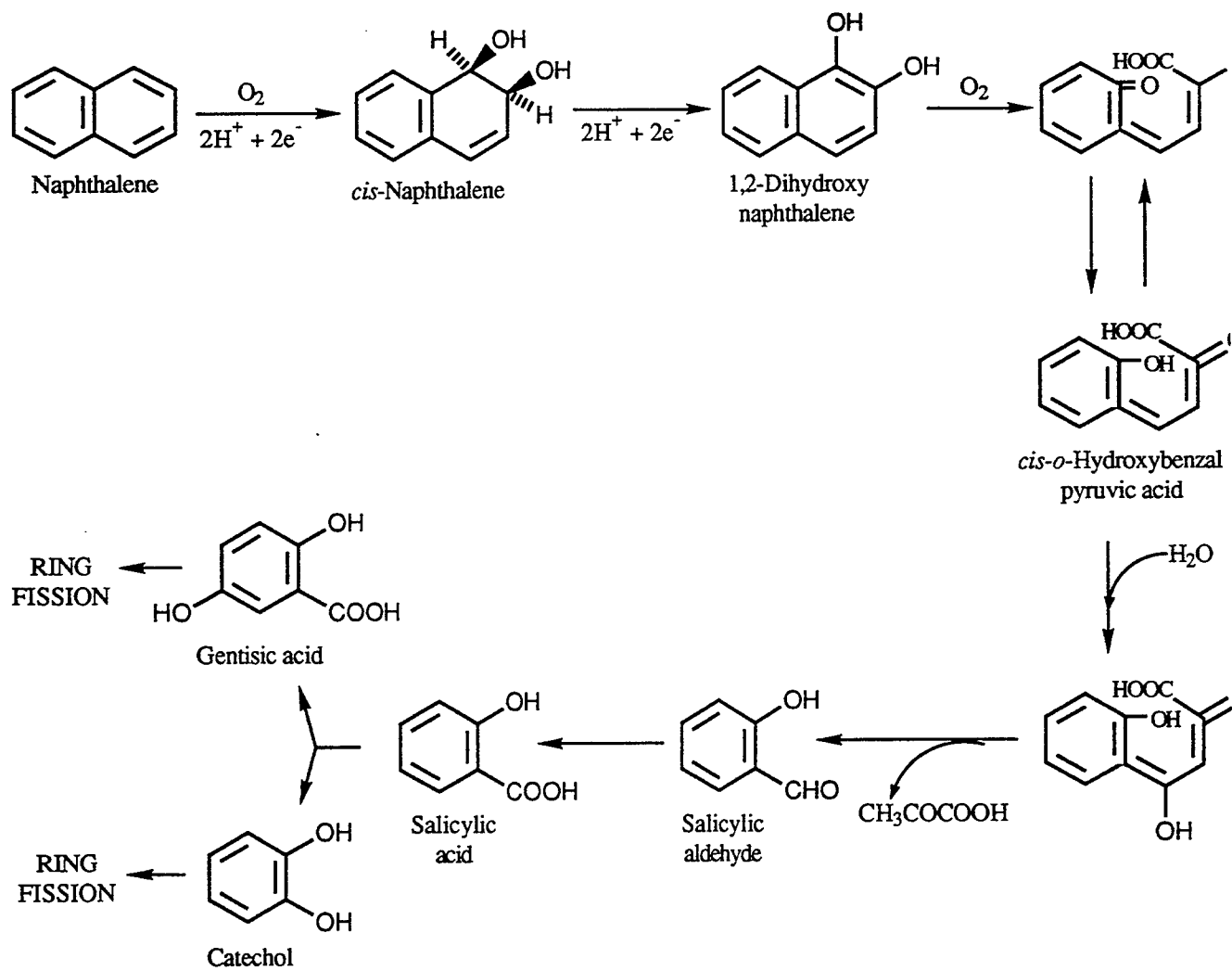


Figure 25. Biodegradation pathway for benzene.

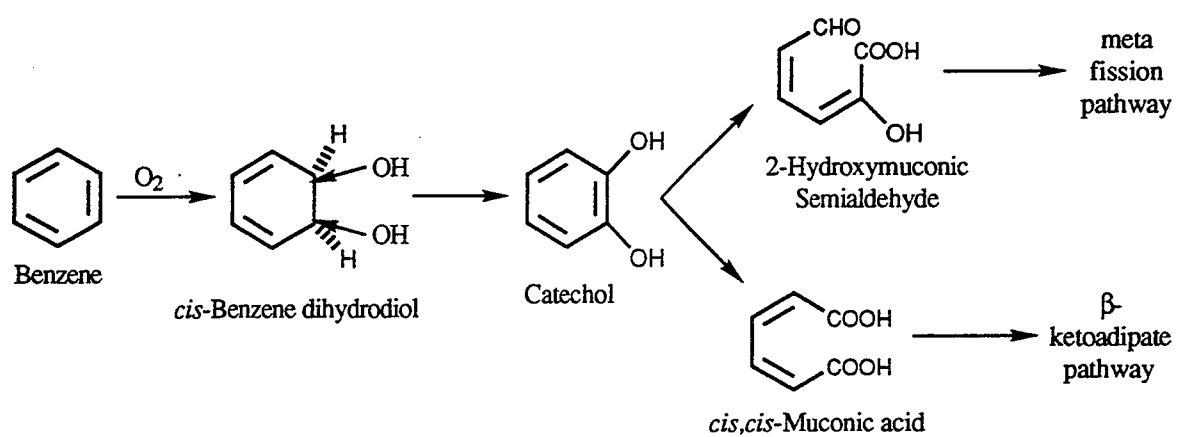


Figure 26. Biodegradation pathway for PAHs.

Acetic acid, generated through β -oxidation, can then proceed through the TCA cycle after it is converted to acetyl CoA; the alcohol also degrades further via the aldehyde-acid route through another β -oxidation. Branching interferes with β -oxidation (in which carbon atoms are cleaved two-at-a-time) because a one-carbon oxidation (α -oxidation) must occur, a more difficult pathway in microbial metabolism.

Aromatic compounds degrade by a dual dioxygenase-catalyzed hydroxylation mechanism in which oxygen is added to form a diol. The diol then proceeds through ring cleavage and the products enter standard metabolic pathways, as illustrated in Figure 25.

Polycyclic aromatic hydrocarbons follow similar pathways of hydroxylation and ring cleavage (Figure 26). However, biodegradation rates of PAH compounds larger than three rings are slowed by their need for specific enzymes to degrade these larger compounds (Gibson and Subramania, 1984). Therefore, the biodegradation of PAHs is a function of the ring size and the enzymatic complement of the microbial consortium. The general consensus is that two and three ring PAHs are readily biodegradable, whereas those containing four or more rings are exceedingly difficult, if not biorefractory. Furthermore, large-ring PAHs are highly hydrophobic and sorption often controls their rates of biodegradation (Mihelcic and Luthy, 1988). Another factor that has been shown to influence the biodegradability of PAHs is the number and positions of substitution groups. Recent studies have documented that the addition of three methyl groups to a number of PAHs resulted in significantly-decreased rates of biodegradation.

Anaerobic biotransformations of PAHs have received less attention relative to aerobic processes. Results to date have shown that two- and three-ring PAHs are biodegraded under denitrifying, sulfate-reducing, and methanogenic conditions (Cookson, 1995).

Aerobic microorganisms require a minimum dissolved oxygen level for maximum growth and metabolism. Although a paucity of information exists on the minimum dissolved oxygen concentration needed to promote the biodegradation of hazardous compounds, trends similar to biological wastewater treatment systems have been

suggested. Activated sludge systems are characterized by negligible metabolism at zero dissolved oxygen, and the rate increases up to approximately 1-to-2 mg/L; above these concentrations, the rate of microbial metabolism is relatively constant.

In order for hazardous compounds to degrade, they must have contact with a species that promotes their transformation. One of the best examples of inaccessibility to degradation is the large pools of petroleum found deep below the earth's surface. These huge reservoirs are in an area where microorganisms do not tend to grow; furthermore, conditions in the interior regions of these hydrocarbon systems are not conducive to microbial growth. If a microorganism found its way to the center of a large pool of oil, it would have more than enough carbon but would be lacking water, nutrients, and the other environmental factors necessary for it to grow and reproduce.

Nonaqueous phase liquids (NAPLs) behave much the same way as the ancient petroleum reserves. These pools of relatively pure materials are not a suitable environment for water-borne reactants such as chemical oxidants or microorganisms. Therefore, minimal transformation of contaminants in pools and lenses of NAPLs may be expected because of their immiscibility with water.

Sorption--the accumulation of contaminants at surfaces--provides an inaccessibility mechanism analogous to the presence of a NAPL phase. Sorption not only retards the rate of migration of hazardous contaminants and lowers the rate of phase transfer to the atmosphere, but also significantly affects rates of abiotic and biotic transformations. The conceptual basis for the effect of sorption is that the agents that transform organic contaminants (e.g., bacteria, oxidants, and reductants) exist in the aqueous phase. In other words, if a contaminant partitions onto soil organic matter or a mineral surface, it is not in direct contact with the agents responsible for its transformation.

In most cases, desorption is believed to control the transformation of hazardous organic contaminants in soils, groundwater, sludge, and treatment systems. For example, Ogram *et al.* (1985) documented that sorption controlled the biological degradation of 2,4-

D; similar results were reported for PAHs (Weissenfels et al., 1992) and PCBs (Guerin and Boyd, 1992). In contrast, other studies have found that, although sorption reduces the rate of biodegradation (and often controls it through desorption), a number of compounds can be biodegraded even when all the chemical is sorbed or when desorption is insignificant over the time biodegradation takes place (Sleinberg et al, 1984; Manilal and Alexander, 1991).

Other studies have shown that some mechanisms can enhance desorption and subsequent transformation. In biological processes, naturally occurring surfactants, such as rhamnolipids, solubilize sorbed contaminants resulting in increased rates of biodegradation (Britton, 1984).

Conclusions

Based on the pilot study conducted on the treatment of vector solids during 1996 through 1997, the following conclusions may be drawn:

1. Piles treated with the addition of fertilizer and turning showed no difference in total petroleum hydrocarbon degradation relative to piles that received water only.
2. Rate of turning of the piles had no effect on total petroleum hydrocarbon degradation, which may have been due to oxygen limitation that could not be overcome, even by weekly turning.
3. Approximately 400 days were required for total petroleum hydrocarbon concentrations to degrade to background levels. The piles were frozen for five months during the study; treatment times may be significantly lower at warm climates.
4. Pretreatment with a surfactant (polysodium vinyl sulfate), sodium carbonate, peroxyhydrate, calcium peroxide, and hydrogen peroxide did not enhance the biodegradability of the total petroleum hydrocarbons under the nutrient, moisture, and turning conditions of this study.

5. Polycyclic aromatic hydrocarbons degraded at approximately the same rates as total petroleum hydrocarbons; these toxic species biodegraded to background levels in 400 days and may be biodegraded faster under warmer climatic conditions.
6. Although a perforated piping system with blowers to supply oxygen would likely provide the most rapid loss of total petroleum hydrocarbons, natural attenuation by keeping the piles moist would provide the most economical treatment.

Implementation

The results of this study show that the turning rate and fertilizer addition for vector solids treatment had no significant effect on the rate of vector solids treatment. In other words, if piles of vector solids are kept moist, the piles are treated effectively by not turning them or adding fertilizer. The use of such intrinsic bioremediation would provide an effective and low-cost method for the treatment of vector solids if land is available for the time required for hydrocarbon treatment. Intrinsic bioremediation has now become the most popular method of treating contaminated soils and groundwater and has been embraced by numerous federal agencies. It has been well proven over the past five years.

Vector solids are often simply stockpiled because no acceptable or economical disposal option exists. A simple and effective implementation plan would be to simply maintain the water content at 50% with sprinklers on a drip system. The time required for the hydrocarbons to change to minimal levels in Pullman, WA was approximately one year. Time requirements for hydrocarbon treatment in other areas that do not experience five months of freezing temperature may be less. The moisture content of the solids was maintained at 50% by daily watering; such a moisture level may also be easier to maintain in Western Washington.

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