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Chemical Oxidation Enhanced Bioremediation of Polycyclic Aromatic Hydrocarbon Contaminated Sediments

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CHEMICAL OXIDATION ENHANCED BIOREMEDIATION OF POLYCYCLIC AROMATIC HYDROCARBON CONTAMINATED SEDIMENTS

By

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This study evaluated the effect of chemical oxidation on the bioremediation of polycyclic aromatic hydrocarbons (PAHs) contaminated sediments. Sediments were treated in sequential steps: biotreatment, chemical oxidation, and biotreatment. The first biotreatment step was initiated via addition of nutrients, microbial seeds, co-metabolites, and/or Tween 80 (surfactant). The chemical oxidation step was conducted using Fenton's Reagent, ozonation, and peroxone (combination of ozone and hydrogen peroxide). The objective was to enhance the PAHs bioavailability via oxidation of natural organic matter and transformation of Heavy PAHs into more biodegradable compounds. Biotreatment was reestablished as a final polishing step to further degrade remaining PAHs and more biodegradable oxidation by-products. The proposed mechanism was proven successful for the less contaminated sediment (Scioto River) and not the highly contaminated and chemically more complex sediment (Lake Superior). Given this mechanism

only worked for the Scioto River sediment, further research is required to determine the mechanisms limiting treatment.

DEDICATION

I would like to dedicate this to my parents, Tiang Hock Leong and Sia Ming Hua.

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CHAPTER I

INTRODUCTION

Background

Petroleum has been used throughout history. The Egyptians used it to coat mummies in order to preserve bodies, while Native-Americans used it for paint and medicinal purposes (Schackne and Drake, 1950). In 1859, Colonel Drake discovered oil in Pennsylvania resulting in 15 petroleum refineries being constructed over the next year. From that point on, the industrial exploitation of oil began. Today, it is estimated that annual global production of crude oil has reached more than two billion metric tons (Jing, 1998). The usage of petroleum has expanded from its use as a fuel to a feedstock for thousands of commercial chemicals.

Crude petroleum is a liquid mixture of literally thousands of compounds, more specifically alkanes, cyclo-alkanes, aromatic hydrocarbons, and small amounts of oxygen, nitrogen, and sulfur containing compounds (Atlas, 1981; Jing, 1998). Petroleum is so complex that the crude form is practically of no commercial value until it is refined into hydrocarbon fractions.

Polycyclic aromatic hydrocarbons (PAHs) are one of the most prevalent petroleum hydrocarbons forms. Many are of concern to the public because of their carcinogenic properties. The National Academy of Sciences has classified eleven of the

forty identified PAHs as being strongly carcinogenic or mutagenic, while ten others are regarded as being weakly carcinogenic and mutagenic (NAS, 1972). Of the 120 compounds defined as priority pollutants by United States Environmental Protection Agency (USEPA), sixteen are PAHs (Keith and Telliard, 1979; Heitkamp and Cerniglia, 1988). Table 1.1 presents the structural and chemical characteristics of the regulated PAHs. USEPA regulated PAHs range from two to six rings, with the higher ringed PAHs (also known as Heavy PAHs) considered carcinogenic (Jones and Leber, 1979; Lehr et al., 1979; Zappi et al., 1993). In general, Heavy PAHs are also known to be recalcitrant to biodegradation; thus, resulting in low removal rates during wastewater and soil treatment.

Human exposure to PAHs may occur from activities such as petroleum refining, coke and aluminum production, coal combustion, and wood preservation (Heitkamp et al., 1987). Contamination of PAHs in groundwater and soil systems can create problems with serious implications to human health and the environment due to the following reasons:

(1) PAHs are relatively toxic with some considered mutagenic and/or carcinogenic, even at low concentrations

(2) PAHs have high bio-accumulation potentials (Park et al., 1990)

(3) The production and usage of PAHs in mass quantities making it impossible to predict the extent of damage to the environment (Dzombak and Luthy, 1984)

(4) Heavy PAHs pose an additional problem of being persistent within soil environments (Zappi et al., 1993; Ye et al., 1996).

Traditional Soil Treatment Options

Treatment of PAH contaminated sediment has generally been limited to incineration, thermal desorption, soil washing, and bioremediation (Averett et al., 1990; Acar and Zappi, 1995). The following sections elaborate on the treatment of PAH contaminated soil and sediment using various techniques. Background on chemical oxidation, a developing process for soil and sediment treatment, is also included because it is key to this research project.

Thermal Approaches

Incineration is a well-developed method of ultimate waste disposal. It is efficient at destroying organic contaminants, such as PAHs; thereby, reducing the waste and destroying their toxicity. Incineration operates at temperatures above 1,800°F in the presence of oxygen to thermally oxidize organic compounds (Long, 1993). USEPA has reported that a good incineration system can have a Destruction Removal Efficiency (DRE) greater than 99.99%. Organic wastes are usually converted into carbon monoxide, carbon dioxide, water, and ash. Since carbon monoxide is hazardous, it is necessary to install secondary treatment facilities, such as afterburners, scrubbers, and filtration units, to treat the carbon monoxide. The drawbacks of using the incineration method are high capital costs and also the possibility of secondary pollution caused by incomplete combustion (USEPA, 1996). Additionally, the use of incinerations are not well received by the public.

Thermal desorption has been proven to be effective for volatile organic and semi-volatile organic contaminants (Downey and Elliott, 1990; Jing, 1998). It uses transferred

heat and the volatility of the pollutants to physically separate organic contaminants from the solid phase. In a thermal desorption chamber, soil is heated within the chamber where the water and organic contaminants are vaporized. Volatilized contaminants and water are then transported via gas emission to an off-gas treatment system. Selection of a gas treatment system is based on the concentration of contaminants, regulations, and the economics involved (Lighty et al., 1993). Drawbacks to thermal desorption system are costs and the partial breakdown of volatile organics resulting in the formation of new organic compounds (e.g., dioxin and furans) that might have an adverse impact on human health (USEPA, 1997).

Soil Washing

Soil washing utilizes water-based solutions to treat excavated soil. This system can be utilized to treat PAHs, pentachlorophenol, and petroleum wastes (USEPA, 1992; Wang, 1999). Contaminants are physically removed using the abrasive scouring action of the particles themselves. The scrubbing process breaks up the soil; thus, freeing the contaminants from the coarser material. Sometimes, surfactant and other agents (e.g., alcohols) can be added to improve the scrubbing process and possibly enhance pollutant release from the soil. Contaminated residual products are treated using thermal desorption, incineration, or bioremediation (Wang, 1999). The advantages of the soil washing system are the high removal efficiency of contaminants from the soil phase and reduction in volume of the waste products. Possible drawbacks to the soil washing system are the high maintenance costs and elevated economics when strongly bonded contaminants are present.

Bioremediation

Bioremediation utilizes microorganisms (i.e., algae, fungi, and bacteria) to degrade organic contaminations into biomass and metabolic products (Mihelcic and Luthy, 1987; Lauch et al., 1992). Given that bioremediation is considered a natural process, bioremediation is generally well accepted by the public as an environmentally friendly alternative.

Microorganisms are vital to bioremediation processes because of their ability to transform organic and inorganic compounds into environmentally benign chemicals. Organic compounds are degraded through natural biochemical reactions to provide energy to sustain growth and metabolic functions. In general, bioremediation processes involve stimulation of microorganisms to biologically degrade organic contaminants present within environmental media (i.e., groundwater aquifers and soils).

Microorganisms have the capability of degrading a wide variety of compounds, including PAHs (Singer and Finnerty, 1984; Cerniglia, 1984; Zappi et al., 1996; Wang, 1999), explosives (Zappi et al., 1995), and pentachlorophenol (Focht and Brunner, 1985; Valo et al., 1986). Bioremediation is easy to implement and generally cost effective. Drawbacks can include long treatment times and the generation of persistent by-products.

Chemical Oxidation

Oxidation-based treatment technologies, such as advanced oxidation processes (AOPs) and ozonation, are based on the use of powerful chemical oxidizers for pollutant removal. They have recently been proposed as alternative and potentially cost competitive methods for soil remediation.

Advanced Oxidation Processes

Processes that destroy organic contaminants using the hydroxyl radical are known as advanced oxidation processes (AOP) (Glaze, 1987). The hydroxyl radical is one of the strongest oxidants known (Zappi et al., 1995). It is stable over a wide range of pH. It has been reported that AOPs have the capacity to oxidize recalcitrant compounds and transform them to potentially less toxic and more readily biodegradable intermediate products (Huang et al., 1993). AOPs have been successfully used for treating chlorinated solvents, polychlorinated biphenyls (PCBs), PAHs, and explosives (Adams and Randke, 1992; Trapido et al, 1994; Zappi 1995; Yao et al., 1996).

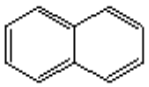
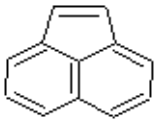
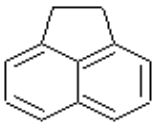
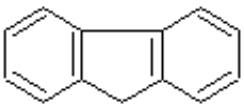
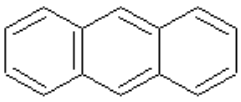
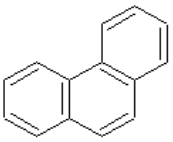
AOPs can be divided into two categories: lighted and dark. AOPs that require ultra violet (UV) light to initiate the hydroxyl radical formation are called lighted AOPs (Hong et al., 1996). Lighted AOPs are unfavorable within a soil system due to limited transmission of UV light that is essential to the formation of the radicals. AOPs that do not utilize UV sources to initiate the formation of hydroxyl radicals are termed as dark AOPs (Hong et al., 1996). Potential dark AOPs that may be useful within soil systems are Fenton's Reagent (hydrogen peroxide and ferrous ion) and peroxone (ozone and hydrogen peroxide).

Ozone

Ozone is an unstable gas that has a characteristic penetrating odor that can be detected at low concentrations (Rice, 1980). Traditionally, ozone has been used to disinfect and decontaminate drinking water and wastewater (Glaze, 1987; Rittmann and McCarty, 2001). Nevertheless, research has shown that ozone has the capability to

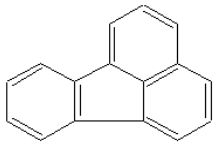
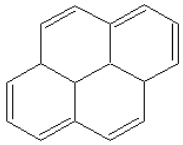
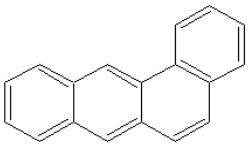
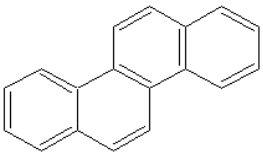
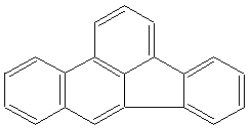
degrade a variety of pesticides and herbicides such as atrazine, cynazine, and metolachlor (Somich et al., 1990; Long, 1993). In addition, ozone has been reported to be an effective oxidant for degrading PAHs (Cornell and Kuo, 1984; Trapido et al., 1994; Beltran et al., 1995).

Table 1.1. Structural and Chemical Characteristics of 16 PAHs Regulated by USEPA[1]

Compound	Molecular Weight	Molecular Formula	Molecular Structure	Aqueous Solubility[2]
Light PAHs				
Two rings:				
Naphthalene	128	$C_{10}H_8$		31,700
Three rings:				
Acenaphthylene	152	$C_{12}H_8$		N/A
Acenaphthene	154	$C_{12}H_{10}$		3,930
Fluorene	166	$C_{13}H_{10}$		1,980
Anthracene	178	$C_{14}H_{10}$		73
Phenanthrene	178	$C_{14}H_{10}$		1,290

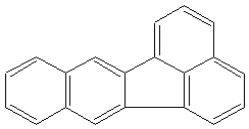
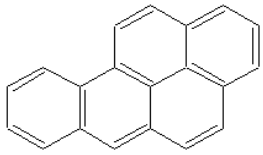
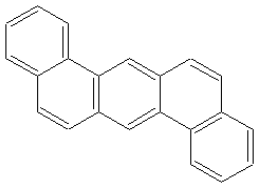
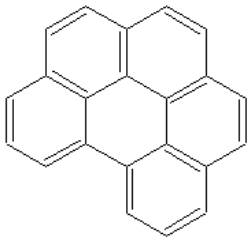
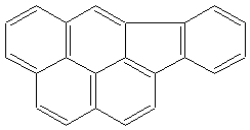
Notes:
[1] United States Environmental Protection Agency
[2] Concentrations are in units of µg/l (ppb) at 25°C
- N/A : Not available
- Adapted from Dzombak and Luthy (1984)

Table 1.1. (Continued)

Compound	Molecular Weight	Molecular Formula	Molecular Structure	Aqueous Solubility[2]
Heavy PAHs				
Four rings:				
Fluoranthene	202	$C_{16}H_{10}$		260
Pyrene	202	$C_{16}H_{10}$		135
Benzo[a]anthracene	228	$C_{18}H_{12}$		14
Chrysene	228	$C_{18}H_{12}$		2
Five rings:				
Benzo[b]fluoranthene	252	$C_{20}H_{12}$		N/A

Notes:
[1] United States Environmental Protection Agency
[2] Concentrations are in units of µg/l (ppb) at 25°C
- N/A : Not available
- Adapted from Dzombak and Luthy (1984)

Table 1.1. (Continued)

Compound	Molecular Weight	Molecular Formula	Molecular Structure	Aqueous Solubility[2]
Five rings:				
Benzo[k]fluoranthene	252	$C_{20}H_{12}$		N/A
Benzo[a]pyrene	252	$C_{20}H_{12}$		3.8
Dibenz[a,h]anthracene	278	$C_{22}H_{14}$		2.49
Six rings:				
Benzo[g,h,i]perylene	276	$C_{22}H_{12}$		0.26
Indeno[1,2,3-cd] pyrene	276	$C_{22}H_{12}$		N/A

Notes:
[1] United States Environmental Protection Agency
[2] Concentrations are in units of µg/l (ppb) at 25ºC
- N/A : Not available
- Adapted from Dzombak and Luthy (1984)

CHAPTER II

PAST RESEARCH EFFORTS

Contaminated Sediment Issues

Reports indicate at least 1.2 billion cubic yards of contaminated sediments in United States. These data are based on surveys conducted from 1980-1993 on contaminated sites that were deemed to be detrimental to human health and to the environment (U.S. House of Representatives, 2002). In addition, between 1980-1983, slightly over half of the 15 million cubic meters of sediments dredged from the Great Lakes to improve the navigation system were placed in confined disposal facilities because of significant contaminants (IAGLR Org., 2002).

Among the identified contamination sources for sediments are sewage treatment plants, disposal of wastes, run-off from mining, farms, construction areas, and urban areas. The contaminants that are washed off via surface transport usually end up in the rivers or lakes. The fate of these contaminants within the sediments varies and depends on the contaminant's susceptibility to microbial degradation. Some contaminants (e.g., polychlorinated biphenyls, PAHs, and heavy metals) are known to resist biodegradation; thus, they persist within the sediments and pose a significant threat to both human health and the aquatic ecosystem.

The contaminants in the sediments have been grouped into five different major categories: nutrients, bulk organics (aliphatic), PAHs, halogenated hydrocarbons, and metals (USEPA, 2002).

Some of the compounds from these categories, such as PAHs (e.g., benzo[a]pyrene), halogenated hydrocarbons (i.e., PCBs), and metals (e.g., arsenic), are considered toxic to humans, animals, and plants. In addition to being toxic and carcinogenic (e.g., benzo[a]pyrene) (NAS, 1972), some are known to posses high bio-accumulation potentials (Park et al., 1990). A variety of aquatic organisms, such as worms and crustaceans, feed off the bottom of the sediments where a significant portion of the contaminants reside. Some toxic contaminants might kill these aquatic creatures; thus, reducing the food source for animals higher up in the food chain. On the other hand, if the aquatic organisms survive the exposure, the contaminants can bio-accumulate within tissues and pose significant threats to both humans and aquatic-dependent predatory wildlife as these aquatic organisms are consumed up the food chain (Averett et al., 1990).

Contaminated sediments issues are addressed by the USEPA, U.S. Army Corps of Engineers, and other federal, state, and local agencies. Among the main issues being addressed are the identification of the contaminated areas, confinement of contaminations, prevention of future contaminations, and also the implementation of remediation technologies. In general, the clean up costs of contaminated sediments are expensive because they include excavation, transportation, treatment, and disposal (USEPA, 2002). The types of remediation technologies chosen vary from site to site, but they are usually dependent on the type of contaminants. For example, among the identified treatment technologies are biological (e.g., composting, bioreactors, and enzymes), chemical (e.g., oxidation of organics and inorganics, reduction of organics and inorganics, and chelation), extraction (e.g., soil washing, steam stripping, and surfactants), immobilization (e.g., organic polymerization, sorption, and encapsulation), radiant energy (e.g., photolysis), and thermal

treatment(e.g., incineration, low-temperature thermal stripping, and pyrolysis) (Averett et al., 1990). Specifically for this study, both biological and chemical oxidation treatment technologies were evaluated for incorporation into the proposed process.

Bioremediation of PAHs

A wide variety of natural microorganisms have the capacity to degrade PAHs. These organisms have been identified to be algae, fungi, and bacteria (Dzombak and Luthy, 1984; Heitkamp and Cerniglia, 1988). PAHs can be degraded under aerobic and anaerobic conditions (Zappi et al., 1996; McNally et al., 1998). However, aerobic degradation has been found to be the optimal approach for selected compounds of wood-preserving wastes consisting mainly of PAHs (Hurst et al., 1996, McNally et al., 1998). This is due to the efficient and rapid reaction of oxygenases with the PAHs (Heitkamp and Cerniglia, 1988).

The first step in the degradation of PAHs inserts oxygen molecules into the aromatic structure (via oxygenases), resulting in the formation of dihydrodiols (Heitkamp and Cerniglia, 1988). Incorporation of oxygen molecules into the aromatic nucleus increases the solubility and makes it more biologically appealing. Further degradation of dihydrodiols results in the production of cathechol-like structures and ring cleavage products.

Light PAHs (i.e., two- and three-ring) are relatively easy to degrade (Bauer and Capone, 1985; Karimi-Lotfabad et al., 1996). These PAHs should disappear before the Heavy PAHs (i.e., > four-ring) are removed during bioremediation. In addition, it has been proven that Light PAHs can be mineralized (Bauer and Capone, 1985; McNally et al., 1998). Unlike Light PAHs, Heavy

PAHs are known to resist bioenzymatic attack. Nevertheless, Heavy PAHs have been shown to biodegrade through the process of co-metabolism (Kazunga et al., 2001). Co-metabolism of Heavy PAHs occurs when other more biodegradable co-metabolites are degraded as primary carbon sources to provide energy for a further biosynthesis, while producing non-specific enzymes that may attack the PAHs. Co-metabolite is an external carbon substrate (e.g., glucose) added to enhance the biodegradation of recalcitrant organics (i.e., PAHs). Additionally, the product of bio-emulsifiers improves PAH removal (Kanga et al., 1997).

Naturally occurring microorganisms are usually present in sufficient amounts within soil to achieve the required bioreactions for mineralization of the desired compounds (i.e., PAHs) (Jing, 1998). However, environmental factors such as nutrients, temperature, and pH are known to affect the ability of these microorganisms to degrade PAHs within soil. Therefore, in order to increase and optimize biodegradation rates, it is necessary to understand how the environmental factors affect PAH biodegradation within the targeted matrix. Thus, environmental factors affecting biodegradation in soil are discussed in the following section; followed by case studies on the biodegradation of PAHs.

Factors Affecting Biodegradation

Microorganisms: A considerable population of microbes capable of degrading the targeted compound(s) must be present before significant bioremediation can be initiated. Most native bacteria that are found within contaminated soil and sediment are usually found in a semi-dormant state; thus, they can be stimulated through the addition of electron acceptors and/or nutrients (Zappi

et al., 1991; Wang, 1999). The microbial population can also be increased by introducing exotic microorganisms to the contaminated site. The introduction of microorganisms into a different environment is called bioaugmentation or simply inoculation (Jing, 1998). During the acclimation period, there is usually a competition between the native and the seeded microorganisms for nutritional resources. Thus, exotic microorganisms are usually added in an overwhelming amount to ensure survival.

Electron Acceptors: Dissolved oxygen is used as the terminal electron acceptor during aerobic respiration and it has been identified to be the rate-limiting variable during aerobic degradation of hydrocarbons (i.e., PAHs) within soil (Dibble and Bartha, 1979). Thus, to warrant successful PAHs degradation during bioremediation, dissolved oxygen should be maintained at levels greater than 2 mg/l to maintain healthy aerobic conditions (Fan and Tafuri, 1994). The requirement is critical because oxygenases are the key enzymes used in the biodegradation of PAHs (Heitkamp and Cerniglia, 1988).

Carbon Sources: Carbon sources can be divided into two categories; organic and inorganic. Bacteria that have the ability to use organic compounds, such as PAHs, as their carbon sources are called heterotrophs (Rittmann and McCarty, 2001). On the other hand, bacteria that utilize inorganic carbons, such as carbon dioxide, as their carbon sources are called autotrophs.

Bacteria utilize carbon to sustain their metabolic functions, which include cell maintenance and reproduction. It is known that a carbon source must be in the dissolved state before appreciable biodegradation rates can be observed (Wodzinski and Coyle, 1974; Mihelcic and

Luthy, 1991; Guerin and Boyd, 1992; Wang, 1999). Unfortunately, organic carbon sources, such as Heavy PAHs, have low solubilities in water. The low solubility and high hydrophobicity of the PAHs make them less susceptible to bacterial attack. The ease of the accessibility of PAH to bacteria is called bioavailability. Bioavailability controls the rate of degradation by the means of physical limitations associated with poor mass transfer conditions (i.e., adsorption). Adsorption of a PAH occurs when PAH adheres to naturally occurring organic matter on the surface of the soil particle and/or mineral surfaces. However, the dominant sorption mechanism is the affinity of a PAH for natural organic matter (LaGrega et al., 1994). The sorption process is reversible (desorption), but this step is usually limited especially in soil with elevated amount of natural organic matter (LaGrega et al., 1994). Fortunately, the bioavailability of a PAH can be enhanced by adding surfactants (e.g., Tween 80) which acts as a solubilizing agent (Volkering et al., 1998).

When Heavy PAHs are in adequate supply, they are not always readily utilizable as carbon sources. Alternative supplementary carbon sources, such as glucose and sodium acetate, can be added to satisfy the carbon source demands. The supplementary carbon sources have been shown to improve the biodegradation of Heavy PAHs through the process of co-metabolism (Kazunga et al., 2001). As mentioned earlier, high carbon loadings may also induce production of bio-emulsifiers which basically act as natural surfactants.

Nutrients: Microorganisms are generally made of the elements: carbon, hydrogen, oxygen, nitrogen, and phosphorus. It is reported that the chemical structure of a typical bacterium can be expressed as $C_{60}H_{87}O_{23}N_{12}P$ with minor traces of other elements such as calcium, sodium,

magnesium, and iron (Metcalf and Eddy, 1991). Microbial metabolisms are highly dependent on these essential elements which can be categorized into two groups: micronutrients and macronutrients (Jing, 1998). Micronutrients, such as calcium and sodium, are required to support bioremediation and are naturally present within the environment in sufficient amounts (Baker and Herson, 1994). On the other hand, macronutrients, such as nitrogen and phosphorus, are usually limited in dissolved state; thus, limiting microbial synthesis and growth. In theory, the amount of nitrogen and phosphorus to be added is based on a carbon: nitrogen: phosphorus (C:N:P) weight ratio similar to the estimated composition of a bacterium, which is $C_{60}N_{12}P$ or approximately 100:20:2 (Hoover and Porges, 1952; Metcalf and Eddy, 1991).

Moisture: Water is vital to cell growth, distribution of substrates, and the removal of toxic waste by-products (Stotzky, 1972; Hoeppel and Hinchee, 1994). It has been concluded by Stotzky (1972) that availability of water is more important to microbes than total water content. Availability of water can be expressed as the activity of water (a_w):

$$a_w = P_s / P_w \qquad (2.1)$$

where:

P_s = vapor pressure of the solution, torr
P_w = vapor pressure of pure water at the same temperature as the solution, torr

Stotzky (1972) concluded that various microorganisms have different acceptable ranges of a_w, with bacteria requiring a range of 0.93 to 0.99. At a higher a_w, it is reported that there is a decrease in the length of a lag phase and an increase in the rate of growth.

Temperature: Temperature influences the metabolic activity of bacteria. In other words, temperature affects the metabolic rate of biodegradation. Normally, both metabolic activity and biodegradation rates diminish in response to a temperature drop (Burchell, 1996). At low temperatures, the activity of enzymes that are responsible for degrading carbon sources to provide energy is reduced; thus, slower biodegradation rates are usually observed. Since it is established that temperature plays a vital role in biodegradation, reports showed that the optimum temperature range for aerobic degradation of hydrocarbons (e.g., PAHs) using most native soil bacteria occurs between 20°C and 30°C (Atlas, 1981; Song et al., 1990; Jing, 1998).

pH: Cell functions and inter-membrane transport are strongly influenced by pH (Jing, 1998). pH also influences the solubility of nutrients that are vital to cellular growth. It is accepted that an increase in pH causes precipitation of some essential ions, such as iron, calcium, and sodium, which are essential to the biodegradation of PAHs. Since, extreme pH values are not favorable for PAH biodegradation, thus it is suggested that the optimum pH for bioremediation lies between 6.5 and 7.5 (Metcalf and Eddy; 1991; Englert et al., 1993; Wang, 1999).

Sediment properties: The chemical and physical properties of a sediment that affect the interaction between sediment and contaminants include the type and amount of clay, natural organic matter (NOM), pH and the metals (i.e., iron and manganese) present within the sediment. These properties most impact bioremediation strategies by adversely impacting contaminant desorption and amendment addition (Bajpai et al., 1994).

Case Studies

The USEPA (1993) presented two case studies involving bioremediation of creosote contaminated soil and petroleum contaminated waste sludge (both of which contained PAHs). In the first case study, five 64-L stainless steel bioreactors were used to assess the bioremediation of creosote contaminated soil. The soil contained a significant amount of PAHs. The Light and Heavy PAHs were reported to be 1,490 mg/kg and 960 mg/kg, respectively. The bioslurry reactors were aerated and mixed. In order to increase the population density of the microbes, a concentrated culture of indigenous bacteria (*Pseudomonas stutzeri*, *Pseudomonas fluorescens,* and *Pseudomonas stuzeri strain* FLN-1) was inoculated and sufficient nutrients were added to promote growth. Results of the pilot study showed that Total PAHs removals were up to 87% within 12 weeks. The degradations of the Light and Heavy PAHs were 98% and 72%, respectively.

In the second case study, a 1-million gallon concrete clarifier was reconfigured into a bioreactor to assess the bioremediation of a waste petroleum sludge. The waste petroleum sludge contained total petroleum hydrocarbons (TPHs), volatile organics (e.g., benzene, toluene, ethylene, xylene (BTEX), and styrene), and and PAHs. The sludge was constantly mixed and aerated with float-mounted mixers and aerators. The batch bioslurry reactor was inoculated with a mixed culture of hydrocarbon degraders and nutrients were added according to the C:N:P ratio of 100:5:1 to promote growth. Results showed that the removal rates of BTEX and styrene were reduced to below detectable limits within one day and it was reported that most of the loss was due to volatilization. In addition, the batch treatment achieved a 50% removal of TPHs in 80 - 90 days;

meanwhile, Total PAH removal was 90 % within 56 days. Reported concentrations for the Light and Heavy PAHs were 119 mg/kg and 47 mg/kg, respectively. Their respective degradations were 92% and 87%.

Lauch et al. (1992) used 64-L continuously-stirred, tank-bioslurry reactors to evaluate the bioremediation of PAHs from creosote contaminated soil. The soil contained significant amounts of volatile compounds (2-butanone, benzene, toluene, ethylbenzene, styrene, and xylenes) and semi-volatiles (naphthalene, fluorene, pyrene, chrysene, and benzo[a]pyrene). The slurry reactors were inoculated with the *organisms from Genus Pseudomonas*, aerated, mixed, and nutrients added using a carbon: nitrogen: phosphorus (C:N:P) ratio of 100:10:1 to promote microbial growth. Results of pilot studies showed that 90% of the Total PAHs were removed within 14 days. The biodegradation of the Light and Heavy PAHs were 96% and 83%, respectively.

Zappi et al. (1996) presented a case study where bioslurry reactors were used to assess the bioremediation of a total petroleum hydrocarbon (TPH) contaminated soil. The soil contained small amounts of TPHs, volatile organic carbons (i.e., benzene, toluene, ethyl benzene and xylenes-BTEX compounds), and PAHs. The bioslurry reactors were aerated, mixed, and sufficient nutrients were added to promote growth of the native soil microbes. Results of the pilot study showed that 98 % of the BTEX compounds were degraded within 2 days and 82 % of the TPHs were degraded within 22 days. The observed degradation of the 2-ring, 3-ring, and 4-ring PAHs were 96%, 75%, and 41%, respectively, which was achieved within 22 days. No biodegradation was observed for the 5 and 6 ring PAHs. On about Day 50 of biotreatment, co-metabolites (e.g., sodium acetate and phenanthrene) and surfactant (e.g., Tween 80) were added to the bioslurry

reactors to enhance the bioremediation of the 5 and 6 ring PAHs. Results showed that both co-metabolites and Tween 80 addition did not enhance the biodegradation of the 5-ring and 6-ring PAHs. The authors suggested that the poor removal rates of the 5 and 6 ring PAHs at low concentrations were attributed to the limited desorption of the PAHs from the soil and also the absence of suitable microorganisms. It was concluded that the results of the pilot study demonstrated the ability of bioslurry systems to bioremediate soils containing TPHs, VOCs, and PAHs with four or less aromatic rings.

Banerji et al. (1995) conducted two bench- and pilot-scale case studies where slurry-phase bioreactors were used to remediate total petroleum hydrocarbon (TPH) contaminated soils. The soils contained TPHs, VOCs, and PAHs. During the bench-scale study, ten 5-L capacity bioreactors were used to assess the bioremediation of PAHs. All the bioslurry experiments were conducted in duplicate with the reactors being aerated, mixed, and maintained at 25°C. The test conditions evaluated were a biotic control, abiotic control (i.e., $HgCl_2$ dosed), bioaugmentation, surfactant addition, and combination of bioaugmentation and surfactant addition. Sufficient nutrients were added to the bioslurry reactors with microbial activity to promote microbial growth. Results from the bench-scale study showed that a high degree of BTEX and TPH removal was believed to be due to volatilization. Despite the significant BTEX and TPH losses due to volatilization, a high PAH removal was reported (attributed to biodegradation). However, the addition of the surfactant and bacteria capable of utilizing specific PAH compounds did not improve PAH degradation. During the pilot-scale study, 60-L continuously-stirred, tank-slurry reactors were used to assess the bioremediation of PAHs. The bioslurry reactors were aerated, mixed, and sufficient nutrients

were added to promote microbial growth. In this system, a novel gas recirculation system was employed to keep all volatile pollutants within the system until they were biodegraded. Results of the pilot study showed that TPHs, volatile organics (e.g., benzene, toluene, ethylbenzene, and xylene), and PAHs removal were significant with most of the concentrations below detectable limits within 48 days. TPHs removal were about 91%, with the volatile organics removed to below detection limits. Total PAHs removals were up to 91% within 48 days. The biodegradation of the Light and Heavy PAHs were 93% and 87%, respectively.

In the second case study by Banerji et al. (1995), a similar bench-scale bioreactor setup was utilized. The conditions were a biotic control, abiotic control, combination of bioaugmentation and surfactant at two different levels (i.e., 1.5% and 3% by weight). Results showed that BTEX removals were mostly due to volatilization. In spite of significant BTEX losses due to volatilization, significant TPHs and PAHs removals due to biodegradation were observed. In addition, the amending with Tween 80 at 1.5 % by weight resulted in higher PAH removal rates. This trend was not observed in the earlier bench-scale study. The authors stated that the discrepancy could be due to the lesser amount of surfactant addition (125 mg/l) compared to this bench-scale study. Despite the positive results, the pilot-scale was conducted without the surfactant. The same pilot-scale bioslurry reactor setup was used. Results of this pilot study showed that TPHs, volatile organics (e.g., BTEX, methylene chloride, chlorobenzene, acetone, butanone, chloroform, and hexanone), and PAHs removals were significant. TPHs removals were reported to vary from 69% to 82% within twenty- seven days. Volatile organics removals were reported to vary from 50% to 97% within six days. Total PAH removal was reported to be 65% within a five-week period.

Chemical Oxidation Processes

Potential chemical oxidation processes of interest to this study are Fenton's Reagent, peroxone, and ozone. These oxidizers were chosen because they have been shown to degrade PAHs within aqueous or soil systems (Cornell and Kuo, 1984; Trapido et al., 1994; Beltran et al., 1996). In order to maximize the oxidation rate, it is essential to understand the mechanisms associated with the oxidation of the PAHs. Thus, the following section elaborates on these chemical processes and associated reactions with PAHs.

Fenton's Reagent

Fenton discovered that by adding a soluble iron salt and hydrogen peroxide, organic compounds could easily be oxidized (Walling, 1975). More recent studies have shown that the main mechanism was that the hydroxyl radical is generated which in turn reacts with organic chemicals (Bigda, 1995). The reactions associated with radical formation via Fenton's Reagent are described as follows:

$$H_2O_2 + Fe^{2+} \bullet \quad OH^- + OH^{\bullet} + Fe^{3+} \tag{2.2}$$

$$Fe^{2+} + OH^- \bullet \bullet Fe^{3+} + OH^{\bullet} \tag{2.3}$$

with the overall stoichiometry being:

$$2Fe^{2+} + H_2O_2 + 2H^+ = 2Fe^{3+} + 2H_2O \tag{2.4}$$

The resulting oxidation reaction step with organic substrates:

$$RH + OH^- \bullet \quad R^- + H_2O \tag{2.5}$$

where:

R is an organic substrate

According to the mechanism pathways, radical generation begins when a ferrous ion, acting as catalyst, comes in contact with hydrogen peroxide. Ferrous ions split the hydrogen peroxide into a hydroxyl ion and hydroxyl radical. In the absence of organic substrates, such as the targeted contaminants, free radical oxidizes another molecule of a ferrous ion to a ferric ion. Fenton's Reagent has been found to be effective in oxidizing organic compounds, such as BTEX, formaldehyde, ethylenediamine, pesticides, gasoline and diesel range organics, PCPs, PCE, and PAHs (Kelley et al., 1991; Leung et al., 1992; Kemenade et al., 1995, Schulte et al., 1995; Wang, 1999). Kawahara et al. (1995) also utilized Fenton's Reagent to oxidize PAHs within the contaminated soil. It was reported that the extractability for most of the PAHs was increased after an hour of treatment. The authors conclude that the increase was due to the oxidation of the humic sorptive bonds, which released the PAHs into the aqueous phase. They conclude that 72% and 93% of naphthalene and acenaphthylene were removed, respectively.

Ozone

As mentioned in Chapter I, ozone has the ability to oxidize a variety of organic compounds. The oxidation of any compound by ozone is called ozonation. Figure 2.1 illustrates the reaction scheme for the ozonation of organic chemicals. Ozonation of organic compounds generally involves two mechanisms: direct oxidation and radical oxidation. From Figure 2.1, when ozone is sparged into an aqueous system, it either oxidizes the organic contaminants directly and/or decomposes into hydroxyl radicals, which then oxidize the pollutant into an oxidation by-product.

It has been reported that the decomposition rate of ozone can be strongly dependent on the pH of the solution (Qiu, 1999). At neutral to high pH, ozone decomposes into hydroxyl radicals through the following initiation steps:

$$O_3 + OH^{\bullet} \bullet \quad HO_2^{\cdot} + O_2^{\cdot} \qquad (2.6)$$

$$O_3 + H_2O \bullet \quad HO_3^{+} + OH^{\cdot} \qquad (2.7)$$

Above initial steps suggest that oxidation rates by ozone within alkaline media are several orders of magnitude greater than those in acidic media (Huang et al., 1993). According to the initial steps, hydroxyl radical is the major oxidation species. Due to its high oxidative potential, (E^o = 2.33v), hydroxyl radical reacts more rapidly with organic substrates than molecular ozone (E^o = 2.08v).

Ozone has been suggested to be an excellent chemical oxidant for degrading PAHs because of both cost and degree of effectiveness (Bailey, 1982; Cornell and Kuo, 1984; Trapido et al., 1994; Beltran et al., 1995). Recent studies of ozonation on 3-ring PAHs have shown that fluorene seems to be degraded due to both direct and hydroxyl radical mechanisms, while oxidation of phenanthrene and acenaphthene are due to direct mechanisms (Beltran et al., 1995). Common by-products of PAHs are polar aliphatic compounds, mainly carboxylic acids and aldehydes (Helleur et al., 1979; Legube et al., 1986). Both carboxylic acids and aldehydes are easily biodegraded (Wang 1999).

Peroxone

Combination of ozone and hydrogen peroxide as a treatment process is termed peroxone. It has been reported that hydrogen peroxide can initiate the formation of hydroxyl radicals by decomposing ozone via a single electron transfer (Huang et al., 1993; Wang, 1999). The initiating species is the hydroperoxide ion, HO_2^-. It is formed via the dissociation of hydrogen peroxide within aqueous media as follows.

$$H_2O_2 + 2H_2O \bullet \quad 2HO_2^{\cdot} + 4H^+ \qquad (2.8)$$

As shown below, the hydroperoxide ion then reacts with ozone to generate the ozonide ion, O_3^- and HO_2.

$$HO_2^{\cdot} + O_3 \bullet \quad O_3^{\cdot} + HO_2 \qquad (2.9)$$

The transitional products would further initiate OH· formation through the following steps:

$$HO_2 \bullet \quad H^+ + O_2^{\cdot} \qquad (2.10)$$

$$O_2^{\cdot} + O_3 \bullet \quad O_3^{\cdot} + O_2 \qquad (2.11)$$

$$O_3 \bullet + H^+ \bullet \quad HO_3 \qquad (2.12)$$

$$HO_3 \bullet \quad OH^{\cdot} + O_2 \qquad (2.13)$$

Peroxone treatment was found be effective for tetrachloroethylene, pesticides, explosives, and PAHs (Glaze and Kang, 1989; Allemance, 1994; Trapido et al., 1994; Zappi et al., 1995; Beltran et al., 1996).

Chemical Oxidation Enhanced Bioremediation

Hydrophobic contaminants are known to adsorb onto the surface of soils (Dzombak and Luthy, 1984; Pignatello, 1989). Adsorption is known to hinder the ability of biotreatment to remediate polluted soils (Dzombak and Luthy, 1984). Since PAHs are hydrophobic contaminants, they strongly adsorb onto the surface of the soil which leads to limited bioavailability; thus, hindering biodegradation. The desorption of PAHs from the soil has been identified to control the fate of the biodegradation (Pignatello, 1989). It has been demonstrated that the addition of strong chemical oxidizers increases the desorption mechanism of contaminants from soil; thus, potentially increasing biodegradation of PAHs in soil (Kawahara et al., 1995).

A strong chemical oxidizer, such as ozone, has been determined to posses the capability to improve the bioavailability of a PAH in the aqueous phase, which is a known limitation associated with bioremediation, via the destabilization and oxidation of NOM (Chandrakanth and Amy, 1996). Note that the details of the proposed impact of ozonation on enhancing the degradation of PAHs are discussed in Chapter III. Research has shown that soils containing elevated amount of natural organic matter show greater adsorption capacities for PAHs (Dzombak and Luthy, 1984). This organic matter also has been observed to easily react with chemical oxidizers (Yuteri and Gurol, 1991; Zappi et al., 2000). The reaction may cause a significant problem during the oxidation of contaminated sediments containing elevated amounts of the organic matter. In addition to the presence of organic matter, reaction of chemical oxidizers with reduced cations which are generally present in sediments also has been observed (Yuteri and Gurol, 1991;

Zappi et al., 2000). Similar to naturally occurring organic matter, the presence of reduced cations at elevated levels may also cause scavenging resulting in reduced PAH degradation. Chandrakanth and Amy (1996) found manganese and iron both reacted with ozone during ozonation of NOM-coated particles in the aqueous phase. Similar observations were also made by Zappi et al. (2000) during the enhancement of bioremediation utilizing hydrogen peroxide as an oxygen source. The authors concluded that the Ferrous ion was one of the primary constituents scavenging the hydrogen peroxide.

Kelley et al. (1991) experimented with Fenton's Reagent as a pretreatment step prior to biological degradation of PAHs within contaminated soil. Degradation of PAHs utilizing Fenton's Reagent was found best to occur under acidic conditions (pH~4.0). Results showed that almost 99% of the PAHs were removed from both the aqueous and soil phases. They found after the Fenton's Reagent treatment, 25% of the PAH was recovered as carbon dioxide, 50% as an oxidized non-polar compounds, and 12% as oxidized polar (water-phase) compounds.

Brown et al. (1995) conducted a bioslurry study to remediate PAHs contaminated soil. Two 60-liter bioslurry reactors and a 10-liter bioslurry reactor were used in sequence. The first 60-liter bioslurry reactor was a pre-biotreament step, where fresh salicylate and succinate were added as co-metabolites to enhance the bioremediation of the Heavy PAHs. Then the slurry from the first reactor was fed to the second 10-liter unit, where Fenton's Reagent was added to oxidize the recalcitrant Heavy PAHs. After the Fenton's Reagent treatment step, the slurry was fed into the second 60-liter bioslurry reactor where biological activities in the slurry were reestablished to

biodegrade the remaining contaminants. The three bioreactors connected in series system demonstrated an average Total PAHs removal of 95% (84% of the carcinogenic PAHs removed).

Wang (1999) successfully integrated bioremediation and chemical oxidation technologies for the removal of the heavy petroleum fraction (motor oil) and light petroleum fraction (diesel fuels) contaminated soils. This study was separated into three phases: 1st stage biotreatment / 2nd stage chemical oxidation / 3rd stage bioremediation. The first stage of biotreatment was conducted with the intention of eliminating the lighter petroleum fraction, followed by the introduction of chemical oxidizers, such as Fenton's Reagent, ozone, and peroxone. Followed by the addition of the chemical oxidizers during the 2nd stage chemical oxidation step to enhance the removal rate of the heavy petroleum fraction through the oxidation of the carbon sorption bonds, which bind the petroleum fractions to the soil phase and limit bioavailability. In addition, the chemical oxidizers were also used for the cleavage of the heavy petroleum fraction into more biodegradable and soluble by-products. Finally, the 3rd stage of biotreatment served as a polishing step, where biological activities were reestablished by adding nutrients and activated sludge. In the last stage of biotreatment, the intent was to further biodegrade the remaining petroleum fraction including the oxidation of the by-products. The integration of bioremediation and chemical oxidation was successful in enhancing the removal of both the light and heavy petroleum fractions within soils. The author reported that the slurry that was treated with biological methods alone achieved 42% and 50% removals of the light and heavy petroleum fractions in soils. On the other hand, the chemical primed slurries achieved an average of 85% and 90% removals of light and heavy petroleum fractions in the soils.

Kemenade et al. (1995) used ozone as a pre-treatment step to enhance biodegradation of phenanthrene. Biotic controls that were not subjected to chemical pre-treatment had removal rates ranging from 0 to 8.6%. However, results showed that after 24 hours pre-treatment using 5 g/l of applied ozone, followed by 5 days of bioremediation, the degradation of phenanthrene within the soil was enhanced by 115% over the controls.

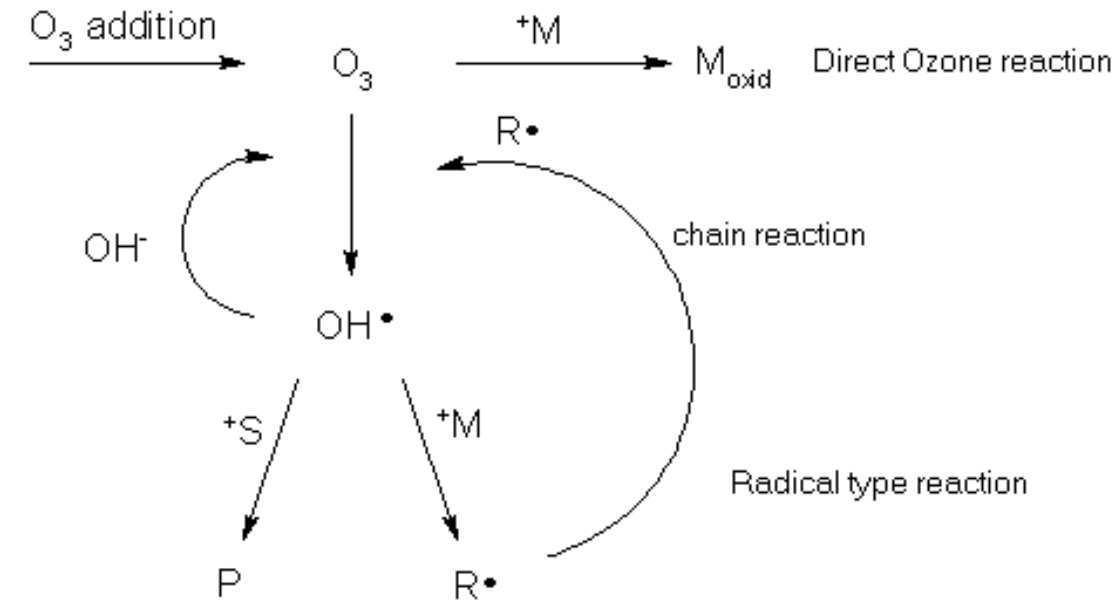


Figure 2.1. Reaction Scheme for Ozone Addition to an Aqueous Solution (Hoigne and Bader, 1975)

CHAPTER III

RESEARCH HYPOTHESIS AND OBJECTIVES

Research Hypothesis

The combination of both bioremediation and chemical oxidation technologies is promising for enhancing the degradation of PAHs within soils and sediments. Thus, it is hypothesized that the integration of both chemical oxidation and bioremediation technologies into a single-step treatment strategy could result in the development of an aggressive treatment process that is far superior to the use of either process as stand-alone systems.

Figure 3.1 illustrates the mechanism of ozonation in enhancing the biodegradation of pyrene within the sediment. The low bioavailability of pyrene in sediment has always been attributed to the limited desorption of the pyrene into the aqueous phases. The introduction of ozone molecules into the system is expected to enhance the desorption through the oxidation of the adsorption link; thus, increasing bioavailability. At the same time, ozone is expected to improve the biodegradability of the pyrene molecules via the oxidation of pyrene into a more biodegradable by-product. This is further illustrated in Figure 3.2, where it can be seen that the presence of the carboxylic groups suggests that the by-product should be more biologically appealing, which leads to the improved removal of pyrene over that achieved with biodegradation alone.

Research Objectives

The primary objective of this research is to evaluate the integration of a chemical priming step (via chemical oxidizers) with bioremediation to form a novel treatment process to be used for the remediation of PAH contaminated sediments. Since all of the past efforts were done using surface soils that contain comparatively little reduced chemical species and natural organic matter (NOM), it is of interest to challenge this concept using sediments which are highly reduced and contain much more NOM. The development of this new treatment process may result in a new and innovative process that may eliminate problems associated with the treatment of PAHs within soils and sediments using current technology.

The specific objectives of this study were the following:

1. Formulate enhancement strategies to optimize the biotreatment of PAHs in sediment by utilizing nutrients, surfactant, co-metabolites, and exotic microorganisms

2. Evaluate various dosing strategies for chemical oxidation for use as a chemical priming step

3. Investigate the feasibility of the combined bioremediation and chemical priming to treat a PAH contaminated sediment within 5-L bioslurry reactors, which mimic actual full-scale reactor units.

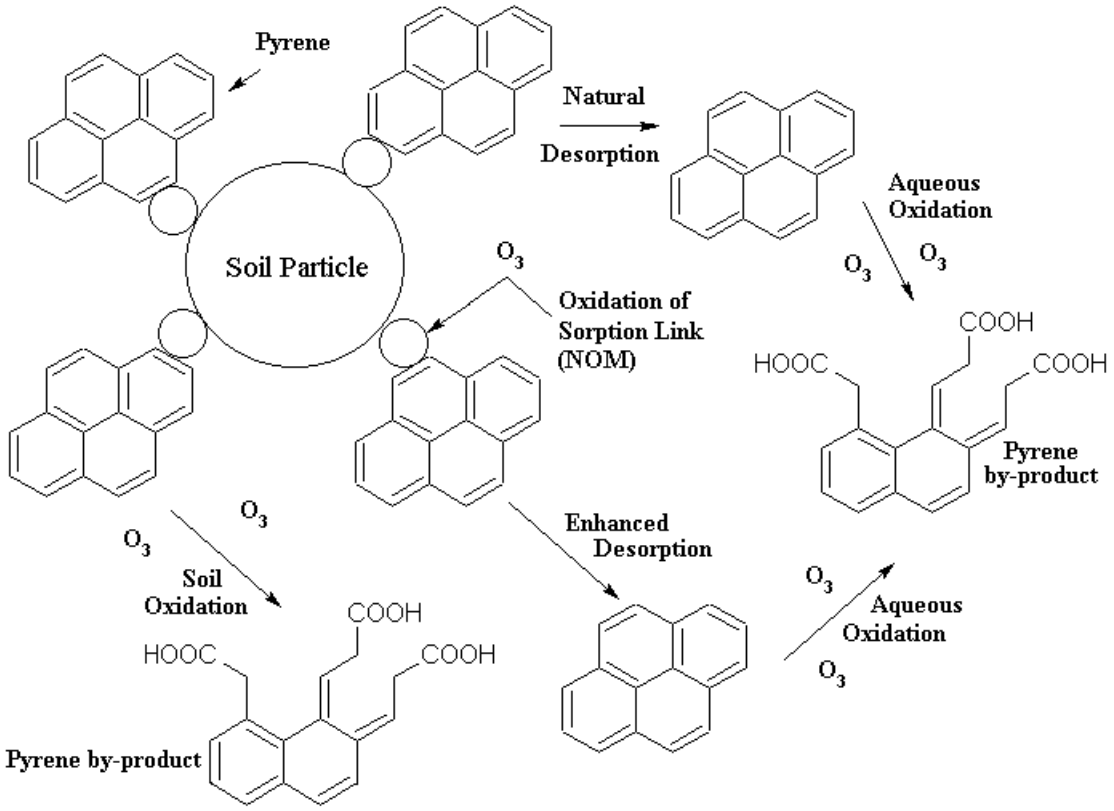


Figure 3.1. Potential Impacts of Ozonation on Enhancing the Bioremediation of a Pyrene Contaminated Sediment

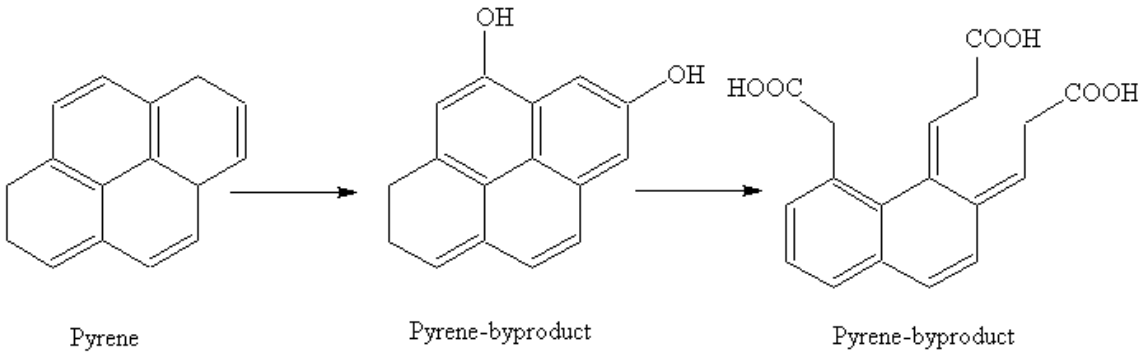


Figure 3.2. Proposed Decomposition Reaction Pathway of Pyrene via Chemical Oxidation

CHAPTER IV

METHODS AND MATERIALS

This study is composed of two experimental phases. Phase I involved shake-flask experiments, while Phase II involved bio-slurry reactor experiments. Phase I served as a screening phase to optimize test conditions for both bio- and chemical-oxidation degradation of the PAHs. Once optimal conditions were established, these conditions were implemented in Phase II involving 5-L bioslurry reactors.

Materials

Sediments

Two sediments were used in this study. The first sediment was collected from Lake Superior by the U.S. Army Engineer Waterways Experiment Station (WES) in Vicksburg, Mississippi. Dr. Elizabeth Fleming, of the WES, provided this sediment to Mississippi State University (MSU) as a partnering effort between the two research entities. Lake Superior Sediment was transported to MSU from WES in four 25-gallon plastic buckets. Foreign debris and large stones were hand picked and removed from the sediment sample. The second sediment was collected from the Scioto River by personnel from the University of Akron. Scioto River sediment was shipped within ten 1-liter plastic bottles to MSU in three ice chests filled with Blue

Ice™. Again, foreign debris (i.e., leaves, plastics) was removed from the sediment sample. The main difference between the Lake Superior and Scioto River sediments is the amount of the PAHs present. The amount of PAHs present within the Lake Superior sediment is at least a magnitude higher than the Scioto River sediment. A summary of the detected PAHs and other selected results for both sediments are listed in Table 4.1. A summary of which sediments were utilized in the various experiments conducted during this study is presented in Table 4.2.

Nutrients

During the biotreatment stages of this study, ammonium nitrate (NH_4NO_3), ammonium hydrogen phosphate ($(NH_4)_2HPO_4$), potassium nitrate (KNO_3), and potassium phosphate (K_3PO_4) were utilized as nitrogen and phosphorus sources. They were purchased from Fisher Scientific. These compounds easily dissolve in water and are used by microorganisms as macronutrients (Dibble and Bartha, 1979; Harris and Arnold, 1995; Wang, 1999).

Surfactant

Tween 80 (polyoxyethlene sorbitan ester) was used during some of the biotreatment experiments to assess the benefits of surfactant dosing towards enhancing the bioavailability of PAHs in the sediments. Tween 80 is a nonionic, nontoxic, and biodegradable surfactant. It was purchased from Fisher Scientific. The chemical formula for Tween 80 is $C_{64}H_{124}O_{26}$.

Co-Metabolites

Naphthalene, sodium acetate, and glucose were added as co-metabolites to selected

bioreactor systems. These chemicals were all purchased from Fisher Scientific. The chemical formulas for naphthalene, sodium acetate, and glucose are $C_{10}H_8$, $NaC_2H_3O_2$, and $C_6H_{12}O_6$, respectively.

Ferrous Sulfate

Ferrous sulfate was used as a catalyst for hydroxyl radical formation during Fenton's Reagent application. It was purchased from Fisher Scientific. Ferrous sulfate is a soluble reagent making it an excellent choice for an iron salt for use in soil remediation. The chemical formula for ferrous sulfate is $FeSO_4.7H_2O$.

Hydrogen Peroxide

Hydrogen peroxide was added when applying Fenton's Reagent and peroxone. Hydrogen peroxide stock solutions of 3% and 30% by weight were purchased from Fisher Scientific. The chemical formula for hydrogen peroxide is H_2O_2.

Bioslurry Reactors

Eight 5-L bioslurry reactors were used during Phase II of this study. These reactors were constructed of glass and mounted in steel support frames. A schematic of a bioslurry reactor is shown in Figure 4.1. A photograph of the complete system (including steel support frames) is shown as Figure 4.2. Three built-in sparging points were located at the bottom of the reactors for supplying air to the slurries. Six outlets located on the top of the reactor for used for venting off-gases, inserting probes, and extension of the mixing shaft into the slurry. The reactors were

purchased from NDS Technologies Inc, New Jersey. A 1/15 horsepower Lightnin LabMaster™ Mixer (Model L1U10) with digital readout was mounted on each reactor.

Ozone

Ozone was generated using a laboratory scale ozone generator (Model LC-1234) manufactured by Ozonology Inc. (Evanston, Illinois). The generator has a built-in Airsep Corporation Model AS-12 oxygen generator with the capacity of producing 90% +/- 5% pure oxygen up to 24 standard cubic feet per hour (scfh). Ozone is generated when high purity oxygen is passed through an electrically-charged corona discharge tube which is comprised of a steel electrode inside a borosilicate glass dielectric with copper jacketing. The generator was equipped with four independent corona cells. Ozone produced within the four cells are independently controlled by a primary single voltage autotransformer (supplies up to 10.5KV). The gas flow through each cell was controlled by a rotameter with volumetric metering capacity. The ozone output of this generator is capable of reaching air-phase ozone concentrations as high as 5% (w/w) ozone. Figure 4.3 shows a graph of ozone concentration versus flowrate at 100% voltage setting. This chart was used for setting the ozone generator to the required ozone inlet gas composition. The actual ozone gas phase concentration is monitored using an ozone gas monitor. Once the desired ozone gas phase concentration is achieved (3% by weight), the voltage setting and the oxygen volumetric flowrate were recorded.

Methods

Phase I: Biotreatment Screening Experiments

All of the shake-flask experiments were performed using an orbital agitation table (Model M49235, Barnstead/Thermalyne, Bubuque, IA) set at 250 rounds per minute (rpm). All the biotreatment experiments were conducted in 500 ml Erlenmeyer flasks at room temperature. Note that all of the shake flasks were capped with porous foam stoppers to allow air into the flasks, but prevent splashing from flask to flask. All slurries were made by mixing wet sediment and distilled water to form a 30% by weight slurry. The moisture content of the wet sediment was determined prior to the addition. The amount of wet sediment required to make the 30% (wt dry soil/ total wt) slurries was added based on the water content of the sediment.

Biotreatment Screening Shake-Flask Experiments

Optimal bioremediation conditions were not known for both Lake Superior and Scioto River sediments. Thus, test conditions in this study phase were formulated to test for variables that would optimize PAH biodegradation. The effects of nutrients, bacterial seeding, and surfactant on the biodegradation of PAHs were examined. The experiments were conducted in duplicate. A summary of the bio-treatment conditions is shown in Tables 4.3 and 4.4. The duration of these experiments was 4 weeks. Three types of bacterial inocula were utilized in these experiments; activated sludge from the return line of a local wastewater treatment plant (approximately 5,500 mg/ volatile suspended solid), activated sludge from the return line of a swine waste treatment project conducted at MSU (approximately 3,000 mg/s volatile suspended solid), and a culture of

multi-ring PAH degraders produced by Dr. Hamid Borazjani of the Department of Forest Products, MSU. The activated sludge from the wastewater treatment plant and the swine project were seeded on the 1st day of the experiment using a liquid volume 10 ml and 30 ml, respectively. The mixture of multi-ring PAH degraders was inoculated using of seed volume 40 ml once a week over the entire study period. The actual number of bacteria present in this inoculum was not known. Lake Superior sediment samples were collected once a week for PAH analysis only; meanwhile, the Scioto River sediment samples were sampled once a week for PAH and pH analyses.

Bioavailability Experiments

The sediment utilized for this set of experiments was the Lake Superior sediment. This test was formulated to examine the biodegradation of naphthalene in both the aqueous and soil slurry matrices. The bioavailability experiments were conducted to verify that the limiting factor in the biodegradation of naphthalene was indeed bioavailability and not bacterial enzyme limitations. The duration of these experiments was three days. These experiments were conducted in duplicate 1 liter glass bottles. The microbial inoculum utilized in this set of experiments was prepared by Dr. Lewis Brown, MSU. A summary of the treatment conditions used with these experiments is shown in Table 4.5. In the first condition, 25 mg/l naphthalene was added to 250 ml of the concentrated microbial inoculum. In the second condition, 31.25 gram of dry sediment that contained approximately 284.73 mg/kg of naphthalene was added to 250 ml of the concentrated microbial inoculum. Samples for both the liquid and soil phases were taken at 0, 1.6, and 70.1 hours and

5 ml of 10% hydrochloric acid added to every sample to stop microbial activity that would result in further naphthalene biodegradation prior to analysis. The slurry samples for the second condition were centrifuged at 3,000 rpm for 30 minutes. Both the equilibrated liquid and sediment samples from these tests were analyzed for naphthalene content.

Phase I: Chemical Oxidation Screening Experiments

The purpose of the chemical oxidation experiments was to evaluate the effectiveness of various chemical processes, such as Fenton's Reagent, ozone, and peroxone, on the oxidation of PAHs in the sediments.

Ozonation and Peroxone Experiments

Ozonation and peroxone treatments of the Lake Superior sediment were conducted in 2-L Erlenmeyer flasks. This set of experiments was designed to examine the efficacy of ozone and peroxone in treating PAHs within the sediment slurries. Mixing was achieved using Fisher Thermix Model 120 S stirrer. The experiments were conducted in duplicate. Figure 4.4 shows the setup for both the ozone and peroxone experiments. Ozone was diffused into the reactors at 2.5 scfh at 100% voltage generator setting through air-stones yielding a gas phase ozone concentration of 3% by weight ozone. The gases exiting via the off-gas outlet from the flask was directed into a glass container containing Carulite, a catalyst that decomposes ozone into oxygen via catalytic reaction. A 5-L foam trap was installed in between the slurry reactor and Carulite to trap foam that might interfere with the ozone destruction clogging or coating of the catalyst.

A summary of the ozone and peroxone experiments performed are listed in Table 4.6. A

summary of the hydrogen peroxide dosing sequence used with the peroxone experiments is listed in Table 4.7. PAH samples for the ozone experiments were collected after 2 hours of oxidation. The PAH samples for the peroxone experiments were sampled prior to each hydrogen peroxide dosing.

Fate of Hydrogen Peroxide in Equilibrated Water Solutions

This test was designed to examine the reactivity of hydrogen peroxide in the aqueous phase due to biotic and abiotic reactions associated with sediment components present in equilibrated water samples. The Lake Superior sediment was utilized in this experiment. The equilibrated water samples were prepared by mixing 75 grams of sediment (on a dry weight basis) and 175 ml of DI water in a 500 ml Erlenmeyer flask to make a 30% by weight slurry. The slurry was allowed to shake on the orbital agitation table (described earlier) for at least 48 hours to allow indigenous microorganisms and other soluble materials (i.e., dissolved and reduced cations, and NOM) to desorb from the surface of the soil particles into the liquid phase. Next, the slurry was centrifuged and the equilibrated liquid was extracted for use in the experiments. The amount of equilibrated liquid extracted was replaced by fresh distilled water to allow further desorption of soluble matter (reduced cations, NOM, and microorganisms). A thousand mg/l of H_2O_2 was added and the concentration in the liquid phase was tracked over a twenty four hour period. The above steps were repeated six times. Two replicates were conducted for every equilibrated water sample run. The equilibrated water solution prepared the first five runs was not autoclaved and utilized to examine the hydrogen peroxide reactivity due to biotic process. The equilibrated water solution

prepared on the sixth run was autoclaved to examine the hydrogen peroxide reactivity due to abiotic reactions. The sample for the abiotic reaction run was prepared by autoclaving. The detailed summary of the autoclaving conditions is listed in Table 4.8. The sample was prepared by the research team of Dr. Lewis Brown, MSU. A single replica of 1,000 mg/l hydrogen peroxide solution was conducted in each run, which served as a control, yielding a total of six replicas.

Fate of Hydrogen Peroxide within the Sediment

This experiment was designed to examine the reactivity of hydrogen peroxide with soluble sediment constituents and the effect of hydrogen peroxide addition on removal of PAHs within the Lake Superior sediment. A 30% (w/w) slurry samples were prepared by mixing 75 grams of sediment (on a dry weight basis) and 175 ml of DI water within a 500 ml Erlenmeyer flask. The slurry samples were homogenized for 24 hours. The sediment samples that required sterilization were autoclaved at 121°C and 15 psi for at least 15 minutes in Dr. Brown's laboratory. The operating conditions for this set of experiments are summarized in Table 4.9. The 1,000 ppm hydrogen peroxide experiments were dosed with 1,000 mg/l hydrogen peroxide at 0, 2, 6, 24, 30, 48, and 60 hours of the reaction yielding an applied total unreacted dose of 7,000 mg/l hydrogen peroxide. The 10,000 ppm hydrogen peroxide experiments were dosed with 10,000 mg/l hydrogen peroxide at 0, 6, 24, 30, 48, and 60 hours of the treatment yielding an unreacted total applied dose of 60,000 mg/l hydrogen peroxide. The 100,000 ppm hydrogen peroxide experiments were dosed with 100,000 mg/l hydrogen peroxide at 0, 20, 41, 61, 64, 83, 91, 105, 130, 149 and 173 hours of the reaction yielding an applied total unreacted dose of 1,100,000 mg/l

hydrogen peroxide. Slurry sample was collected for H_2O_2 analysis. Additionally, slurry samples were also collected before and after each hydrogen peroxide treatment for PAHs analysis.

Fenton's Reagent Experiments

This set of experiments was designed to examine the efficacy of Fenton's Reagent for removing PAHs within the Lake Superior sediment. The Fenton's Reagent experiments were conducted in 500 ml Erlenmeyer flasks. Ferrous sulfate was added at least 24 hours prior to H_2O_2 addition. The 24-hour equilibration period allows the ferrous sulfate to become homogenous in the sediment and also to diffuse into the pores of the soil particles. A summary of Fenton's Reagent experiments performed on the Lake Superior sediment is shown in Table 4.10 and the detailed summary of Fenton's Reagent additions is listed in Table 4.11. Soil samples for PAH analysis were collected after every hydrogen peroxide dosing.

Phase I: Integrated Experiments

This set of experiments was designed to examine the efficacy of Fenton's Reagent for removal of PAH within a previously biotreated sediment. The sediment utilized was Scioto River sediment. These experiments were conducted similar to the Fenton's Reagent experiments. A summary of Fenton's Reagent additions within the Scioto River sediment is presented in Table 4.12. Soil samples for PAH analysis also were collected after every hydrogen peroxide dosing.

Phase II: Bench-scale Bioslurry Experiments

As stated earlier, Figure 4.2 presents a photograph of the bioslurry reactor setup used in this study. The mixing rate of the mixer was set at 300 rpm, which provided mixing conditions where the sediment was gently turned over continuously. The temperature in the bioreactors was controlled by maintaining the temperature of the room between 70°F and 75°F. Aeration was provided to all bioreactors by diffused air supplied through sparging frits (Q_{air} = 10 scfh) located on the bottom of the reactor.

The sediment utilized was the Lake Superior Sediment. Prior to testing the untreated sediment, samples were collected for initial characterization (i.e., PAHs, total solid content, dissolved oxygen, oxygen uptake rate, pH, and total heterotrophs). The slurry samples were collected from the bioslurry reactor using a Tygon tubing and peristaltic pump (Masterflex Model EZ-Load II). The Tygon tubing was inserted via one of the outlets located on top of the bioslurry reactor. During the sampling of the slurry, the mixer was stopped to prevent the Tygon tubing from tangling up with the propeller. The slurry samples were not collected from the sampling ports located on the side or the bottom because of clogging problems. The slurry samples collected were analyzed for PAHs, total solid content, dissolved oxygen, oxygen uptake rate, pH, and total heterotrophs. A portion of the slurry samples was centrifuged and the supernatant liquid was extracted and analyzed for nitrate, ammonia, and ortho-phosphate. In addition, the presence of volatile organic carbon, carbon dioxide, and oxygen in the column headspace of the bioslurry reactors also were analyzed using a multi-gas

analyzer.

Four different conditions were evaluated using duplicate bioslurry reactors (yielding a total of 8 reactors). For each bioslurry reactor, 1.5 kg of contaminated sediment (on a dry weight basis) was mixed with 3.5 kg of distilled water to form a 30% by-weight slurry.

A summary of treatment conditions used for this experiment is listed in Table 4.13. No nutrients, microbial or growth substrates were added to Reactors 1 and 2; thus, they served as biotic controls. Reactors 3 and 4 were dosed with nutrients only. Reactors 5 and 6 were dosed with nutrients and a microbial inoculum (provided by Dr. Brown of the Department of Biological Sciences, MSU). The microbial inoculum was cultured specifically for the degradation of naphthalene as a growth substrate. The population density of the naphthalene degraders in the inoculum was approximately $1x10^8$ CFUs/ml. Twnety ml of the microbial inoculum was added on the 1st and 11th day of the experiment. Meanwhile, 500 ml of the microbial inoculum was added on the 50th day of the experiment. Reactors 7 and 8 were dosed with nutrients, the microbial inoculum, co-metabolites (e.g., glucose, sodium acetate, naphthalene), and surfactant (e.g., Tween 80). Twenty ml of the microbial inoculum was added on the 1st and 11th day of the experiment. One thousand mg/l glucose was added as an external growth substrate on the 1st, 11th and 23rd day of the experiments. Followed by 100 mg/l sodium acetate addition on the 50th and 63rd day of the experiments. Next, 1 liter of 25 mg/l of naphthalene was dosed on the 53rd and 65th day of the experiments. Finally, Tween 80 was dosed at 5 % by weight on the 74th and 86th day of the experiments, and at 2.5% by weight on the 107th and 116th day of the experiments. Note that the details on this dosing strategy are discussed in Chapter 8.

Phase II: Integrated Chemical Oxidation Experiments

The chemical oxidation experiments were conducted using the same setups utilized in the chemical oxidation screening phase. Fenton's Reagent, ozone, and peroxone were all tested on slurry samples collected from Reactors 3 and 4, which involved nutrients addition only. This set was chosen because of minimal differences noted between the various test systems. Reactors 3 and 4 were also chosen because it was believed that the foaming would be minimal when oxidizing the slurry since there was no external microorganisms inoculated nor surfactant added. Equal portions of slurry from the two replicate bioreactors were pumped out using the Masterflex peristaltic pump and mixed together. Then the mixture was divided into several portions and the various chemical oxidation strategies applied. After the applications of the chemical oxidizers, biological activity was reestablished. Note that the details on this post-oxidation step are discussed in the next segment.

Fenton's Reagent also was tested on slurry samples collected from Reactors 5 and 6, which involved the addition of nutrients and bio-augmentation. Reactors 5 and 6 were chosen to prove the fact that naphthalene biodegradation was hindered due to limited bioavailability and can be enhanced by adding Fenton's Reagent. After this oxidation step, the chemical primed slurry was mixed and poured back in equal portions into Reactors 5 and 6.

Ozonation and Peroxone Treatments

Both ozone and peroxone experiments were conducted in duplicate at an ozone volumetric flowrate of 2.5 scfh at 100% voltage, which yields a 3% (w/w) ozonated oxygen stream.

Summaries of conditions used with ozone and peroxone treatments are listed in Table 4.14. The summary for hydrogen peroxide dosing sequences used during the peroxone treatments is listed as Table 4.15. Samples for both ozone and peroxone treatments were taken for PAH, total solids, dissolved oxygen, oxygen uptake rate, pH, nitrate, ammonia, ortho-phosphate, temperature, and total heterotrophs analyses every four hours.

Fenton's Reagent Treatments

Hydrogen peroxide and ferrous salt were dosed at a concentration ratio of $H_2O_2 : Fe^{2+}$ = 10 : 1. All Fenton's Reagent experiments were conducted in duplicate. A summary of Fenton's Reagent treatments is shown in Tables 4.16. For the slurry from Reactors 3 and 4, a total of 350,000 mg/l H_2O_2 and 35,000 mg/l Fe^{2+} were applied to each replicate, respectively. One the other hand, the slurry from Reactors 5 and 6 had a total of 450,000 mg/l H_2O_2 and 45,000 mg/l Fe^{2+} added to each replicate, respectively. For both experiments, the Fenton's Reagent was applied over six dosing events. The distribution of the Fenton's Reagent dosing and the treatment conditions are also summarized in Table 4.16. The slurry samples were collected for PAH, total solids, dissolved oxygen, pH, nitrate, ammonia, ortho-phosphate, temperature, and total heterotrophs analyses after each dosing.

Phase II: Post Oxidation Experiments (Re-established Biotreatment)

After chemical oxidation, the slurries from Reactors 3 and 4 were poured back into the bioslurry reactors. Then, the pH was adjusted back to about 7 by adding appropriate amount of 2M sodium hydroxide solution. Biological activity within the slurry system was re-established by

adding 40 ml of the microbial inoculum. At this same time, nutrients were dosed at 1,000 mg/l and 400 mg/l of nitrates and ortho-phosphate, respectively. Samples were then periodically collected for PAH, total solids, dissolved oxygen, oxygen uptake rate, pH, nitrate, ammonia, ortho-phosphate, temperature, and total heterotrophs.

For Reactors 5 and 6, biological activity within the sediment was not reestablished and the PAH levels within the sediment were not monitored. This is because it was believed that the post-oxidation results of the chemical primed slurries (Reactors 3 and 4) would give a good representation of the success of combining bioremediation and chemical oxidation into a single-step treatment strategy.

Analytical Methods

Dissolved Oxygen

Dissolved oxygen (DO) was measured using a YSI™ Dissolved Oxygen Portable Meter Model 52 and a biochemical oxygen demand (BOD) probe (Model 5905/5010). The BOD probe features a self-stirring mechanism (i.e., stir paddle) that keeps the contents in a BOD bottle well mixed. The BOD probe was calibrated daily using air calibration. In between samples, the DO probe was rinsed and blot-dried with tissue. Lower detectable limit for the BOD probe is 0.01 mg/l.

Oxygen Uptake Rate (OUR)

In order to perform this test, 350 ml of sample was poured into a biochemical oxygen

demand bottle and the initial DO recorded. After 10 minutes, final DO was measured and the OUR (mg O_2/liter-hr) calculated using the following equation:

$$OUR = \frac{60x\,(DO_i \cdot DO_f)}{t} \qquad (4.1)$$

where:

DO_i = Initial dissolved oxygen, mg/l
DO_f = Final dissolved oxygen, mg/l
t = time interval, min

Headspace Gas Analysis

A portable multi-gas analyzer (Gas Tech Inc.) was utilized during this study to measure % oxygen, % carbon dioxide, lower explosive levels (LEL) and parts per million (ppm) of hydrocarbons in the head-space of the bench-scale bioslurry reactors. The multi-gas analyzer is equipped with an electrochemical oxygen sensor, an infrared carbon dioxide sensor, and a catalytic hydrocarbon sensor. The oxygen, carbon dioxide, and hydrocarbon sensors were calibrated to 12 % volume oxygen, 2.5 % volume carbon dioxide, and 50 % of LEL, respectively. Lower detectable limits for oxygen sensor, carbon dioxide, and VOCs are 0.1%, 0.1%, and 1 ppm.

Iron

Iron in the liquid phase was determined using an Iron-Phenanthroline Method (HACH™). The contents of a Hach brand phenanthroline reagent pillow are added to 5 ml of sample in a 20 ml tube and the mixture thoroughly mixed. During reaction, the test reagent reacts with the iron in the sample to yield a red-orange color. The intensity of the color is measured and compared to

a color coded scale. When necessary, samples were diluted with distilled water to reduce the concentrations to levels that are lower than the upper detection limit of the test (5 mg/L). Lower detectable limit for this method is 0.1 mg/l.

Manganese

Manganese in the liquid phase was determined using a Periodate Method (HACH^{TM}). The contents of a Hach brand Citrate reagent pillows are added to 5ml of sample in a tube and thoroughly mixed. Then, the same steps are repeated except that the contents of a Hach brand sodium periodate reagent pillow are used. During reaction, sodium periodate reagent oxidizes the manganese in the sample to yield a purple permanganate color. The intensity of the color is measured and compared to a color coded scale. When necessary, samples were diluted with distilled water to reduce the concentrations to levels that are lower than the upper detection limit of the test (3 mg/l). Lower detectable limit for this method is 0.1 mg/l.

Liquid-Phase Hydrogen Peroxide Concentration

The desired hydrogen peroxide concentrations were achieved by adding the concentrated stock solutions to the slurry. The amount of hydrogen peroxide added was formulated based on the total volume of the slurry (i.e., mg of H_2O_2 / liter of slurry volume). The hydrogen peroxide concentration in the liquid phase was analyzed using a RQflex Meter (EM Science^{TM}). The RQflex Method uses specially designed hydrogen peroxide test strips containing an organic redox indicator. In order to measure hydrogen peroxide, the strip is immersed in the supernatant liquid

for 2 seconds to thoroughly moistened the tip. During a 15-second reaction time, the oxygen from hydrogen peroxide decomposition converts the redox indicator into a blue oxidation product. The intensity of the blue oxidation product is measured by inserting the tip into the RQflex meter and a reading taken. When necessary, the supernatant liquid samples were diluted with distilled water to reduce the concentrations to levels lower that are lower than the upper detection limit for this method (20 ppm). Lower detectable limit for the hydrogen peroxide strip 0.2 mg/l.

Microbial Enumeration (Total Heterotrophs)

Total heterotrophic microbial enumerations were used to measure active aerobic bacterial populations within the sediments and slurries. Counts were accomplished using a pour plate technique amended with nutrient agar (Hach Company). Enumeration of heterotrophs was done by transferring 1 ml of slurry into 99 ml of phosphate buffered contained in a dilution bottle resulting in 1:100 dilution. The dilution step was repeated until the desired dilution factor was achieved. Then 1 ml of each dilution and moderate amount of agar was added onto pour plates and incubated for 48 hours at 35°C within an incubator (Fisher Scientific Isotemp Standard 600 Series). Colonies formed on the plates were visible as distinct circles and countable plates were characterized as those having visible separate colonies. Counting was accomplished by physically counting the total amount of visible and separate colonies using a lighted colony counter (Leica Model 3325, New York). Counts were expressed as colony forming units per gram of dry soil (CFUs/g soil) and calculated using the following equation:

$$\text{Microbial Counts (CFUs / g)} = \frac{N \times DF}{C_{slurry} \times \frac{(100 \cdot MC)}{100}} \quad (4.2)$$

where,

N = Counts, CFUs/ml
DF = Dilution factor
C_{slurry} = Slurry concentration, g/ml
MC = Moisture content of the soil, %

Nitrate and Ammonia

Both nitrate and ammonia concentrations were measured using appropriate ion selective probes and an Accumet Model 15 Meter. Both the nitrate and ammonia probes were calibrated using standards of 0.001M, 0.01M and 0.1M prepared from a stock solution of 10M. Standards and samples were prepared for analysis by adding 1 ml of ionic strengthener adjuster (ISA) per 100 ml of standard or sample. The probes were calibrated prior to analyses. Lower detectable limit for both probes is 0.001 mol/l.

Ortho-Phosphate

Ortho-Phosphate (OP) concentration was determined using the Hach™ Phosver 3 Method. This colorimetric technique utilizes the Hach™ No. 5010 Spectrophotometer for testing. To perform this test, 5 ml of sample and 4 ml of distilled water were mixed in a test vial. The mixture was then placed in the spectrophotometer to zero the machine. Then the Phosver 3 reagent powder pillow was added to the tube and rigorously mixed with the sample. During the

two-minute reaction, the reagent powder reacts with the phosphate in the sample to yield a blue molybdenum-complex. The intensity of the blue molybdenum complex is measured by placing the tube into the spectrophotometer and a reading was obtained. When necessary, samples were diluted with distilled water to lower the concentrations to the identifiable upper detection limit of 2.5 mg/l. Lower detectable limit is 0.01.

pH

The pH in the liquid phase and slurry were measured using a pH probe and Accumet Meter Model 15 (Fisher Scientific). The meter was calibrated using standard buffers of pH-4, pH-7, and pH-10. In between analyses, the pH probe was rinsed with distilled water and blot-dried with paper towel. The probe was calibrated prior to analysis.

Total Organic Carbon

Total organic carbon (TOC) was determined using a Shimadzu TOC analyzer (Model TOC-5000A CE) coupled with a Solid Sampling Module (SSM). The SSM provides the TOC analyzer the capacity to analyze for solid samples, such as soil and sediment. In order to prepare for this test, samples were dried in a desiccator before weighing in ceramic boats. Two boats are required for a TOC analysis because the TOC analysis is separated into two sections; measurement of total carbon (TC) and inorganic carbon (IC). In the TC phase, a known amount of sample is inserted into a furnace set at 900 °C. In the furnace, all of the carbon is oxidized into carbon dioxide and channeled to the TOC analyzer using ultra-high purity helium. The carbon dioxide is analyzed by matching the generated spectrum against a TC calibration curve. In the IC

section, 0.5 ml of phosphoric acid is injected onto the sample before inserting it into a different heating chamber set at 200°C. Phosphoric acid reacts with the inorganic carbon in the chamber to yield carbon dioxide. Similar to TC, the carbon dioxide generated is channeled into the analyzer, where the concentration was determined by matching the spectrum against an IC calibration curve. The results obtained from both TC and IC are reported as mg carbon/ kg of dry soil. Finally, TOC is determined by subtracting IC from TC.

Moisture Content

Moisture content was determined by weighing a known amount of sample before and after the soil is dried in a laboratory oven set at 105 °C for 12 hours. Then moisture content is calculated using the following equation:

$$\text{Moisture Content, \%} = \frac{W_{total} \cdot W_{dry}}{W_{total}} \times 100\% \qquad (4.3)$$

where,

W_{total} = Weight of the wet sediment, gram
W_{dry} = Weight of the dry sediment, gram

Total Solid Content

All slurries were mixed to achieve a total solid content of 30% by weight. Slurry and distilled water were mixed according to the following equation:

$$\text{Total Solid Content, \%} = \frac{W_{Total}\left(1 \cdot \frac{MC}{100}\right)}{(W_{Total} + DI)} \times 100\% \qquad (4.4)$$

where,

W_{Total} = Weight of the wet sediment, gram
DI = Weight of distilled water, gram
MC = Moisture content (refer to Equation 4.3)

Heavy Metals Analysis

The metal analysis was performed by the research team of Dr. Mark Bricka of Swalm School of Chemical Engineering at MSU. The sediment was prepared for metals analysis according to EPA Method 3051. Initially, a known weight of sediment is dried in a laboratory oven at 105°C for twelve hours and the moisture content is calculated based on Equation 4.3. Then, the sample is grounded in mortar and pestle. The sediment is then sieved using ASTM E-11 No. 35 sieve (500• m). The dried sample is placed into a vessel where 10 ml of concentrated nitric acid was added and heated in a multiwave (digestion) according to EPA Method 3501. After that, the digested sample is filtered using 0.45 millipore cellulose filter. The vessel and the filtering unit are rinsed using 2% (v/v) nitric acid solution. The filtered sample is then diluted to 100 ml using 2% (v/v) nitric acid solution. Finally, the filtered sample is analyzed for metals using on Induced Coupled Plasma (ICP). The concentration of a metal was determined by matching the spectrum against a calibration curve. The results obtained from the ICP are reported as mg metal/liter. The metal concentration in mg/kg is then determined using the following equation:

$$[\text{Metal}],\ \text{mg/kg} = \frac{[\text{ICP}] \times \text{DF}}{W_{Total} \times (1 \bullet \frac{MC}{100})} \qquad (4.5)$$

where,

[Metal] = Metal concentration, mg metal / kg of dry soil
DF = Dilution factor
[ICP] = Metal concentration, mg metal / liter
W_{Total} = Weight of wet sediment, kg
MC = Moisture content (refer to Equation 4.3)

Preparation and Analysis of PAH Samples

Prior to analysis, PAHs analysis requires sample preparation, extraction, and clean-up. PAHs were analyzed according to EPA Method 8100 using gas chromatography (GC) equipped with a flame ionization detector (GC/FID). Most current GC methods for hydrocarbon based products are coupled with FID, primarily because FID is universal and sensitive for most hydrocarbons (Xiang and Morgan, 1995).

Soil Phase Extraction: In this study, PAHs were extracted using ASE 200 Accelerated Solvent Extractor equipped with ASE 200 Solvent Controller (Dionex Corporation, USA). The Dionex Accelerated Solvent Extraction 200 (ASE^{TM}) system is a newly developed technology made for extraction of organics (i.e., PAHs) from solid wastes. This technology meets the requirements of USEPA SW-846 Method 3545 for PAH analysis (USEPA, 1996). ASE was chosen over the traditional extraction methods (i.e., Soxhlet and sonication) for the following reasons:

a. Reduced sample preparation and extraction time (minutes vs. hours)

b. Minimal use of solvents (<15 ml for a 10 g sample)

c. Elimination of interferences caused by variation in temperature encountered in Soxhlet and sonication

d. Analytes recoveries from ASE are equivalent to that of the Soxhlet method (EPA, 1997)

e. The extraction process is fully automated

In order to prepare for the ASE extraction, slurry samples were mixed with diatomaceous earth (DE) in a beaker before loading into the 33ml ASE 200 cell. The amount of DE added to the soil samples was adjusted according to the recommendations given in ASE 200 Operator's Manual. Then the cell was loaded on the ASE and extracted according to the following program:

Solvent:	Acetone / Hexane = 1/1 (by volume)
Oven temperature:	100°C
Pressure:	1,500 psi
Heat-up time:	5 minutes
Static time:	5 minutes
Static cycle:	3
Flush volume:	60%
Purge time:	180 seconds

Upon completion, the extractant was transferred from the heated cell to a standard collection 60-ml vial. The extracts collected in the vial had two separate layers. The water/acetone layer was discarded and the anhydrous sodium sulfate was added to PAHs/ hexane layer in the vial to absorb moisture. Then, sodium sulfate was filtered out by simple gravity filtration technique using Whatman™ filter paper (110 mm diameter). Finally, the PAHs/hexane layer was concentrated to 5 ml using an isothermal water-bath set at 40°C.

Liquid Phase Extraction: PAHs concentrations in the water phase was extracted using a sonication technique. In order to perform this test, 5 ml of sample and 10 ml of the hexane and acetone solution were mixed together. Then, the mixture was sealed and sonicated in a Branson™ Ultrasonic Cleaner for 12 hours with periodic venting of vapor. After sonication, the water/acetone layer was discarded and anhydrous sodium sulfate was added to absorb the moisture and the sodium sulfate filtered out using the same filtration technique described in the soil phase extraction.

Gas Chromatography Analysis: Gas Chromatograph (GC) analysis was performed on a Hewlett Packard 6890™ (HP) series capillary column gas chromatography equipped with a FID detector and an automatic liquid sampler (HP G1512A controller and HP G1513A injector). A fused silica capillary column was used and the total system operated as follows: Column:

J&W Scientific™ Fused Silica Capillary Column;

DB-5 30m x 0.25 mm i.d. x 0.25 •m df (Catalog# 122-5032);

temperature limits: -60°C to 350°C

Inlet: 1ml; Splitless; 10 psi at 80°C;

45 cm/sec with Ultra-High Purity Hydrogen Carrier;

1.5 ml/min in Constant Flow Mode

Oven Program: 80°C (1 min)

25°C/min to 160°C (0 min)

3°C/min to 300°C (0 min)

20°C/min to 325°C (1 min)

Detector: FID, 325°C

PAHs standard mixture purchased from Accustandard Inc. (New Haven, CT) was used as the calibration standard for the GC-PAHs analysis. The PAH solution mixture was diluted using hexane and calibration was conducted by matching each peak to the known concentrations. The R^2 values for all 16 PAHs were 0.98 or better. The summation of all 16 PAH concentrations extracted from the sediment is called Total PAHs. A known amount of PAH solution mixture was analyzed after every 150 extracted samples to verify the retention of the 16 PAHs (approximately after 100 samples) and a blank sample (hexane) was injected after every three samples into the GC to clean the column and to check for PAH residual. The lowest PAH standard concentration calibrated on the GC was 1 ng/• l.

A summary of the detected PAHs as analyzed by the Swalm C. School of Chemical Engineering (E-Tech) at MSU, Department of Forest Products at MSU (FP) , and WES at Vicksburg is presented in Table 4.17. This comparison was done to ensure the adequacy of the PAH analytical techniques by comparing the analytical results from this study to those generated by two well-established laboratories. First of all, the results show that most of the PAHs detected by E-Tech are in the same magnitude, in comparison to the other laboratories, with the exceptions of acenaphthylene, benzo[g,h,i]perylene, and indeno[1,2,3-cd]pyrene. The amount of two to four rings PAHs obtained by E-Tech matches closely to the values reported by WES with the exception of acenaphthylene. On the other hand, the amount of five-ring and six-ring PAHs detected by E-Tech is higher than the values reported from both WES and FP. The discrepancy in the PAH amount could have resulted from heterogeneous properties of the Lake Superior

Sediment. Finally, the Total PAH amount detected by E-Tech is slightly higher than the Total PAH detected by FP and also an order of magnitude lower than the Total PAH reported by WES. The magnitude in difference between the Total PAH detected by E-Tech and WES is mainly attributed to acenaphthylene. This trend could have resulted from heterogeneous properties of the sediment. Overall, the amount of PAHs detected in the sediment by E-Tech matches closely to the amount of PAHs detected by FP and reported values by WES with the exception of the acenaphthylene amount.

Table 4.1. Summary of PAHs in Lake Superior and Scioto River Sediments

Analysis	Lake Superior	Scioto River
Naphthalene	181.91	1.33
Acenaphthylene	6.41	0.21
Acenaphthene	27.79	0.02
Fluorene	23.36	0.24
Anthracene	29.35	4.38
Phenanthrene	62.75	1.03
Fluoranthene	52.94	4.53
Pyrene	38.02	2.24
Benzo[a]anthracene	26.60	4.38
Chrysene	23.90	1.70
Benzo[b]fluoranthene	24.06	0.46
Benzo[k]fluoranthene	18.69	1.57
Benzo[a]pyrene	27.13	1.80
Benzo[g,h,i]perylene	13.73	1.73
Indeno[1,2,3-cd]pyrene	15.80	2.01
Total PAHs, mg/kg	572.43	27.63

Notes:
- The PAH amount is reported as mg of PAH / kg of dry soil

Table 4.1. (Continued)

Analysis	Lake Superior	Scioto River
Total Heterotroph Counts, CFUs/g	9433	12166
Moisture, Content, %	50	52
Total Organic Carbon, mg/kg	96627.2	44764.5
pH	7.2	7.6

Notes:
- The PAH amount is reported as mg of PAH / kg of dry soil

Table 4.2. Summary of Sediments Utilized in the Experiments Conducted in this Study

Phase	Treatment Type	Experiment	Sediment
I	Biotreatment	Bioavailability of Naphthalene	Lake Superior
		Biotreatment of Scioto River Sediment	Scioto River
		Biotreatment Lake Superior Sediment	Lake Superior
		Impact of Tween 80 and Glucose Amending on PAH Degradation	Lake Superior
	Chemical Oxidation	Ozonation of PAHs Contaminated Sediment	Lake Superior
		Peroxone Treatment of PAHs Contaminated Sediment	Lake Superior
		Fate of Hydrogen Peroxide in Equilibrated Water Solutions	Lake Superior
		Fate of PAHs and Hydrogen Peroxide within the Sediment	Lake Superior
		Impact of Fenton's Reagent Addition on PAHs Contaminated Sediment	Lake Superior
	Integrated	Fenton's Reagent Treatment	Scioto River
II	Biotreatment	Bioslurry Reactors	Lake Superior
	Integrated	Ozone Treatment	Lake Superior
		Peroxone Treatment	Lake Superior
		Fenton's Reagent Treatment	Lake Superior

Table 4.3. Operating Conditions for Phase I: Shake-Flask Biotreatment, Scioto River Sediment (Performed in duplicate)

Condition	Nutrients	Microbes	Surfactant
a	–	Native	–
b	N & P[1]	Native	–
c	N & P[1]	Inoculated[2]	–
d	N & P[1]	Inoculated[2]	Tween 80[3]

Notes:
[1]PAH:N:P = 100:20:5 addition once a week
[2]Activated sludge from the return line of a local wastewater treatment plant
[3]0.5% (w/w) the first week and 0.25% (w/w) the following weeks

Table 4.4. Operating Conditions for Phase I: Shake-Flask Biotreatment Tests, Lake Superior Sediment (Performed in duplicate)

Condition	Nutrients	Microbes	Surfactant	External Growth Substrate
a	–	Native	–	–
b	N & P[1]	Native	–	–
c	N & P[2]	Native	–	–
d	N & P[1]	Inoculated[4]	–	–
e	N & P[1]	Inoculated[5]	Tween 80[7]	–
f	N & P[3]	Inoculated[6]	Tween 80[8]	–
g	N & P[3]	Inoculated[6]	–	Glucose[9]

Notes:
[1]PAH:N:P = 100:20:5
[2]PAH:N:P = 1:32:13
[3]N & P concentrations of 100 mg/l and 20 mg/l, respectively
[4]Activated sludge from the return line of a local wastewater treatment plant
[5]Activated sludge from the return line of a swine operation
[6]Multiringed PAH degraders
[7]0.5% (w/w) the first week and 0.25% (w/w) the following weeks
[8]3% (w/w) the first two weeks and 1.5 % (w/w) the following weeks
[9]100 mg/l glucose addition once a week

Table 4.5. Operating Conditions for Phase I: Shake-Flask Bioavailability Experiments (Performed in duplicate)

Condition[1]	Microbes[2]	Naphthalene addition[3], mg/l	Dry sediment[4], g
1	Inoculated	25	-
2	Inoculated	-	31.25

Notes:
[1]All samplings were conducted at 0, 1.6, and 70.1 treatment hours
[2]Naphthalene degraders
[3]Analyzed for naphthalene in the liquid phase
[4]Analyzed for naphthalene in both the liquid and soil phases

Table 4.6. Operating Conditions for Phase I: Ozone and Peroxone Treatments, Lake Superior Sediment (Performed in duplicate)

Flowrate:2.5 scfh at 100 % voltage setting		
Treatment type	Peroxone	Ozone
Percent ozone, %	3	3
Amount of H_2O_2 added, mg/l	2,687[1]	Not Applicable

Notes:
[1]Hydrogen peroxide dosing sequences are listed in Table 4.7.

Table 4.7. Summary of the Hydrogen Peroxide Dosing Sequences for Phase I:Peroxone Treatments, Lake Superior Sediment (Performed in duplicate)

Treatment Time[1] (hr)	Amount of H_2O_2 added, mg/l	Cumulative Total H_2O_2, mg/l
0	62.5	62.5
2	62.5	125
4	62.5	187.5
6	500	687.5
9	500	1,187.5
12	500	1,687.5
15	500	2,187
18	500	2,687.5
21	-	-

Note:
[1]Denotes soil sampling for PAHs analysis

Table 4.8. Operating Conditions for the Fate of Hydrogen Peroxide in Equilibrated Water Test, Lake Superior Sediment

[1]Run	Control [2,3]	Not-autoclaved [2,4]	Autoclaved [2,4,5]
1st	HP	HP	-
2nd	HP	HP	-
3rd	HP	HP	-
4th	HP	HP	-
5th	HP	HP/THC	-
6th	HP	-	HP/THC

Notes:
[1]Described in the Method section
[2]1,000 mg/l hydrogen peroxide addition
[3]Single replicate
[4]Duplicate
[5]Autoclaved at 121°C and 15 psi for 15 minutes
- HP: Hydrogen peroxide analysis, mg/l
- THC: Total heterotrophic counts, CFUs/ml

Table 4.9. Operating Conditions for Testing the Fate of Hydrogen Peroxide within Sediment Compartment, Lake Superior Sediment.

Condition	Hydrogen peroxide dosing concentration, mg/l	Cumulative Total H_2O_2, mg/l
Not autoclaved	1,000	7,000
Not autoclaved	10,000	60,000
Not autoclaved	100,000	1,100,000
Autoclaved[1]	100,000	1,100,000

Notes:
[1]Sediment that was autoclaved at 121°C and 15 psi for 15 minutes
- Hydrogen peroxide analysis was conducted in triplicate
- Soil samples for PAHs analysis were conducted in duplicate
- Total heterotrophic counts were conducted in duplicate

Table 4.10. Operating Conditions for Phase I: Fenton's Reagent Treatments, Lake Superior Sediment (Performed in duplicate)

Condition	$[H_2O_2]$, mg/l	Fe^{2+}, mg/l	Number of applications	H_2O_2/Fe^{2+} ratio
A	25,000	2,500	7[1]	10:1
B	100,000	10,000	7	10:1

Notes:
[1]Dosing for steps 4-7: 100,000 mg/l H_2O_2 and 10,000 mg/l Fe^{2+}

Table 4.11. Test Schedule for Phase I: Fenton's Reagent Additions, Lake Superior Sediment (Performed in duplicate)

Step Number	Time, hr	A		B	
		HP	Fe	HP	Fe
1st	0[1]	-	2,500	-	10,000
	24	25,000	-	100,000	-
2nd	48[1]	-	2,500	-	10,000
	72	25,000	-	100,000	-
3rd	96[1]	-	2,500	-	10,000
	120	25,000	-	100,000	-
4th	144[1]	-	10,00	-	10,000
	168	100,000	-	100,000	
5th	192[1]	-	10,000		10,000
	216	100,000	-	100,000	-
6th	240[1]	-	10,000	-	10,000
	264	100,000	-	100,000	-
7th	288[1]	-	10,000	-	10,000
	312	100,000	-	100,000	-
Total, mg/l		475,000	47,500	700,000	70,000

Notes:
[1]Soil sampled for PAH analysis
- HP: Hydrogen peroxide addition, mg/l
- Fe: Ferrous sulfate addition, mg/l

Table 4.12. Operating Conditions for Phase I: Integrated Fenton's Reagent Treatments, Scioto River Sediment (Performed in duplicate)

Dosing Step Number	Timing, hr	H_2O_2/Fe^{2+} ratio = 10:1	
		HP	Fe
1st	0[1]	-	2,000
	24	20,000	-
2nd	48[1]	-	5,000
	72	50,000	-
3rd	96[1]	-	5,000
	120	50,000	-
4th	144[1]	-	10,000
	168	100,000	-
5th	192[1]	-	10,000
	216	100,000	-
6th	240[1]	-	10,000
	264	100,000	-
7th	288[1]	-	10,000
	312	100,000	-
8th	336[1]	-	10,000
	360	100,000	-
	384[1]	-	-
Total amount		620,000	62,000

Notes:
[1]Soil sampling for PAH analysis
- HP: Hydrogen peroxide addition, mg/l
- Fe: Ferrous sulfate addition, mg/l

Table 4.13. Operating Conditions for Phase II: Biotreatment Tests, Lake Superior Sediment (Performed in duplicate)

Reactor No.	Nutrient	Microbes	External Growth Substrates	Surfactant
1	–	Native	–	–
2	–	Native	–	–
3	N & P[1]	Native	–	–
4	N & P[1]	Native	–	–
5	N & P[1]	Inoculated[2]	–	–
6	N & P[1]	Inoculated[2]	–	–
7	N & P[1]	Inoculated[2]	Glucose[3]/Acetate[4]/Nap[5]	Tween 80[6]
8	N & P[1]	Inoculated[2]	Glucose[3]/Acetate[4]/Nap[5]	Tween 80[6]

Notes:
[1]Nitrate and Phosphate additions at 100 mg/l and 40 mg/l, respectively, the first three weeks, and increased to 1,000 mg/l and 400 mg/l the following weeks
[2]Naphthalene degrader (Days 1 and 11 of the experiments)
[3]Glucose dosing at 1,000 mg/l (Days 1, 11, and 23 of the experiments)
[4]Sodium acetate dosing at 100 mg/l (Days 50 and 63 of the experiments)
[5]1 liter of 25 mg/l naphthalene addition (Days 53 and 65 of the experiments)
[6]Initial Tween 80 addition at 5% by weight, (Days 74 and 86 of the experiments) followed by 2.5% by weight (Days 107 and 116 of the experiments)

Table 4.14. Operating Conditions for Phase II: Integrated Ozone and Peroxone Treatment Tests, Lake Superior Sediment (Reactors 3 and 4) (Performed in duplicate)

Flowrate:2.5 scfh at 100% voltage setting		
Treatment type	Peroxone	Ozone
Percent ozone, %	3	3
Amount of H_2O_2 added, mg/l	2,400[1]	-

Notes:
[1]Hydrogen peroxide dosing sequences is summarized in Table 4.15

Table 4.15. Summary of Hydrogen Peroxide Dosing Sequences for the Phase II: Integrated Peroxone Treatment of Lake Superior Sediment Tests (Performed in duplicate)

Treatment Time, hr	Amount of H_2O_2 added, mg/l	Cumulative Total H_2O_2, mg/l
0	100	100
1	100	200
2	100	300
3	100	400
4[1]	500	900
5	500	1,400
6	500	1,900
7	500	2,400
8[1]	-	-

Note:
[1]Soil sampled for PAH analysis

Table 4.16. Operating Conditions for Phase II: Integrated Fenton's Reagent Treatment, Lake Superior Sediment (Reactors 3 through 6) (Performed in duplicate)

Step No.	Timing, hr	Reactors 3 & 4		Reactors 5 & 6	
		HP	Fe	HP	Fe
1st	0[1]	-	2,500	-	2,500
	24	25,000	-	25,000	-
2nd	48[1]	-	2,500	-	2,500
	72	25,000	-	25,000	-
3rd	96[1]	-	5,000	-	10,000
	120	50,000	-	100,000	-
4th	144[1]	-	5,000	-	10,000
	168	50,000	-	100,000	-
5th	192[1]	-	10,000	-	10,000
	216	100,000	-	100,000	-
6th	240[1]	-	10,000	-	10,000
	264	100,000	-	100,000	-
	288[1]	-	-	-	-
Total, mg/l		350,000	35,000	450,000	45,000

Notes:
[1]Soil sampled for PAH analysis
- HP: Hydrogen peroxide addition, mg/l
- Fe: Ferrous sulfate addition, mg/l

Table 4.17. PAH Results of Lake Superior Sediment

PAH Compound	Amount in mg of PAH / kg of dry soil		
	E-Tech[1]	Forest Products[2]	WES[3]
Two rings:			
Naphthalene	181.91	168.02	194.67
Three rings:			
Acenaphthylene	6.41	2.830	7,100.00
Acenaphthene	27.79	16.20	26.02
Fluorene	23.36	12.65	21.57
Anthracene	29.35	17.98	31.05
Phenanthrene	62.75	39.08	71.40
Four rings:			
Fluoranthene	52.94	33.45	54.95
Pyrene	38.02	24.15	50.25
Benzo[a]anthracene	26.60	15.18	24.47
Chrysene	23.90	12.88	23.50
Five rings:			
Benzo[b]fluoranthene	24.06	ND	24.45[4]
Benzo[k]fluoranthene	18.69	ND	
Benzo[a]pyrene	27.13	14.58	14.95

Notes:
[1]Swalm C. School of Chemical Engineering, MSU
[2]Department of Forest Products, MSU
[3]U.S. Army Engineer Waterways Experiment Station, Vicksburg
[4]Reported as benzo[k&b]fluoranthene
- ND: Below detectable limit

Table 4.17. (Continued)

Compound	Amount in mg of PAH/kg of dry soil		
	Chem[1]	Forest Product[2]	WES[3]
Six rings:			
Benzo[g,h,i]perylene	13.73	5.40	6.20
Indeno[1,2,3-cd]pyrene	15.80	ND	7.82
Total PAHs	572.43	362.37	7651.36

Notes:
[1]Swalm C. School of Chemical Engineering, MSU
[2]Department of Forest Products, MSU
[3]U.S. Army Engineer Waterways Experiment Station, Vicksburg
[4]Reported as benzo[k&b]fluoranthene
- ND: Below detectable limit

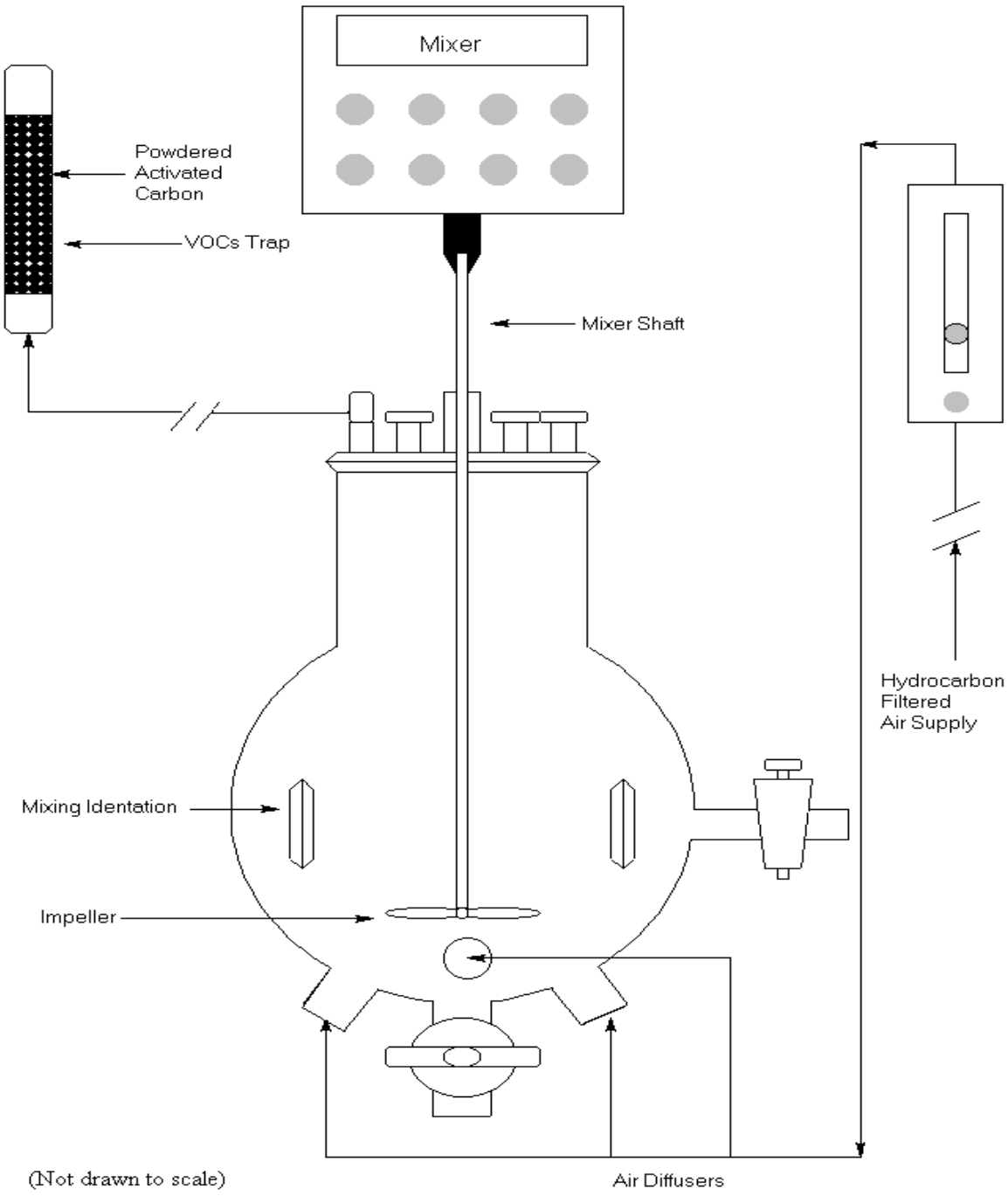


Figure 4.1. Schematic Drawing of a Bench-Scale Bioslurry Reactor Setup

Figure 4.2. Photograph of the Bioslurry Reactor Setup

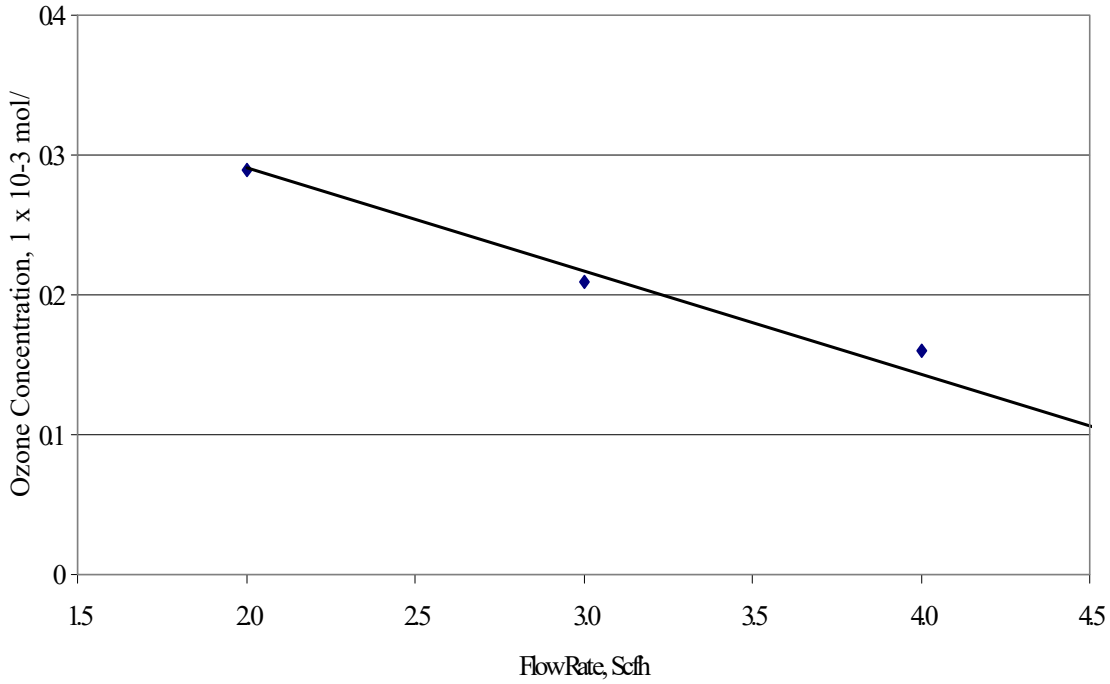


Figure 4.3. Ozone Concentration as a Function of flow rate (112V)

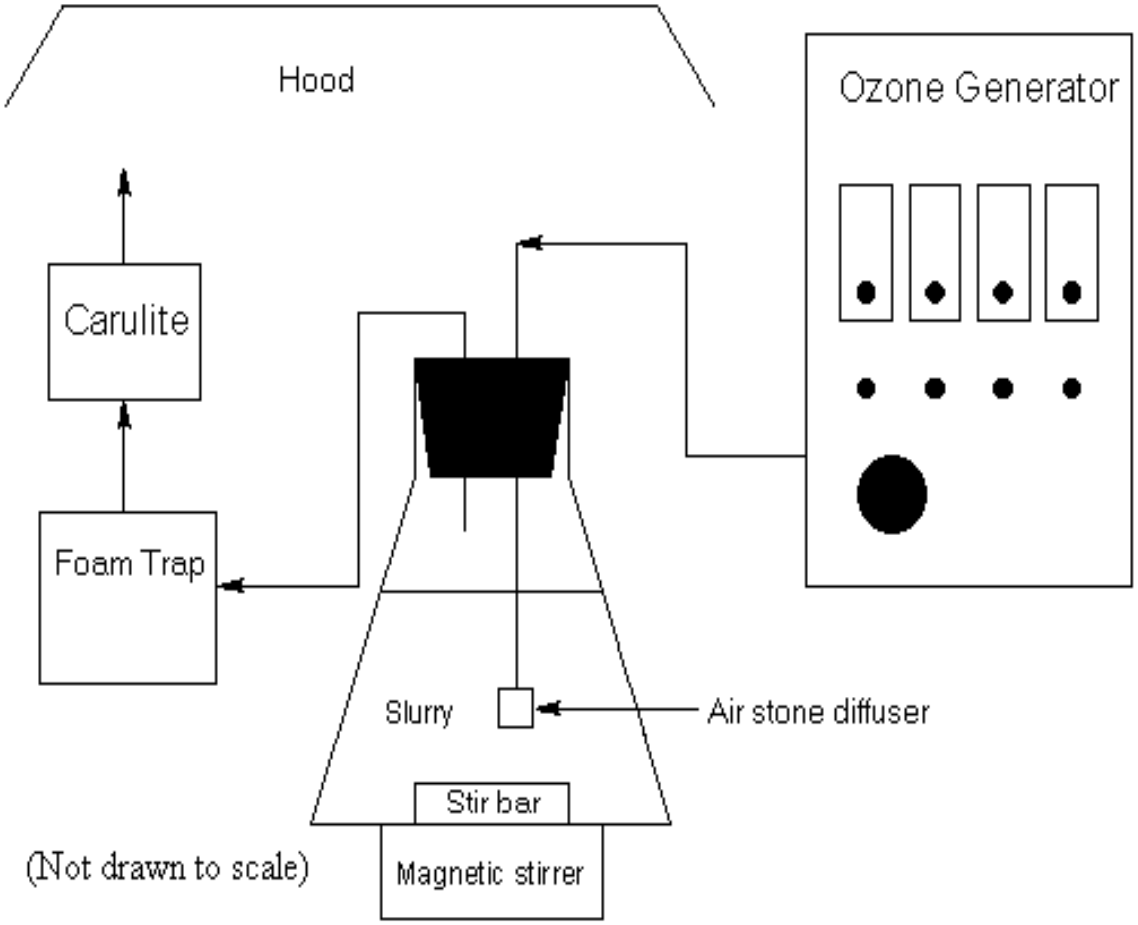


Figure 4.4. Experimental Setup for Ozone and Peroxone Treatment Experiments on Contaminated Slurry

CHAPTER V

PHASE I: BIOTREATMENT SCREENING RESULTS

This series of shake-flask experiments was performed on both the Lake Superior and Scioto River sediments to screen numerous candidate biological conditions as a means of determining the optimal conditions for PAH removal to be utilized in the bench-scale bioslurry study (Phase II). This series of experiments also was done as an effort to determine the amount of time needed to allow bioremediation sufficient time to perform as a stand-alone process or as a pre-treatment step.

Bioavailability Experiment Results

The objective of this test was to evaluate the mechanisms controlling PAH biodegradation within the bioslurry systems. Note that the Lake Superior sediment was utilized for this study. Appendix A presents the raw data along with the standard deviation associated with these data. In the liquid system, naphthalene degraders were added to flasks along with 25 mg/l naphthalene. Only the naphthalene degraders were added to the sediment slurry system because the sediment in this experiment already contained 284 mg/kg of naphthalene. Table 5.1 presents the liquid phase and the soil phase naphthalene degradation results for this experiment. The data reveal that naphthalene biodegradation in the liquid phase by the naphthalene degraders was significant within the first two hours. The liquid set showed 86% biodegradation of the naphthalene within the first

two hours. The naphthalene in the liquid phase for the slurry set (derived from naphthalene in the sediment) was totally consumed within the first two hours of testing. Despite the significant biodegradation of naphthalene in the liquid phase, the naphthalene levels in the sediment remained relatively unchanged over seventy hours of testing. These findings prove that the low bioavailability of naphthalene in the liquid phase to be the limiting factor for the biodegradation of PAHs in the sediment. Additionally, these data show that the enzymatic capability of bacteria for PAH biodegradation was not limiting. Therefore, it is concluded that mass transfer limitations are controlling the overall fate of PAHs within the sediment slurry systems and not the reaction kinetics associated with bacterial enzymes.

Biotreatment Screening Results for the Scioto River Sediment

The objective of this test series was to screen various bioremediation strategies for eventually selecting a narrower evaluation scheme in later testing. Note that the different treatment conditions were examined in duplicate flasks and the data shown in this chapter represent an average of the replicate data. Appendix A presents the raw data along with the standard deviation associated with these data.

Table 5.2 presents the pH measurements for these tests. Most of the pH values remained relatively constant throughout the four weeks of testing (7.0 +/- 0.5), with the exception of the set involving Tween 80. This neutral pH range is optimal for biological activity (Metcalf and Eddy, 1991). The constant decrease in pH for the set involving Tween 80 addition was attributed to the formation of organic acids as by-products of Tween 80 biodegradation. No attempt to buffer this

pH change was attempted because of interests associated with determining how dramatic the pH would change from Tween 80 degradation.

In terms of Total PAH removal (Figure 5.1), during the first week of bioremediation, a slight drop in the Total PAH concentration was observed with all treatments. The decrease in the PAH levels may be attributed to heterogeneous contaminant distribution within the slurry and the rapid biodegradation of the easily solubilized PAHs. It is known that when sediment and fresh water mix together, the soluble fractions (i.e., NOM, reduced cations, organic contaminants, etc.) disperse into the aqueous phase and become homogenized within the slurry (Wang, 1999); thus, destabilizing adsorption equilibria. On the third week, the sets amended with activated sludge and nutrients and nutrients only were the only systems showing any further decrease in Total PAHs prior to an increase during the fourth week. The decrease in Total PAHs was not observed in the biotic control, indicating that this disappearance in the Total PAHs was very likely due to biodegradation. The increase in the Total PAHs on the fourth week observed with all the systems, except the controls, was attributed to natural biosurfactants produced due to an increased level of bacterial activity. In a study conducted by Kanga et al. (1997), aqueous phase naphthalene levels were increased after the addition of a glycolipid, which is a biosurfactant produced by *Rhodococcus* Species H13-A. It was concluded that this increase was attributable to biosurfactants and the erosion of the soil particles into smaller fractions; thus, exposing new surface area.

The set involving Tween 80 addition once a week resulted in an increase in Total PAHs over the course of this test. This trend also was observed with Wang (1999) during the

biotreatment of TPHs from soil and Tiehm et al. (1997) during the bioremediation of PAHs contaminated soil. Wang (1999) reported that an increase in the TPH concentration was recorded after the addition of Tween 80 on the 21st day of the biotreatment experiments. On the other hand, Tiehm et al. (1997) reported that an increase in PAHs in the aqueous phase was observed after the addition of surfactants (e.g., Arkopal –300 and Sapogenat T-300). This increase observed by Tiehm et al. (1997) later did improve the rate and extent of PAHs biodegradation.

In terms of Light PAH removal (Figure 5.2), the biodegradation of the Light PAHs followed the trend observed with the biodegradation of Total PAHs (see Figure 5.1). The Light PAHs for the sets amended with activated sludge and nutrients and nutrients alone disappeared during the second week prior to a slight increase on the fourth week. Again, the disappearance of Light PAHs was likely due to biodegradation because the Light PAHs in the control system were not removed. The increase in Light PAHs on the fourth week also was believed to be attributable to the production of natural biosurfactants and sediment particle erosion.

In terms of Heavy PAH removal (Figure 5.3), the biodegradation of Heavy PAHs also appears to generally follow the trend observed with the Total PAHs (see Figure 5.1). The results show that the increase in the Total PAHs in the sets involving activated sludge and nutrients and nutrients alone was mainly Heavy PAHs, as witnessed by a dramatic increase in these PAHs at Week 4 and the minimal change seen with the Light PAH data (see Figure 5.2).

Biotreatment Screening Results for the Lake Superior Sediment

Figures 5.4 through 5.8 present the results from the experiments that evaluated various bioremediation strategies for the time-course removal of the various fractions of PAHs from the Lake Superior sediment. Note that these data represent an average of the data from the duplicate sets. Appendix A lists the raw data and standard deviations associated with these average data.

From Figure 5.4, the results show that during the first week of bioremediation, a slight drop in the Total PAHs was observed with all treatments, except the set involving nutrients amending at a PAH:N:P concentration ratio of 1:32:13. Note that the reason for dosing the nutrients at a 1:32:13 ratio will be discussed in the following section. Like the Scioto River data, the slight decrease in the Total PAHs was likely attributed to the heterogeneous distribution of the PAHs within the sediment. Despite that decrease during the first week, the amount of Total PAHs increased during the third week prior to a slight drop by the fourth week. The increase in the Total PAHs was likely again attributable to the production of natural biosurfactants associated with the increased levels of microbial activity stimulated by the nutrients dosing. The addition of the activated sludge and nutrients at a PAH:N:P concentration ratio of 100:20:5 did not enhance the degradation of the PAHs. Since the seeding of this bacterial source into the Scioto River sediment did not result in an improvement in PAH removal, this suggests that the reactor environment was not suitable for the seeded bacteria to grow within the reaction times evaluated.

The results shown in Figure 5.4 reveal that the set involving nutrients addition at a dose of 1:32:13 provided slow but consistent biodegradation of Total PAHs within the sediment (in comparison with the biotic control). The TOC content in the Lake Superior sediment was around

100,000 mg/kg (see Table 4.1). This value is higher than the reported values for most sediments (around 7,500 mg/kg) (Zappi et al., 2000). Based on this TOC value, there is a significant amount of organic constituents other than PAHs within this sediment. Since the PAHs make up a small fraction of this high TOC, then dosing nutrients using a C:N:P ratio based on PAHs (i.e., C = [PAHs]) was believed to be too small. The rationale was that the high TOC likely contains a portion of organics that represents a significantly higher amount of additional substrate. Therefore, the system has a much higher demand for nutrients than associated with the PAHs value alone. The need for nitrate and phosphate increases with the total amount of degradable organic constituents present in the test system. Thus, the nitrate and phosphate dosages were elevated over the PAH concentration-based dosing strategies used with the other test systems. The data generated clearly support this hypothesis. Clearly, this approach yielded steady removal of the PAHs from the sediment slurry.

Figure 5.5 presents the Total PAHs results for the set involving the addition of activated sludge, nutrients, and Tween 80. These data were segregated from the other data to better visualize the trend associated with Tween 80 addition. The data reveal that the Tween 80 caused an increase in extractable PAHs over time. This was observed in the earlier experiments involving Tween 80 addition during the bioremediation screening activities for the Scioto River sediment (see Figure 5.1). This increase in Total PAHs was likely attributable to the dosed surfactant greatly improving the extractability of the PAHs; plus, the facilitation of a more rapid deagglomeration of sediment particles resulting in a dramatic increase in surface area (and thus, extraction efficiency). The drop in Total PAHs after the 2nd week was believed to have resulted from the resulting

increase in bioavailability. This effect was also observed by Harvey (1997) during the bioremediation of explosives contaminated soils. Harvey (1997) indicated that the addition of Tween 80 increased the desorption of explosive compounds (i.e., TNT and RDX) from the soil; thereby, increasing analytical extractability. This increase observed by Harvey did later improve the rate and extent of TNT biodegradation.

In terms of Light PAH removal (Figure 5.6), the trend observed with the biodegradation of the Light PAHs also followed the trend observed with the Total PAHs (Figure 5.5). On the other hand, the results of the Heavy PAHs (Figure 5.7) show a decrease in Heavy PAHs during the first week of bioremediation for the control system, the sets involving activated sludge and nutrients and nutrients alone showing a less significant decrease in comparison to those observed with the Total PAHs data (Figure 5.4). This indicates that the bioavailability of the Heavy PAHs was still very limited, due to their low water solubility. Obviously, little benefit was observed with some of the systems evaluated.

Figure 5.8 presents the Heavy PAHs results for set involving Tween 80 addition. These data were segregated from the other data to better visualize the trend associated with Tween 80 addition. These data show that the increase in Total PAHs (Figure 5.5) was mainly associated with the Heavy PAHs. Heavy PAHs are known to be hydrophobic and adsorb strongly onto soil surfaces; thus, limiting bioavailability and resulting in poor biodegradation rates (Mihelcic and Luthy, 1987; Zappi et al., 1993). This observation concurs with Volkering et al. (1998) in which the bioavailability of the PAHs and subsequent removal rate increased with the addition of Tween 80. From this set of experiments, the addition of Tween 80 appears to have increased the amount of

Heavy PAHs in solution; thus, improving the rate and extent of Heavy PAH biodegradation.

The biodegradation half-life of naphthalene, in soil and water mixture, under optimum aerobic conditions is reported to be three days (Danish EPA, 2002). Based on these findings, the experiments were conducted over a four week period to allow sufficient time for significant naphthalene degradation to occur. However, the duration of these experiments was shorter (four weeks) in comparison to other studies, such as Lauch et al. (1992), USEPA (1993), and Zappi et al. (1996). These researchers found that the biodegradation-based half-life for PAHs having more than three rings to be greater than 30 days and more specifically, the half-life of benzo[a]pyrene, a four-ring, within acclimated reactors of about 22 days (Sims et al., 1989; Park et al., 1990). These findings indicate that longer treatment times than those used in these studies were required if complete removal of Total PAHs is desired. However, since the objective was simply to screen candidate treatment conditions, it was decided to end the experiments early to allow for focus to be placed on process integration experiments. In general, only the sets with nutrients amended at a PAH:N:P dosing ratio of 1:32:13 exhibited Light PAH biodegradation of about 35%, which is still much lower than the bioremediation success reported by Zappi et al. (1993) for Light PAHs who observed a removal of 89% for the Light PAHs within a 22 day period. However, it is important to point out that Zappi et al. (1993) worked with an upland soil which was chemically much less complex than a sediment.

Impact of Tween 80 and Glucose Amending on PAH Degradation

The objective of this test series was to further evaluate the effect of Tween 80 dosing and evaluate the effect of glucose dosing on the removal of PAHs from the Lake Superior sediment. Note that the duration of these experiments was 20 weeks. The longer incubation times were selected based on the results of the previously discussed experiments. The bacterial seed used in this testing was a culture of multi-ring PAH degraders prepared by Dr. Hamid Borazjani of the Department of Forest Products, MSU, for a treatment plant in Wiggins, MS. This plant is treating low levels of PAHs in a groundwater influent. Additionally, all of the data plots presented herein for these experiments represent an average of the data from the duplicate set. Appendix A lists the raw data and standard deviations associated with these average data.

Figure 5.9 presents the pH levels within the flasks over the course of this test. The results show that the pH for the set with Tween 80 addition remained lower than the set with glucose addition. After 14 weeks of repetitive Tween 80 additions, the pH dropped below six, which is out of the optimum pH range for bioremediation (Metcalf and Eddy, 1991; Englert et al., 1993). This observation concurs with the previous experiments involving Tween 80, indicating the generation of organic acids as by-products of Tween 80 biodegradation. The pH was not adjusted in order to evaluate the effect of pH and unadjusted Tween 80 addition on the Heavy PAH biodegradation.

Figure 5.10 presents the dissolved oxygen concentrations within the slurries over the course of this test. The dissolved oxygen levels for the set involving Tween 80 addition dropped below 2 mg/l during Weeks 6, 14, 20, and 21. However, these DO results show that the systems

generally remained aerobic over the entire study period.

Figure 5.11 presents the Total PAHs degradation within the slurries over the course of this test. The results show that there was a significant increase in the Total PAHs in both sets during the mid point of the test prior to a steady decrease toward the end of the test. Despite the overall increase in the extractable Total PAHs, the results show that during the first three weeks of biotreatment, a drop in Total PAHs was observed with both sets. A significant increase in the concentration of the PAHs was observed for both sets of experiments by Week 4. This trend is similar to those observed in the earlier experiments. This finding indicates that the increase in extractable PAHs is likely due to natural biosurfactants produced from the increased levels of bacterial activity and not the addition of surfactant. Since Tween 80 is highly biodegradable, as is glucose, the benefits of adding these high levels of co-metabolite likely resulted in the production of natural biosurfactants. The results also show that the drop in the pH in the set involving Tween 80 after 14 weeks did not appear to affect the ability of the microorganism to biodegrade the PAHs. Obviously, 20 weeks was not sufficient to remove the PAHs to below detection limits. However, a removal of over 80% was achieved.

Figure 5.12 presents the Light PAHs degradation within the slurries over the course of this test. The results show that Light PAHs degradation generally followed the trend observed with the Total PAH degradation. The set involving Tween 80 addition performed better than the set involving glucose addition with respect to Light PAHs biodegradation; thereby, possibly indicating that some removal was associated with the surfactant properties of the Tween 80. It is also possible that the slightly better performance of the Tween 80 addition may be attributable to the

fact that Tween 80 is a much more complex substrate than glucose; thus, it stimulated enzyme production better suited for Light PAH degradation. Surprisingly, the biodegradation of the Light PAHs appeared to be slower than the Heavy PAHs (Figure 5.13). Light PAHs have been documented to be relatively easy to degrade (Bauer and Capone, 1985; Banerji et al., 1995) in comparison with Heavy PAHs, but in this study, they appeared to have persisted longer than the Heavy PAHs. It is believed that with this study, the high levels of Tween 80 and glucose in the reactors offered a better carbon source than the Light PAHs; thus, the biodegradation of the Light PAHs was hindered. Microorganisms have been documented to selectively degrade a more biodegradable compound (e.g., glucose) over other less biodegradable compounds (e.g., Light PAHs) (Jing, 1998). Thus, both the Tween 80 and glucose were chosen for biodegradation over the Light PAHs. As a result of this selective degradation, only the Heavy PAHs were degraded through the process of co-metabolism that appeared to stimulate natural biosurfactant production.

Figure 5.13 presents the Heavy PAHs removal within the slurries over the course of this test. The results show that the overall Heavy PAH degradation followed the trend observed with both the Total and Light PAHs degradation. The increase in the extractable Heavy PAHs is less pronounced in comparison to the Light PAHs. The set with glucose addition shows a better removal rate of the Heavy PAHs in comparison with the set involving Tween 80 addition. These data tend to contradict the Light PAH data in that glucose provided better removal than the Tween 80. Additionally, it is expected that Tween 80 would have a higher extent and rate of Heavy PAH removal due to its surfactant characteristic. Total removal of the Heavy PAHs was observed with the glucose amended set after 15 weeks of treatment. It took the Tween 80 amended reactors 4

weeks longer to reach these levels. Research has shown that the Heavy PAHs can be biodegraded through the process of co-metabolism with glucose being the sole carbon source (Kazunga et al., 2001).

Summary of the Biotreatment Results

In the Bioavailability Experiment, it was discovered that the biodegradation of naphthalene in the Lake Superior sediment was hindered due to low bioavailability of naphthalene in the aqueous phase and not the enzymatic capability of bacteria for PAH degradation. During the biotreatment of the Scioto River Sediment, it was observed that Tween 80 addition enhanced the bioavailability of both the Light and Heavy PAHs. The results showed that the addition of highly biodegradable substrates, such as Tween 80 and glucose, appeared to have enhanced the Heavy PAH biodegradation in the sediment, but maybe hindered Light PAH biodegradation.

Table 5.1. Results of the Bioavailability Experiments (Performed in duplicate)

Naphthalene degraders + 25 mg/l Naphthalene		
Liquid Phase Analysis		
Time, Hour	Amount of Naphthalene, mg/l	Standard Deviation
0	17.10	7.72
1.6	2.44	0.27
70.1	ND	-
Naphthalene degraders + 31.25 gram of dry sediment:		
Liquid Phase Analysis		
Time, Hour	Amount of Naphthalene, mg/l	Standard Deviation
0	2.81	0.60
1.6	ND	-
70.1	ND	-
Soil Phase Analysis		
Time, Hour	Amount of Naphthalene, mg/l	Standard Deviation
0	284.73	42.62
1.6	219.17	36.06
70.1	244.17	94.67

Note:
- ND: Below detectable limit

Table 5.2. Soil pH during Slurry Phase Bioremediation of the Scioto River Sediment (Performed in duplicate)

Sets	Weeks				
	0	1	2	3	4
Biotic Control	7.58	7.36	7.68	7.39	7.54
100:20:5	7.58	6.67	7.37	7.16	7.32
Bio + 100:20:5	7.58	6.65	7.39	7.14	7.30
Bio + 100:20:5 : Tween 80	7.58	6.07	6.08	5.86	5.66

Notes:
- Bio indicates activated sludge addition on Day 1
- 100:20:5 indicates PAH:N:P ratio
- Tween 80 indicates 3 % by weight of Tween 80 addition once a week (dry sediment basis)

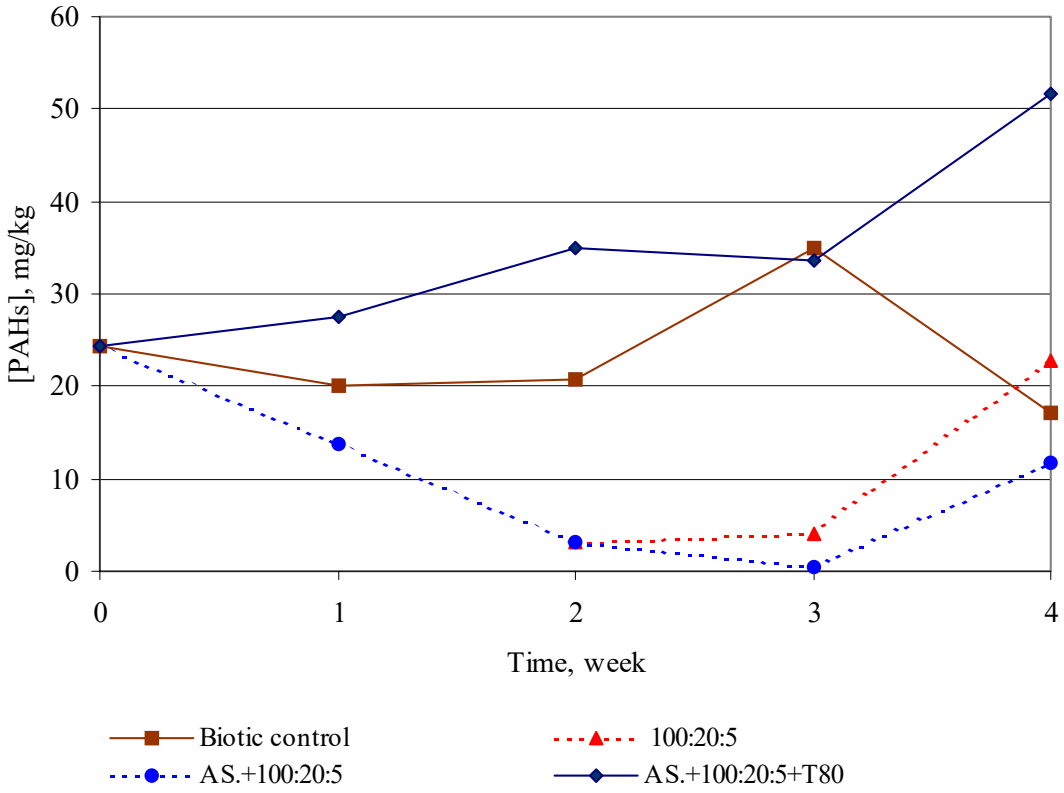


Figure 5.1. Bioremediation Results for Total PAHs in Scioto River Sediment

Notes:
- AS.: Bioaugmentation with activated sludge from the return line of a local wastewater treatment plant
- 100:20:5 represents PAH:N:P ratio
- T80: Tween addition at 0.5% (w/w) the first week and 0.25% (w/w) the following weeks
- These tests were conducted in duplicate

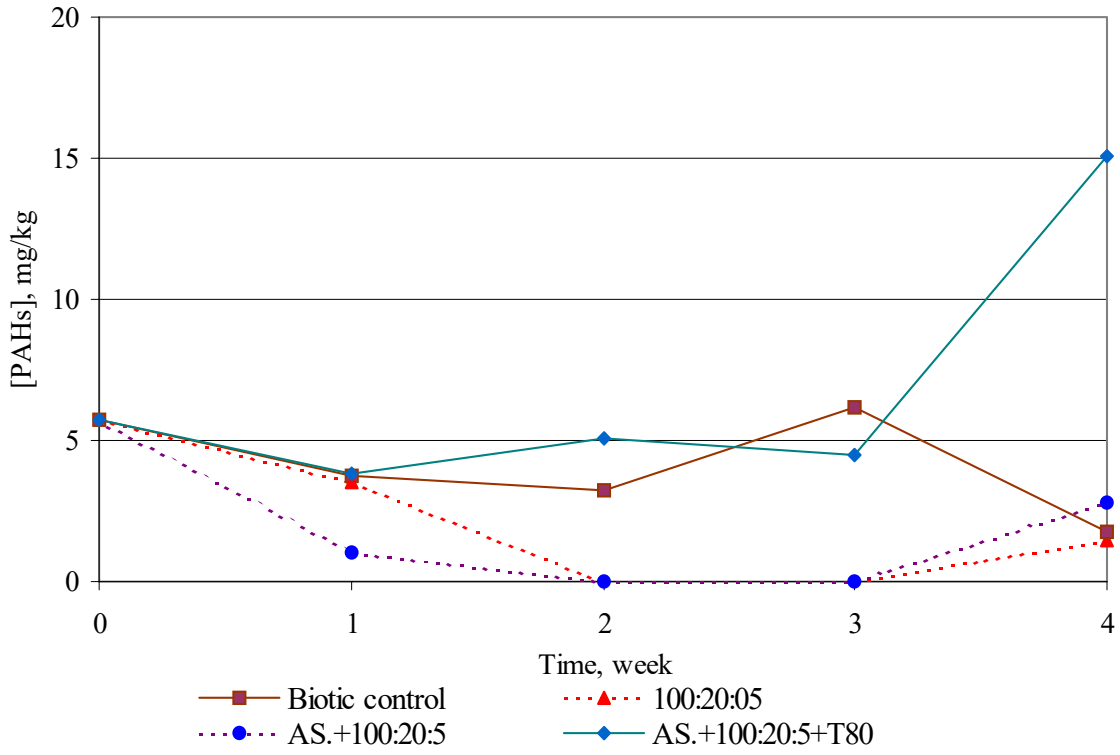


Figure 5.2. Bioremediation Results for Light PAHs in Scioto River Sediment

Notes:
- AS.: Bioaugmentation with activated sludge from the return line of a local wastewater treatment plant
- 100:20:5 represents PAH:N:P ratio
- T80: Tween addition at 0.5% (w/w) the first week and 0.25% (w/w) the following weeks
- These tests were conducted in duplicate

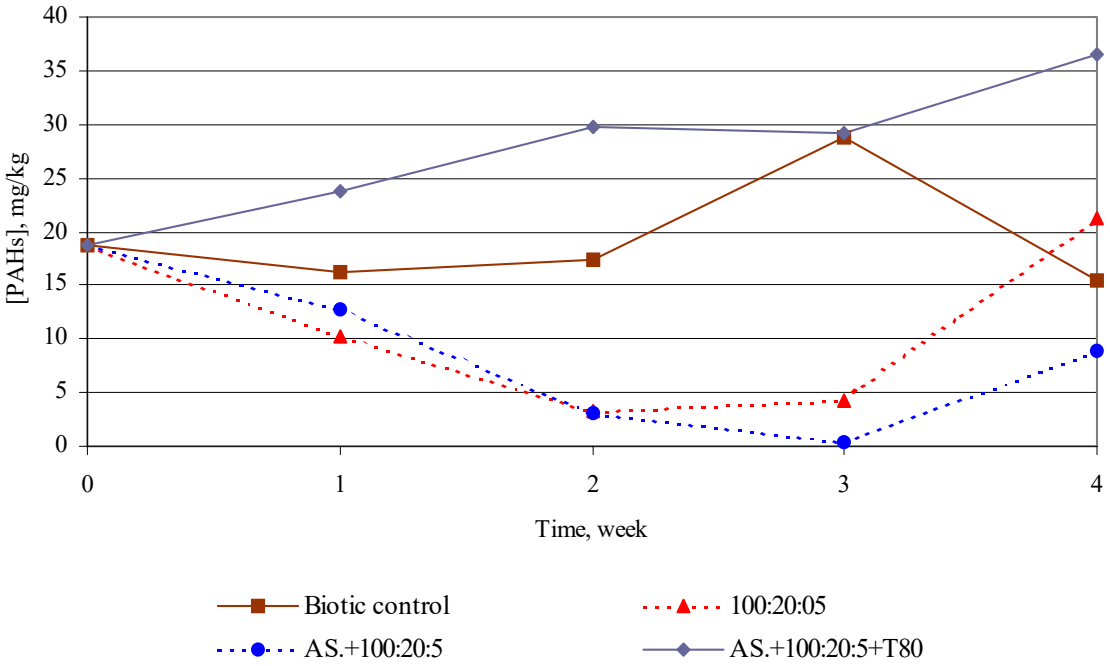


Figure 5.3. Bioremediation Results for Heavy PAHs in Scioto River Sediment

Notes:
- AS.: Bioaugmentation with activated sludge from the return line of a local wastewater treatment plant
- 100:20:5 represents PAH:N:P ratio
- T80: Tween addition at 0.5% (w/w) the first week and 0.25% (w/w) the following weeks
- These tests were conducted in duplicate

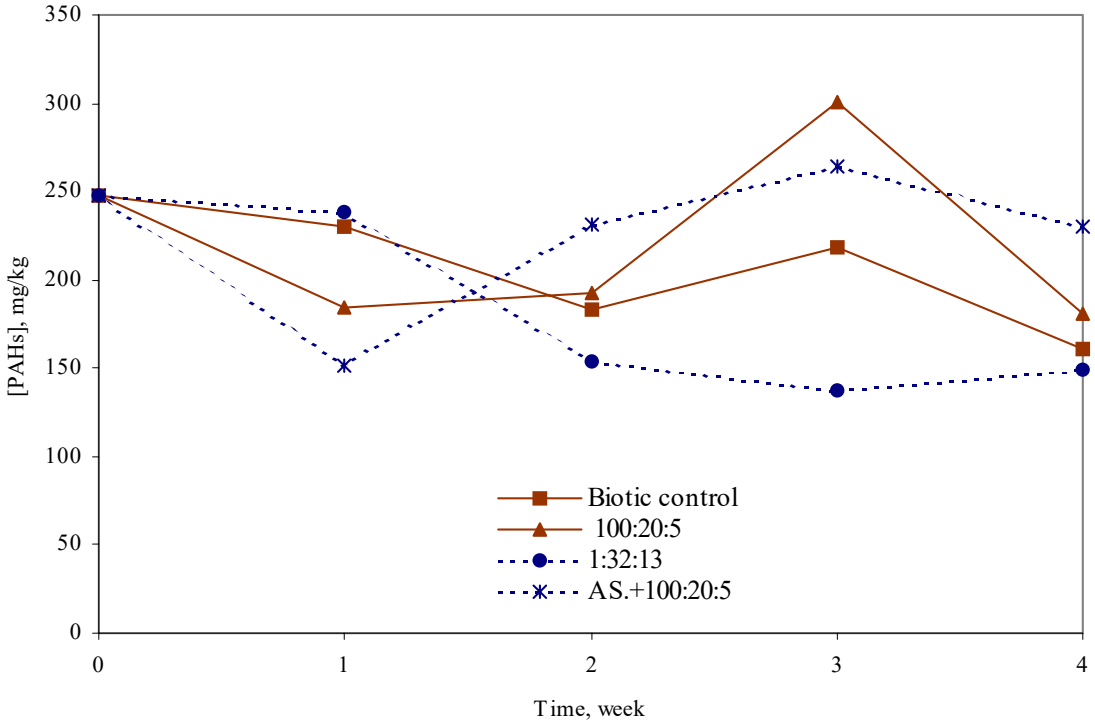


Figure 5.4. Bioremediation Results for Total PAHs in Lake Superior Sediment

Notes:
- AS.: Bioaugmentation with activated sludge from the return line of a local wastewater treatment plant
- 100:20:5 and 1:32:13 represent PAH:N:P ratios
- These tests were conducted in duplicate

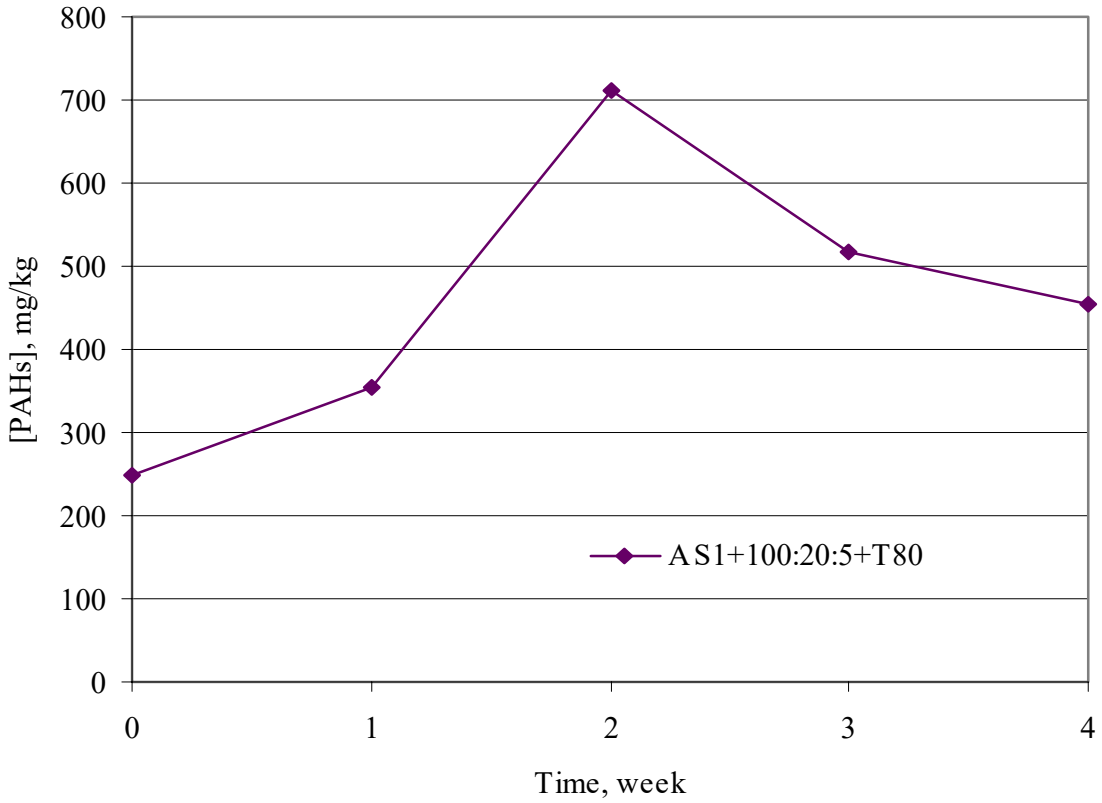


Figure 5.5. Bioremediation Results for Total PAHs in Lake Superior Sediment

Notes:
- AS1: Bioaugmentation with activated sludge from a return line of a swine waste project
- 100:20:5 represents PAH:N:P ratio
- T80: Tween addition at 0.5% (w/w) the first week and 0.25% (w/w) the following weeks
- These were conducted in duplicate

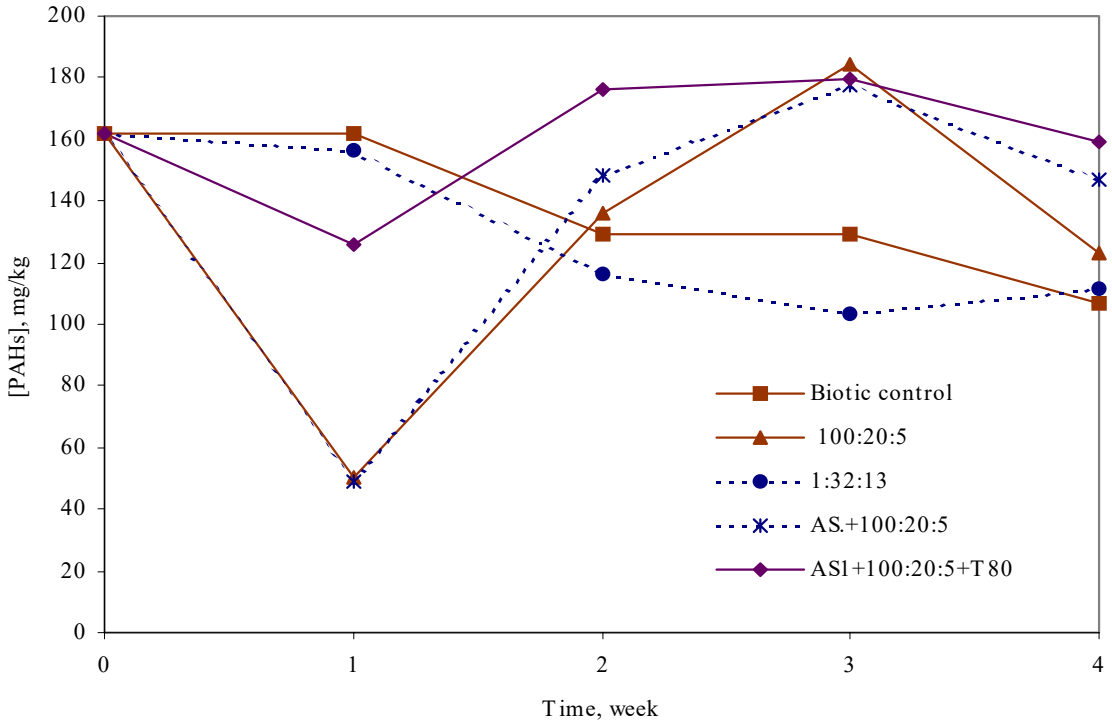


Figure 5.6. Bioremediation Results for Light PAHs in Lake Superior Sediment

Notes:
- AS.: Bioaugmentation with activated sludge from a return line of a local wastewater treatment plant
- AS1: Bioaugmentation with activated sludge from a return line of a swine waste project
- 100:20:5 and 1:32:13 represent PAH:N:P ratios
- T80: Tween 80 addition at 0.5% (w/w) the first week and 0.25% (w/w) the following weeks
- These tests were conducted in duplicate

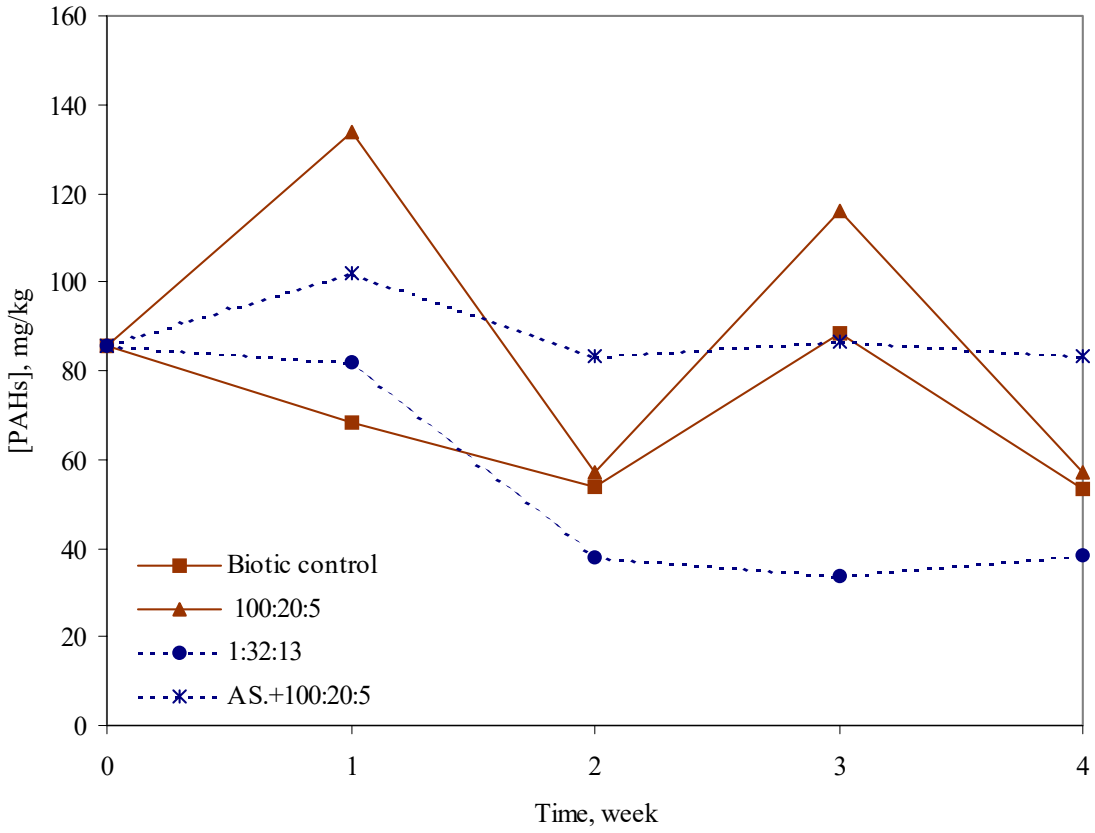


Figure 5.7. Bioremediation Results for Heavy PAHs in Lake Superior Sediment

Notes:
- AS.: Bioaugmentation with activated sludge from a return line of a local wastewater treatment plant
- 100:20:5 and 1:32:13 represent PAH:N:P ratios
- These tests were conducted in duplicate

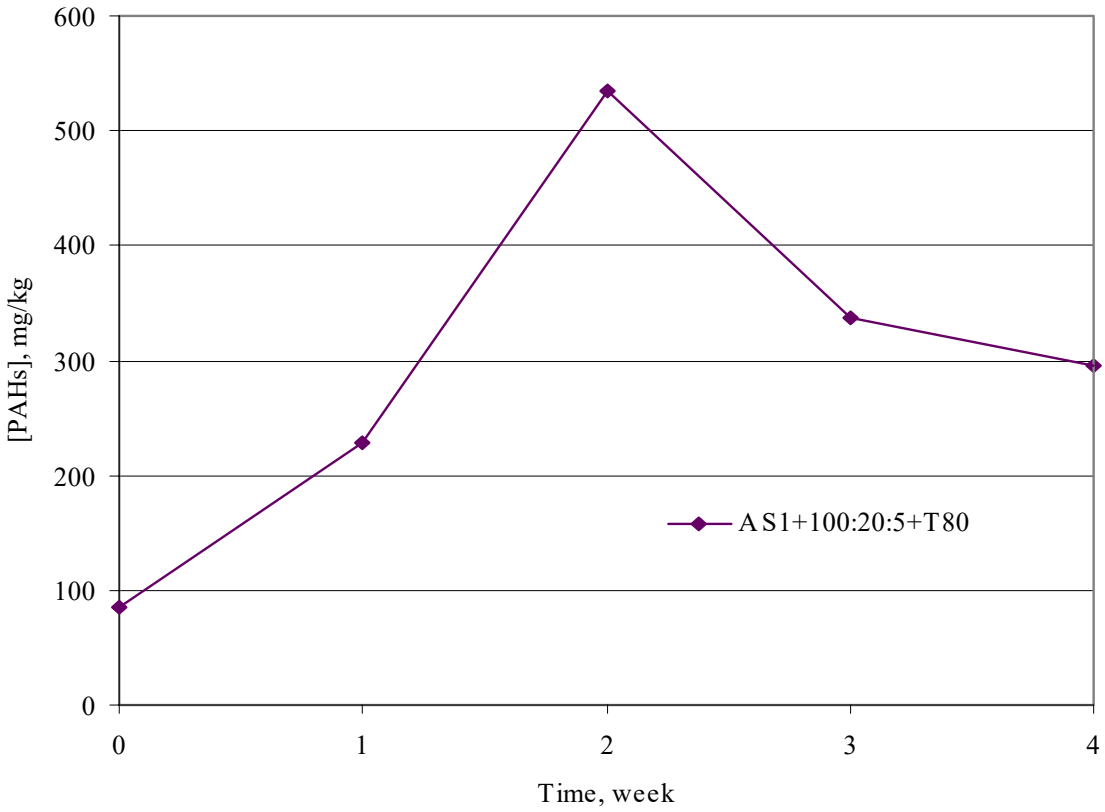


Figure 5.8. Bioremediation Results for Heavy PAHs in Lake Superior Sediment

Notes:
- AS1: Bioaugmentation with activated sludge from the return line of a swine waste project
- 100:20:5 represents PAH:N:P ratio
- T80: Tween 80 addition at 0.5% (w/w) the first week and 0.25% (w/w) the following weeks
- These were conducted in duplicate

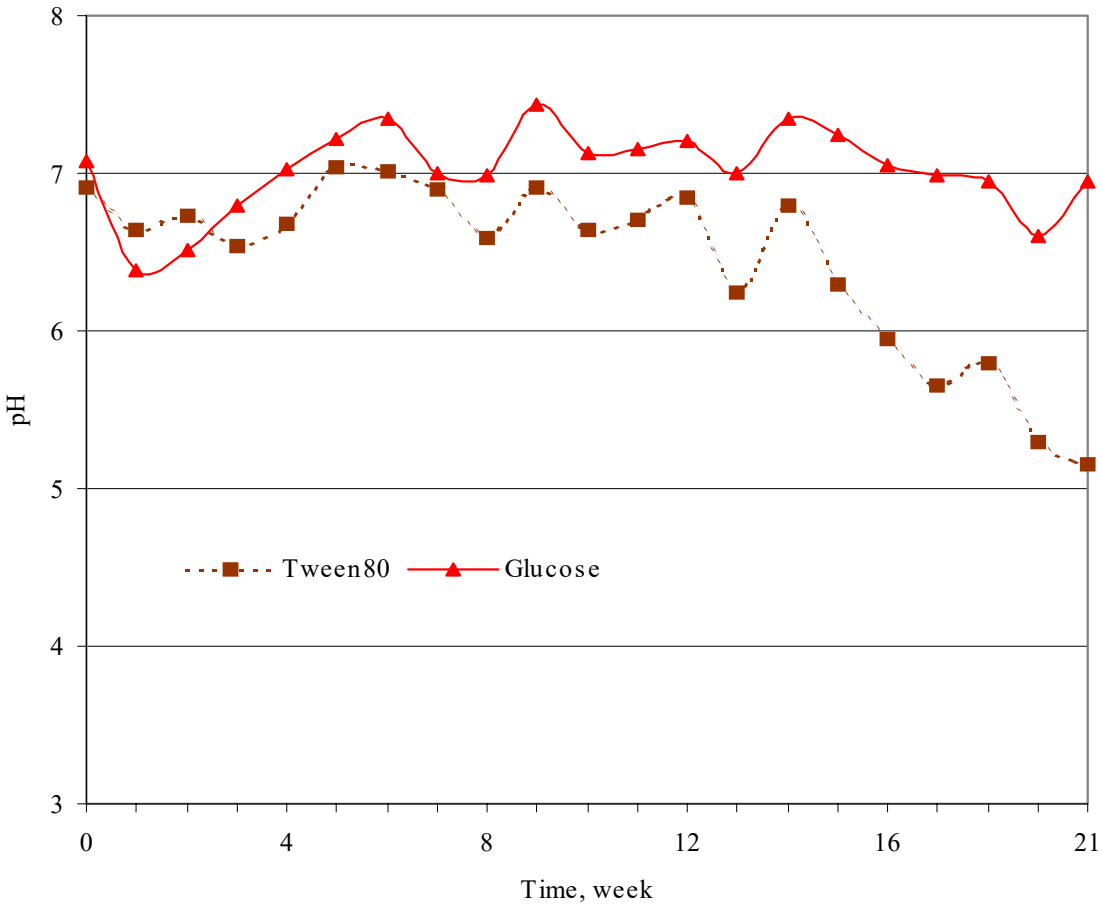


Figure 5.9. pH Measurements for Bioremediation Experiments Involving Tween 80 and Glucose Additions

Notes:
- Glucose : 1,000 mg/l glucose addition once a week
- Tween 80 : 3 % by weight of Tween 80 addition once a week
- These were conducted in duplicate

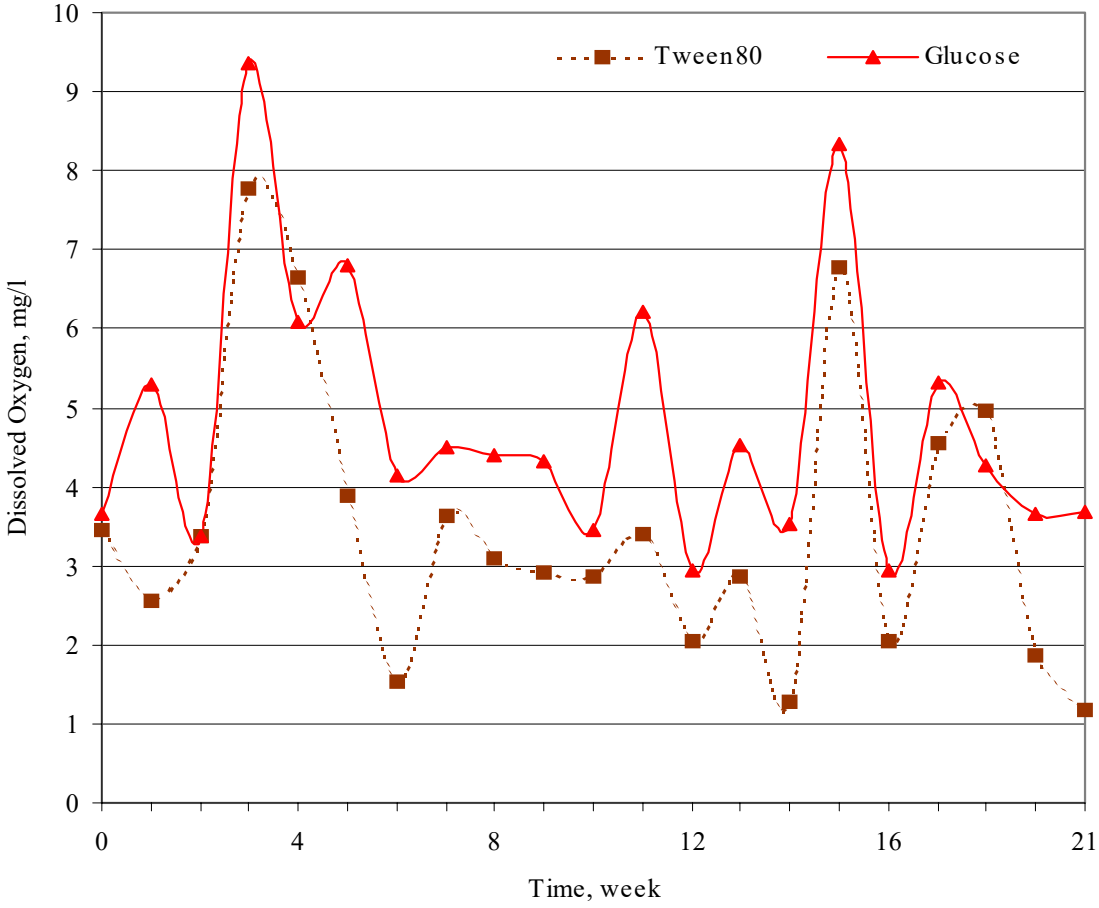


Figure 5.10. Dissolved Oxygen Readings for Bioremediation Experiments Involving Tween 80 and Glucose Additions

Notes:
- Glucose : 1,000 mg/l of glucose addition once a week
- Tween 80 : 3 % by weight of Tween 80 addition once a week
- These were conducted in duplicate

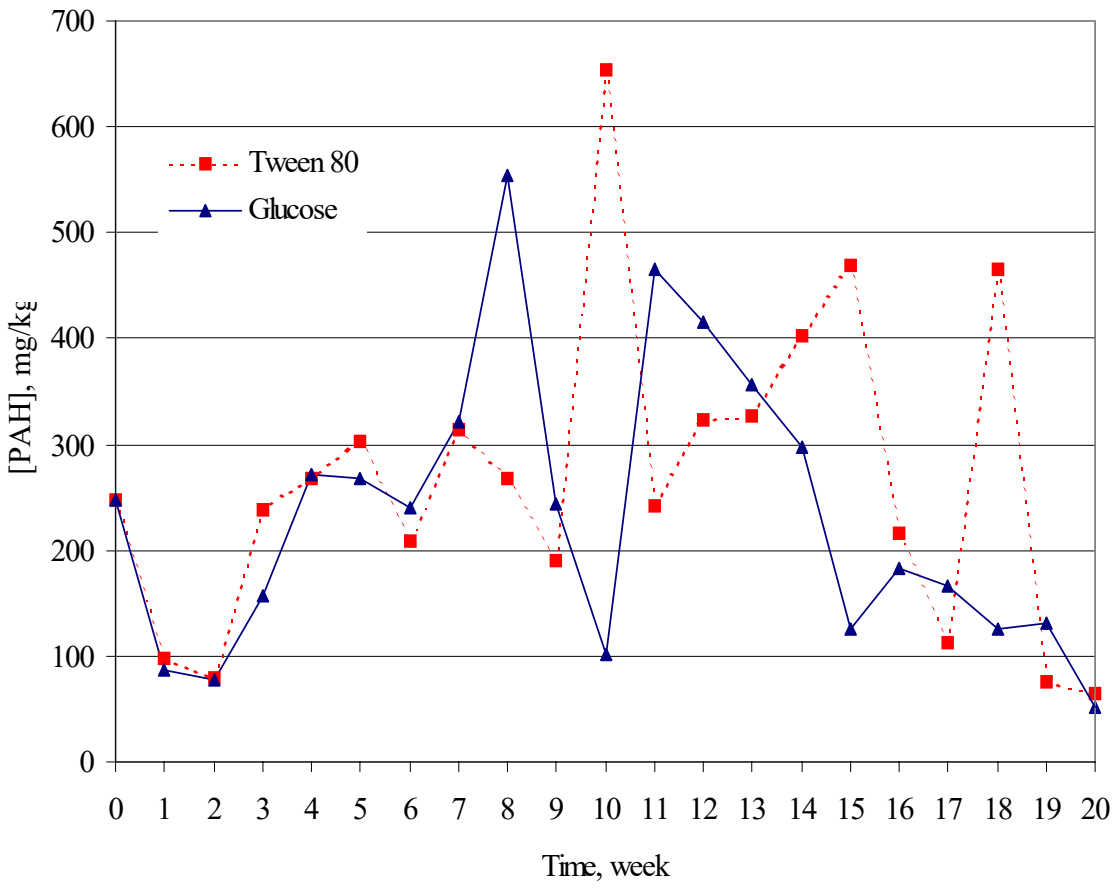


Figure 5.11. Bioremediation Results for Total PAHs in Lake Superior Sediment

Notes:
- Glucose: 1,000 mg/l glucose addition once a week
- Tween 80 : 3% (w/w) Tween 80 addition once a week
- These were conducted in duplicate

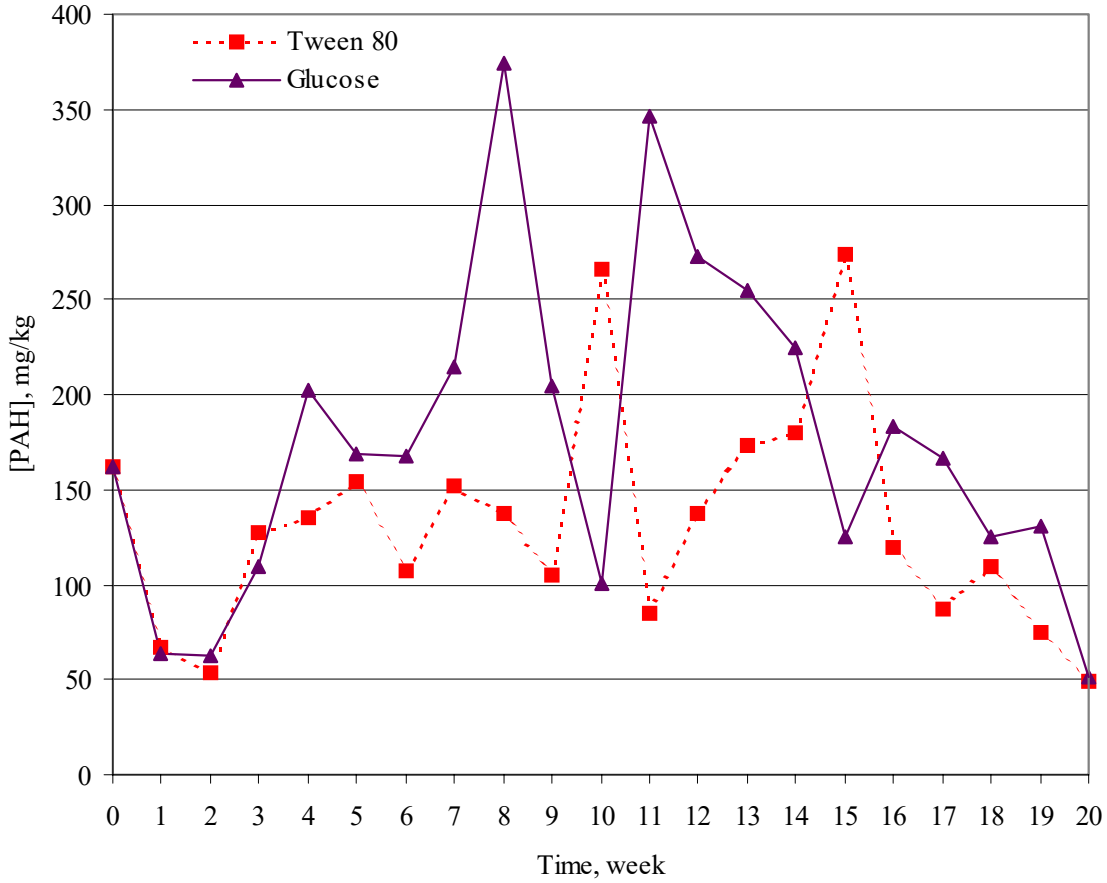


Figure 5.12. Bioremediation Results for Light PAHs in Lake Superior Sediment

Notes:
- Glucose: 1,000 mg/l glucose addition once a week
- Tween 80 : 3% (w/w) Tween 80 addition once a week
- These were conducted in duplicate

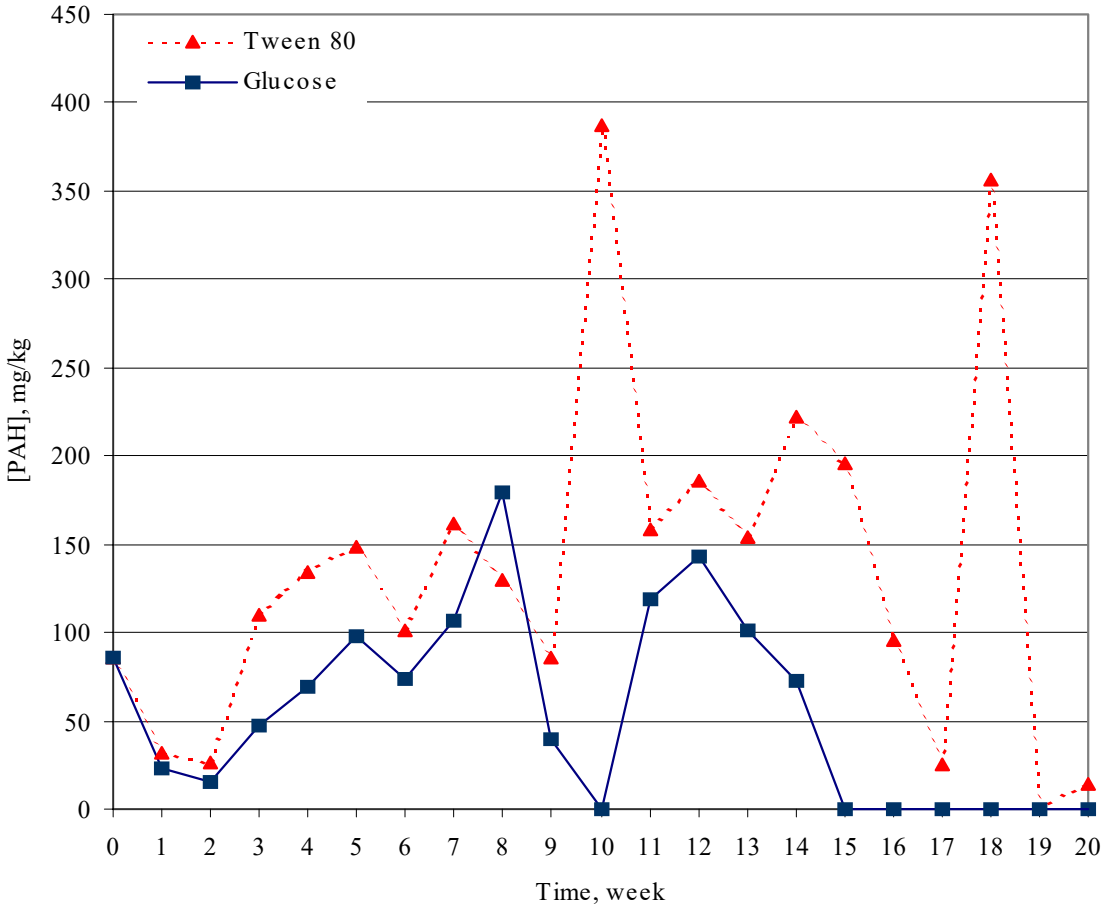


Figure 5.13. Bioremediation Results for Heavy PAHs in Lake Superior Sediment

Notes:
- Glucose: 1,000 mg/l glucose addition once a week
- Tween 80 : 3% (w/w) Tween 80 addition once a week
- These were conducted in duplicate

CHAPTER VI

PHASE I: CHEMICAL OXIDATION SCREENING RESULTS

This series of shake-flask experiments was performed on Lake Superior and Scioto River sediments to determine the impact of chemical oxidation processes, such as ozone, peroxone, and Fenton's Reagent, on the removal of PAHs within the Lake Superior sediment. Additionally, the fate of hydrogen peroxide within these chemically complex sediments systems was studied.

Treatment using Ozone and Peroxone

The objective of these experiments was to evaluate the impact of ozone and peroxone on the removal of PAH within untreated Lake Superior sediment (i.e., no biotreatment). Note that all data represented in x-y plots within this chapter are actually an average of the duplicate sets. The raw data and standard deviations for all of the average data in this chapter are listed in Appendix B.

Figure 6.1 presents the PAH degradation results achieved with ozone. The results show that after two hours of ozonation, approximately 26% of Total PAHs were oxidized. The success with ozone for contaminant removal was also observed by Wang (1999) during the ozonation of soil contaminated with TPH. The author reported that 53% of the TPH in the soil was removed after four hours of treatment. This finding also suggests that further removal of PAHs can likely be achieved with longer ozonation times. This is likely due to the availability of the Light PAHs in the

aqueous phase for reaction with ozone. Light PAHs have a lower affinity for adsorption onto soil than heavier PAHs (Dzombak and Luthy, 1984). The removal of the Light PAHs was 27%. On the other hand, the removal of the Heavy PAHs was 23%.

After the success of the ozone, peroxone was applied for longer treatment times (i.e., 21 hours). Figure 6.2 presents the PAH degradation results achieved with peroxone. The data show that the addition of hydrogen peroxide in the peroxone treatment provided significant degradation of PAH within the first six hours in comparison to the degradation observed in ozone experiments. The removal of the Total PAHs was 43.3%. Light and Heavy PAH removals were 30.4% and 72.9%, respectively. This improved degradation of Heavy PAHs was likely attributable to the availability of these chemicals in the aqueous phase for chemical oxidation. After that, the hydrogen peroxide dosing was increased from 62.5 mg/l to 500 mg/l, with the expectation that the rate of PAHs removal would increase. However, instead of enhancing the degradation, an increase in PAH concentrations was observed. It is speculated that this increase in PAH concentrations is likely due to the attack of the additional hydroxyl radicals on the NOM, and thus, destabilizing the PAH-NOM adsorption bonds resulting in an increase in extractable PAHs. This phenomena was also observed by Kawahara et al. (1995) during the oxidation of PAH-contaminated soils using Fenton's Reagent. Additionally, it is further speculated that an inhibition effect of the PAHs degradation attributed to the scavenging effect of the hydrogen peroxide and scouring action also may have caused these results. Hydrogen peroxide can be a hydroxyl scavenger competing with the PAHs for the hydroxyl radicals; thus, reducing rate of PAH degradation within the slurry (Hong et al., 1996). Although, the actual cause is not known. However, it is noteworthy to point out that

by 18 hours of oxidation a dramatic decrease in PAHs is observed.

Fate of Hydrogen Peroxide in Equilibrated Water Solutions

The objective of this test was to examine the factors controlling the fate of hydrogen peroxide in the equilibrated water solutions. The raw data and standard deviations for all of the average data presented in this section are listed in Appendix B. Table 6.1 lists heavy metals that were detected in both the soil phase and liquid phase of Lake Superior sediment. The results show that the iron concentration was 70 mg/l and that manganese was not present in the liquid phase. This is a high level of iron in terms of potential scavenging effects (Zappi et al., 2000). Given this high amount of iron present, it was expected that reactions between the iron and H_2O_2 would provide a Fenton's type mechanism resulting in PAH degradation during H_2O_2 addition. Among the six types of heavy metals being analyzed in the soil phase, cadmium was not detected. Copper, chromium, lead, zinc, and calcium were detected and present in the sediment at 42.4, 45.3, 64.9, 149, and 10,200 mg/kg, respectively. The amount of calcium in the sediment is below average compared to the reported values for most sediments (around 7,500 mg/kg) (Zappi et al., 2000). The amount of iron in the sediment was not tested because the calibration curve for iron was not available at the time of testing. However, it is expected to be substantial given the amount detected in equilibrated water.

Table 6.1 also lists the total heterotroph counts for the autoclaved and not-autoclaved water samples utilized in the hydrogen peroxide fate experiments. The total heterotroph counts for the not-autoclaved equilibrated water sample was 20 CFUs/ml. On the other hand, no

heterotrophic counts were found in the autoclaved equilibrated water sample and indicating that this water sample was free of bacteria. Since it was free from bacteria prior to the addition of the hydrogen peroxide addition, the hydrogen peroxide consumption in the liquid would be attributed to abiotic process via oxidation of the soluble matters (i.e., reduced cations, NOM, soluble organics, and etc).

Figure 6.3 presents the results from experiments directed toward evaluating the fate of hydrogen peroxide within the equilibrated water samples of Lake Superior. Research has shown hydrogen peroxide is able to oxidize soluble soil-derived matter (reduced cations, NOM, soluble organics, and etc.) in the liquid phase (Zappi et al., 2000). From the data in Figure 6.3, hydrogen peroxide concentrations in the equilibrated water samples that were autoclaved was significantly reduced within the first 30 minutes, before leveling off to about 490 mg/L for the remainder of the test. The reactivity in the hydrogen peroxide is attributable to the oxidation of the soluble matter because of its rapid step-wise character. The results for the equilibrated water samples that were not autoclaved also show the same initial consumption of hydrogen peroxide within the first 30 minutes as that observed with the liquid sample that was autoclaved. This indicates that the initial consumption was also largely due to the abiotic-derived oxidation of soluble matter in the liquid. After 30 minutes, a slow and steady degradation of the hydrogen peroxide concentrations in the biologically active sample was observed. There was 20 CFUs/ml of bacteria present in the equilibrated water samples; thus, this consumption is attributable to bacterial degradation of the hydrogen peroxide. Catalase is an enzyme that is produced as a defense mechanism when bacteria are exposed to hydrogen peroxide, to minimize the damage done to the cell (Zappi et al., 2000).

When catalase comes in contact with the hydrogen peroxide, it converts the hydrogen peroxide into water and oxygen at a very fast rate (Zappi et al., 2000). In general, the hydrogen peroxide consumption in the equilibrated water samples appears to be largely due to abiotic reactions via oxidation of the soluble matter within the sediment.

Figure 6.4 presents the hydrogen peroxide consumption rate (zero-order) obtained for the equilibrated water samples that were not autoclaved (using data from Figure 6.3). As stated before, there were significant amount of metals present in the sediment (see Table 6.1). It is believed that addition of fresh water after each equilibration step breaks apart clumps of soil particles, exposing more soil surface area causing more reduced cations to desorb into the aqueous phase which further degrades the hydrogen peroxide. The results in Figure 6.4 show that the hydrogen peroxide consumption rate increases within the first four equilibration steps prior to a slight decrease on the fifth step. The increase in degradation of the hydrogen peroxide in the liquid phase was due to freshly desorbed cations and humic acids that were easily released within the sediment . On the other hand, the decrease suggests that the rate of desorbed cations was slowing down.

Fate of PAHs and Hydrogen Peroxide within the Sediment

The objectives of these experiments are to determine the factors controlling the fate of hydrogen peroxide in the sediment and the impact of sequential hydrogen peroxide dosing on PAH fate within the sediment. The raw data and standard deviations for all of the average data presented in this section are listed in Appendix B.

1,000 ppm H_2O_2 Experiments

Figure 6.5 presents the zero order rate constant results of experiment directed toward evaluating the fate of hydrogen peroxide within the slurries. The hydrogen peroxide concentration applied each time was 1,000 mg/L. The results show that the highest consumption rate of hydrogen peroxide was observed after the first application. After three consecutive additions of hydrogen peroxide to the sediment, the hydrogen peroxide consumption rate appeared to decrease, in comparison to the first applied dose. Despite the decrease in the consumption rate, the hydrogen peroxide was still being degraded continuously over the entire course of this test (see Table 6.2). This trend also was observed in the previous experiment examining the fate of hydrogen peroxide in equilibrated water solutions. It is believed that the high consumption rate of the hydrogen peroxide within the first three hydrogen peroxide applications was attributable to the oxidation by dissolved cations and humic acids that were easily released in the sediment. Then, the slow consumption rate of hydrogen peroxide after the third dosing application was primarily attributable to bacterial degradation. Pardiek et al. (1992) reported that the hydrogen peroxide concentration between 10 and 1,000 mg/l range inhibits bacterial growth, but does not destroy the microorganisms. This finding suggests that higher amounts of hydrogen peroxide are required to destroy the microorganisms capable of producing catalase before significant reduction in biological decay can be observed.

Figure 6.6 presents PAHs degradation results achieved with the 1,000 mg/l hydrogen peroxide dosing. These data show an increased in PAH concentrations after dosing with the hydrogen peroxide. This increase is likely attributed to the weakening of the adsorption bonds and

erosion of soil agglomerates due to the scouring action caused by the foaming and agitation. Both of these act upon the extraction efficiency of the analytical process. This effect is clearly illustrated by comparing the change in both Light and Heavy PAH concentrations before and after testing. The Light PAHs are not as strongly adsorbed onto the soil particles as are the Heavy PAHs. Degradation of the adsorption bonds clearly increase the extractability of the Heavy PAHs with little impact on the Light PAHs noted.

10,000 ppm H_2O_2 Experiments

Figure 6.7 presents the zero order rate constant results of experiment directed toward evaluating the fate of hydrogen peroxide within the slurries using a 10,000 ppm H_2O_2 dose. This set of experiment was conducted similar to the previous experiments, except that the dosing concentration of the hydrogen peroxide was 10,000 ppm instead of 1,000 ppm.

From Figure 6.7, the highest consumption rate of hydrogen peroxide was observed during the first three applications. After several consecutive additions of hydrogen peroxide to the sediment, the hydrogen peroxide consumption rate appears to decrease, in comparison to the first and third dosing step. Despite the decrease in the consumption rate, the hydrogen peroxide was still being degraded continuously throughout testing (see Table 6.3). This trend also was observed in the previous experiment involving the 1,000 mg/l hydrogen peroxide dosing, suggesting that the consumption of hydrogen peroxide also could be attributed to the combined effect of both abiotic and biotic degradation. It has been reported that hydrogen peroxide is also capable of degrading organic matter (i.e., humic acids) and oxidizing reduced cations (i.e., Fe and Cu) (Yuteri and Gurol,

1991; Zappi et al., 2000). These findings indicate that the consumption of the hydrogen peroxide was likely due to the combination of catalase degradation and the oxidation of the reduced cations and organic matter which are both present in the sediment (see Table 6.1).

Figure 6.8 presents the PAHs degradation results achieved with the 10,000 mg/l hydrogen peroxide dosing. The Light, Heavy, and Total PAHs results show that the addition of hydrogen peroxide at 10,000 mg/l had the similar effect on the removal of PAHs as observed with the 1,000 ppm dose. However, the final amount of Heavy PAHs for this set involving 10,000 ppm hydrogen peroxide addition is slightly lower than the amount observed in the set involving the 1,000 ppm hydrogen peroxide addition. The extent of Light, Heavy, and Total PAHs degradation appears to increase with increasing hydrogen peroxide dosing concentration. This is expected since the higher hydrogen peroxide dose inputs more oxidation capability into the test system.

100,000 ppm H_2O_2 Experiments

This section involves the discussion of results of the experiments directed towards the evaluation of the fate of hydrogen peroxide within the slurries (autoclaved and not-autoclaved sediment samples) using a 100,000 ppm H_2O_2 dose. The total heterotrophic counts for the sediment sample that was not-autoclaved was 4,889 CFUs/g (see Table 6.1). No heterotrophic counts were found on the sediment sample that it was autoclaved, indicating that was free from bacteria prior to the addition of hydrogen peroxide (see Table 6.1). Again, the sediment was autoclaved at 121°C and 15 psi. This indicates that any hydrogen peroxide reactivity within the sediment would likely be attributed to abiotic process via the oxidation of reduced cations (i.e.,

ferrous ion and copper ion) present in the sediment.

Figure 6.9 presents the results of an experiment directed toward evaluating the fate of hydrogen peroxide within the slurries. During the treatment period between 41 and 83 hrs, the sediment that was autoclaved exhibited a slightly higher hydrogen peroxide consumption than the sediment that was not autoclaved. After several repetitive additions of hydrogen peroxide, the hydrogen peroxide consumption for the sediment that was autoclaved showed a slightly slower reactivity in comparison to the sediment that was not autoclaved. However, since testing was not performed to observe the tailing of degradation, an attempt at separating mechanisms of hydrogen peroxide degradation (biotic vs. abiotic) cannot be made. Despite this slight decrease in consumption rate, the hydrogen peroxide was still being very rapidly degraded. The total organic carbon concentration recorded for this sediment is approximately 100,000 mg/kg (see Table 4.1), which is higher than an average value of around 7,500 mg/kg for most sediments (Zappi et al., 2000). Thus, it is believed that the high reactivity of the hydrogen peroxide was attributed to the oxidation of the humic acids and reduced cations found in the sediments. Similar phenomena were observed by Zappi et al. (2000) who noticed the reactivity of the hydrogen peroxide in the equilibrated water samples that contained higher levels of humic acids than for those samples with much lower TOC levels.

Figure 6.10 presents the Light, Heavy, and Total PAHs degradation results achieved with the 100,000 mg/l hydrogen peroxide dosing. It is interesting to note that there was an increase in the level of extractable Total PAHs after the autoclave process. Research has shown organic matter converts into carbon dioxide and water at high temperature conditions (Debellefontaine et

al., 1996). This finding suggests the PAH-organic adsorption bonds were likely degraded under the extreme heat of the autoclave process. Nonetheless, after several consecutive additions of hydrogen peroxide, 72% of the Total PAHs was degraded in the sediment that was autoclaved. Clearly, the degradation of the adsorption sites provided an increase in the availability of the PAHs for chemical oxidation. This finding suggests the significant consumption of the hydrogen peroxide was likely due to the oxidation of the PAHs. On the other hand, the data for the sediment that was not autoclaved did not show degradation of PAHs after the hydrogen peroxide treatment, yielding speculation that adsorptive-based mass transfer limitations greatly impacted the ability of the oxidizer to degrade the PAHs within the sediment.

The results (Figure 6.10) also show that 21% of the Light PAHs were removed from the sediment that was not autoclaved; meanwhile, 16% of the Light PAHs were removed from the sediment that was autoclaved. In terms of the removal of Heavy PAHs, the significant increase in the level of extractable Total PAHs for the sediment that was autoclaved was mainly the Heavy PAHs. No degradation of Heavy PAHs was observed for the sediment sample that was not autoclaved. However, the final amount of Heavy PAHs for this set involving 100,000 ppm hydrogen peroxide addition is slightly lower than the amount observed in the set involving the 1,000 or 10,000 ppm hydrogen peroxide addition. On the other hand, the Heavy PAHs degradation in the sediment that was autoclaved sediment was 81%. Thus, a substantially higher Heavy PAHs removal was observed with the sediment that was autoclaved. Again, this trend was likely attributable to the availability of these chemicals in the aqueous phase for reaction with hydrogen peroxide.

Treatment using Fenton's Reagent

25K-10:1 Ratio and 100K-10:1 Ratio Experiments

Based on the success of the previous experiments on removing some of the PAHs from the sediment, a series of more refined applications of Fenton's Reagent were attempted. The objective of this set of experiments was to determine the impact of Fenton's Reagent on PAH fate within the sediment. Note that these data represent an average of duplicate sets. The raw data and standard deviations for all of the average data are listed in Appendix B. The applied Fenton's Reagent dosages were 25,000 mg/l hydrogen peroxide/2,500 mg/l ferrous sulfate (25K-10:1 ratio) and 100,000 mg/l hydrogen peroxide/10,000 mg/l ferrous sulfate (100K-10:1 ratio). On the 4th dosing, a concentrated ferrous sulfate solution prepared for the 100K-10:1 ratio reactors was accidentally added to one of the 25K-10:1 ratio reactors; thus, both the replicates were spiked with 10,000 ml ferrous sulfate. After 24-hour equilibration time, 100,000 mg/l hydrogen peroxide was added to both replicates. From that point on, the applied dosing concentrations of hydrogen peroxide and ferrous sulfate for the 25K-10:1 ratio experiments were increased to 100,000 mg/l and 10,000 mg/l, respectively.

Figure 6.11 presents the Total PAHs degradation achieved with Fenton's Reagent. The results show that Total PAHs degradation in the 100k-10:1 ratio experiments was relatively better in comparison to the Total PAHs degradation observed in the 25K-10:1 ratio experiments. A slight increase in Total PAHs within the sediment was observed for the 25K-10:1 ratio experiments prior to a decrease after the fourth dosing. This increase was likely attributable to hydroxyl radical

oxidation of the NOM which destabilized the PAH-NOM adsorption bonds resulting in an increase in the extractable PAHs within the sediment. As mentioned before, the dosing concentration of Fenton's Reagent for the 25K-10:1 ratio experiments was accidentally increased to 100,000 mg/l and 10,000 mg/l on the fourth dosing and at the same time, the degradation of PAHs was also observed. This is expected since higher Fenton's Reagent dose inputs more oxidation capability into the test system.

From Figure 6.12, the degradation of Light PAHs followed the trend observed with the degradation of Total PAHs (see Figure 6.11). Additionally, the increase in Total PAHs amount during the fourth dosing application for the both sets of experiments was mainly due to the increase in Light PAHs amount within the sediment. This phenomena was attributable to the increase of extractable PAHs via oxidation of PAH-NOM adsorption bonds.

From Figure 6.13, the results show that the degradation of Heavy PAHs was slightly greater in the 100K-10:1 ratio experiments than the 25K-10:1 ratio experiments. For the 100K-10:1 ratio experiments, Heavy PAHs degradation was observed after the first dosing application. The Heavy PAHs degradation was continuously degraded with further additions of Fenton's Reagent. A slight increase in the Heavy PAHs was observed during the fourth dosing application of the Fenton's Reagent prior to complete removal of the Heavy PAHs during the fifth addition. For the 25K-10:1 ratio experiments, Heavy PAHs degradation became more aggressive after the accidental increase of Fenton's Reagent dosing concentration (25K-10:1 ratio experiments) during the fourth dosing. After seven consecutive additions of Fenton's Reagent to the slurry, complete removal of Heavy PAHs within the sediment was observed.

Overall, 69% and 81% of the Total PAHs were removed from the 25K-10:1 ratio and 100K-10:1 ratio experiments, respectively. The degradation of the Light PAHs was 55% and 73% for the 25K-10:1 ratio and 100K-10:1 ratio experiments, respectively. On the other hand, Heavy PAHs were not detected after the 5th and 7th dosing for the 100K-10:1 ratio and 25K-10:1 ratio experiments, respectively.

In general, the PAH degradation in the sediment is more aggressive and greater in the 100K-10:1 ratio experiments in comparison with the 25K-10:1 ratio experiments. The Light PAHs degradation appeared to be slower than the Heavy PAHs. The Heavy PAHs degradation was faster with the 100K-10:1 ratio experiment. However, the experiment using lower amounts of hydrogen peroxide and ferrous sulfate accomplished the same removal of the Heavy PAHs (25K-10:1 ratio experiment) as the higher dosed system. Thus, the addition of Fenton's Reagent at lower concentrations (25K-10:1 ratio experiment) was comparably as effective and more economical than the higher dosed condition (100K-10:1 ratio experiment). This conclusion is based on the fact that same removal or enhancement efficiency was achieved for the PAHs in both sets.

Summary of the Chemical Oxidation Results

In the ozone and peroxone experiments, the objectives were to determine the impact of ozone and peroxone on PAHs. Ozone was found to result in PAH removal from the sediment. On the other hand, the addition of hydrogen peroxide in the peroxone process appeared to have increased the availability of the PAHs within the sediment via oxidation of the PAH-NOM

adsorption bonds.

In the Fate of Hydrogen Peroxide in Equilibrated Water Solutions Experiments, the objective was to determine the factor controlling the hydrogen peroxide reactivity in the liquid phase. It was discovered that the degradation of hydrogen peroxide in the liquid phase was likely due to abiotic process via oxidation of soluble matter (i.e., reduced cations, NOM, and etc.) with a tailing effect that was observed is attributed to biotic reactions.

From the Fate of Hydrogen Peroxide within the Sediment Tests, the objectives were to determine the fate of hydrogen peroxide within the sediment and assess the impact of the hydrogen peroxide addition on the PAHs. The results showed that the fate of the hydrogen peroxide was influenced by both soluble matter (e.g., NOM) and microbes via catalase degradation. In terms of the PAH removal, PAHs degradation was observed in the set involving 100,000 ppm H_2O_2 dosing concentration (autoclaved sediment) and limited removal observed for the sediment that was not autoclaved. However, the Total PAHs after the addition of hydrogen peroxide is lower than the Total PAHs observed with the 1,000 ppm and 10,000 ppm H_2O_2. This indicates that the removal of Total PAHs is slightly better in the set 100,000 ppm in comparison to the 1,000 ppm or 10,000 ppm H_2O_2.

In the Fenton's Reagent experiments, the objective was to investigate the impact of Fenton's Reagent addition on PAHs. The results showed that the addition of Fenton's Reagent at higher dosing concentration (100,000 ppm H_2O_2 / 10,000 ppm Fe^{2+}) did not improve the degradation of Total PAHs within the sediment over the other set (25,000 ppm H_2O_2 / 2,500 ppm Fe^{2+}) (see Figure 6.11). The Light PAHs degradation in both sets was inhibited. This was likely

attributed to the unavailability of these chemicals for the oxidation. In terms of Heavy PAHs, the addition of Fenton's Reagent with higher dosing concentration (100,000 ppm H_2O_2 / 10,000 ppm Fe^{2+}) yielded better performance in the removal of the Heavy PAHs within the sediment in comparison to the other set (25,000 ppm H_2O_2 / 2,500 ppm Fe^{2+}) (see Figure 6.13). Nonetheless, the Heavy PAHs were not detected within the sediment after 7 applications of Fenton's Reagent at 25,000 ppm H_2O_2 / 2,500 ppm Fe^{2+}. Note that the dosing concentration for this set was accidentally increased to 100,000 ppm H_2O_2 / 10,000 ppm Fe^{2+} during the fourth dosing. The cumulative total amount of hydrogen peroxide and ferrous sulfate utilized for the 100,000 ppm H_2O_2 / 10,000 ppm Fe^{2+} was 700,000 ppm and 70,000 ppm, respectively. On the other hand, the cumulative total amount of hydrogen peroxide and ferrous sulfate utilized for the 25,000 ppm H_2O_2 / 2,500 ppm Fe^{2+} was 475,000 ppm and 47,500 ppm, respectively. Since the same removal of Heavy PAHs was achieved with both dosing concentrations of Fenton's Reagent, it was believed that the addition of Fenton's Reagent at increasing dosing concentration was more economical. The cumulative total amount of hydrogen peroxide and ferrous sulfate utilized for the 100,000 ppm H_2O_2 / 10,000 ppm Fe^{2+} was 700,000 ppm and 70,000 ppm.

Table 6.1. Results of Heavy Metals Analysis and Total Heterotrophic Counts for the Liquid and Soil Phases, Lake Superior Sediment (Performed in triplicate)

Liquid Phase	
Analysis[1]	Amount, mg/l
Iron	70
Manganese	ND
Soil Phase[2]	
Analysis	Amount, mg/kg
Cadmium	ND
Calcium	10,200
Chromium	45.3
Copper	42.4
Lead	64.9
Zinc	149
Total Heterotroph Count	Not-Autoclaved[3]
Liquid Phase, CFUs/ml	20
Soil Phase[1], CFUs/g	4,889

Notes:
[1]Described in the Analytical Methods
[2]Analyzed according to EPA 3051
[3]No CFUs were observed in autoclaved set
- ND: Below detectable limit

Table 6.2. Experimental Results for the 1,000 mg/l Hydrogen Peroxide Reactivity Experiment (Performed in triplicate)

Treatment time, hr	Liquid phase [H_2O_2], mg/l	H_2O_2 added, mg/l	• [H_2O_2], mg/l
0	1000	1000	1000
2	45	1000	2000
4	432	None added	None added
6	142	1000	3000
24	12	1000	4000
26	812	None added	None added
28	413	None added	None added
30	233	1000	5000
48	30	1000	6000
60	7	1000	7000
84	13	None added	None added

Table 6.3. Experimental Results for the 10,000 mg/l Hydrogen Peroxide Reactivity Experiment (Performed in triplicate)

Time, hr	Liquid phase $[H_2O_2]$, mg/l	H_2O_2 added, mg/l	• $[H_2O_2]$, mg/l
0	10000	10000	10000
2	7017	None added	None added
4	4283	None added	None added
6	2167	10000	20000
24	67	10000	30000
26	7467	None added	None added
28	3617	None added	None added
30	2167	10000	40000
48	83	10000	50000
60	83	10000	60000
84	67	None added	None added

Table 6.4. Experimental Results for the 100,000 mg/l Hydrogen Peroxide Reactivity Experiment (Performed in triplicate)

Time, hr	Liquid phase $[H_2O_2]$, mg/l		H_2O_2 added, mg/l	• $[H_2O_2]$, mg/l
	Autoclaved	Not-Autoclaved		
0	100,000	100,000	100,000	100,000
1	94,000	65,667	None added	None added
20	5,833	8,166	100,000	200,000
21	75,500	69,000	None added	None added
23	44,500	42,833	None added	None added
41	500	4,500	100,000	300,000
42	56,000	45,167	None added	None added
43	41,000	45,500	None added	None added
44	26,167	37,833	None added	None added
45	10,166	31,000	None added	None added
46	4,500	26,500	None added	None added
61	500	500	100,000	400,000
62	51,500	48,167	None added	None added
63	30,833	38,833	None added	None added
64	4,666	17,333	100,000	500,000
83	500	833	100,000	600,000
87	10,166	17,000	None added	None added
91	75,000	70,167	100,000	700,000
92	45,333	39,167	None added	None added
105	42,167	40,500	100,000	800,000

Table 6.4. (Continued)

Time	Liquid phase [H_2O_2], mg/l		H_2O_2 added, mg/l	• [H_2O_2], mg/l
	Autoclaved	Not-Autoclaved		
106	29,333	24,500	None added	None added
127	500	500	None added	None added
130	52,167	47,500	100,000	900,000
132	32,000	22,833	None added	None added
135	11,667	7,500	None added	None added
149	1,167	1,166	100,000	1,000,000
150	67,000	53,833	None added	None added
151	49,833	44,667	None added	None added
152	42,333	34,333	None added	None added
154	27,167	22,333	None added	None added
173	1,167	1,000	100,000	1,100,000
174	45,833	52,333	None added	None added
175	40,500	38,667	None added	None added
177	32,667	29,500	None added	None added
222	500	500	None added	None added

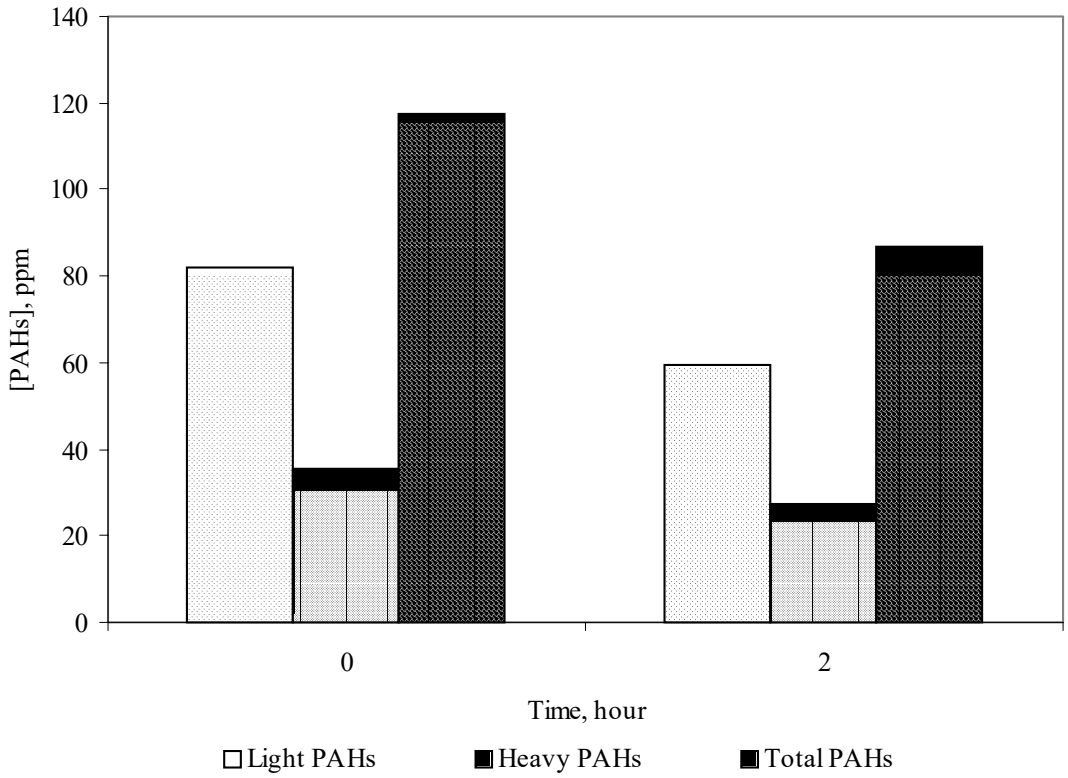


Figure 6.1. Ozone Treatment of PAHs in the Lake Superior Sediment

Condition:
- 3% (w/w) ozone at 2.5 scfh

Note:
- These were conducted in duplicate

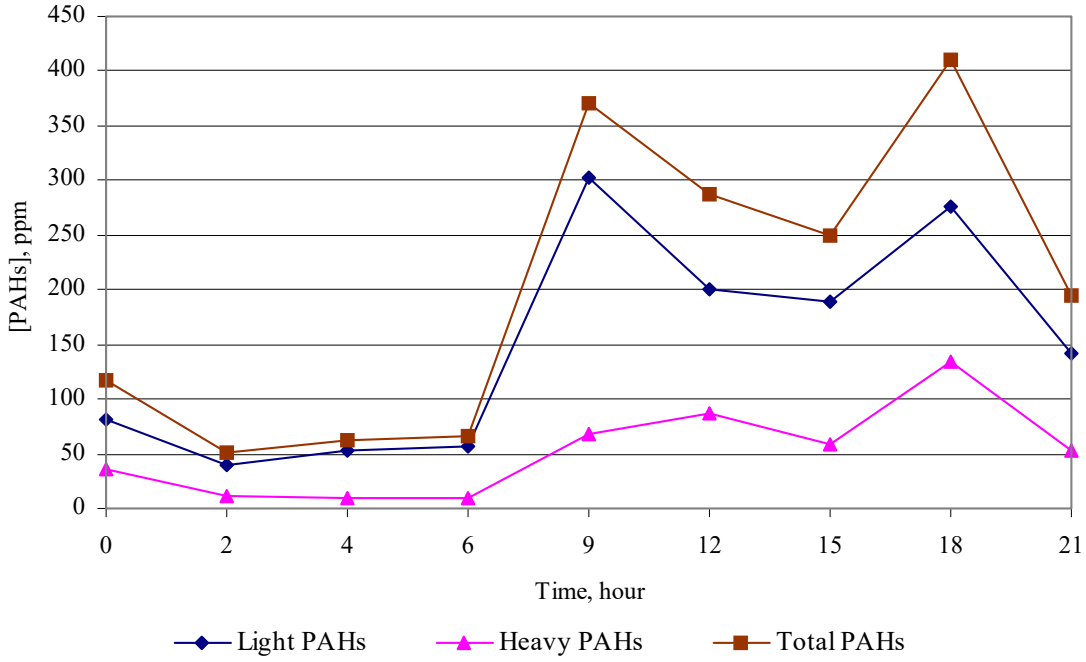


Figure 6.2. Peroxone Treatment of PAHs in the Lake Superior Sediment

Conditions:
- 3% (w/w) ozone at 2.5 scfh
- 65.5 mg/l H_2O_2 addition every two hours for the first six hours and 500 mg/l H_2O_2 addition every three hours for the next 15 hours

Note:
- These were conducted in duplicate

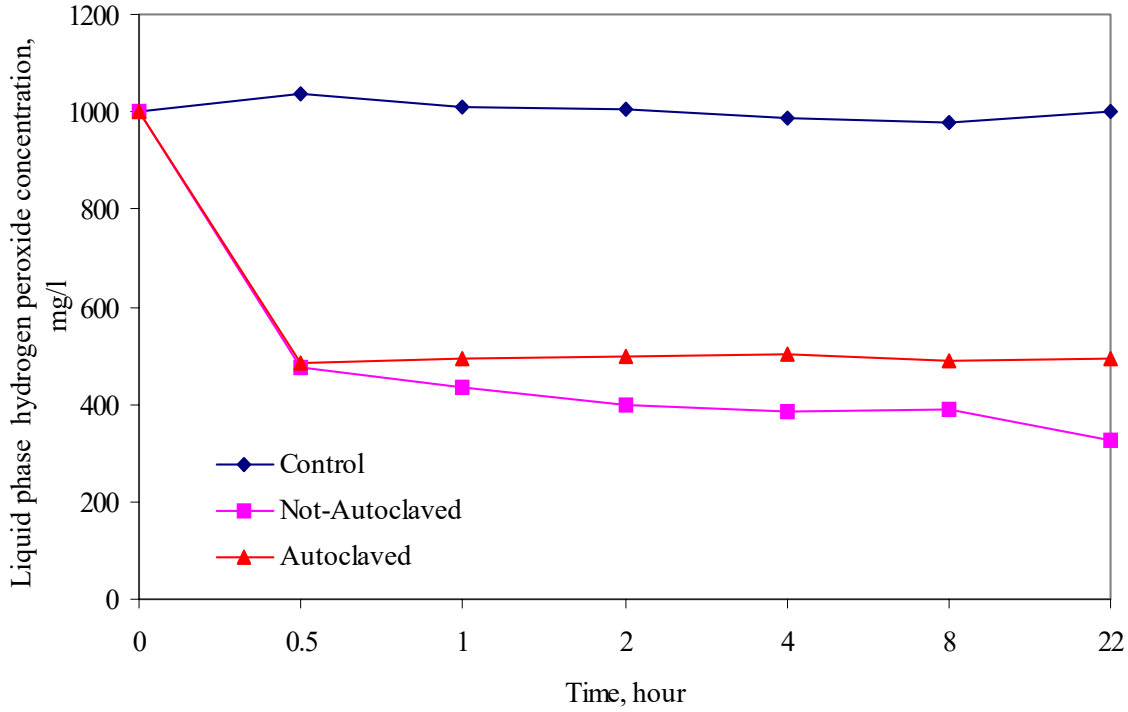


Figure 6.3. Liquid Phase H_2O_2 Reactivity in Equilibrated Water Solution (Lake Superior Sediment)

Notes:
- Control: 1,000 mg/l hydrogen peroxide solution
- Not-Autoclaved: Equilibrated water solution (Ten replicates)
- Autoclaved: Equilibrated water solution that was autoclaved at 121°C and 15 psi steam (Two replicas)

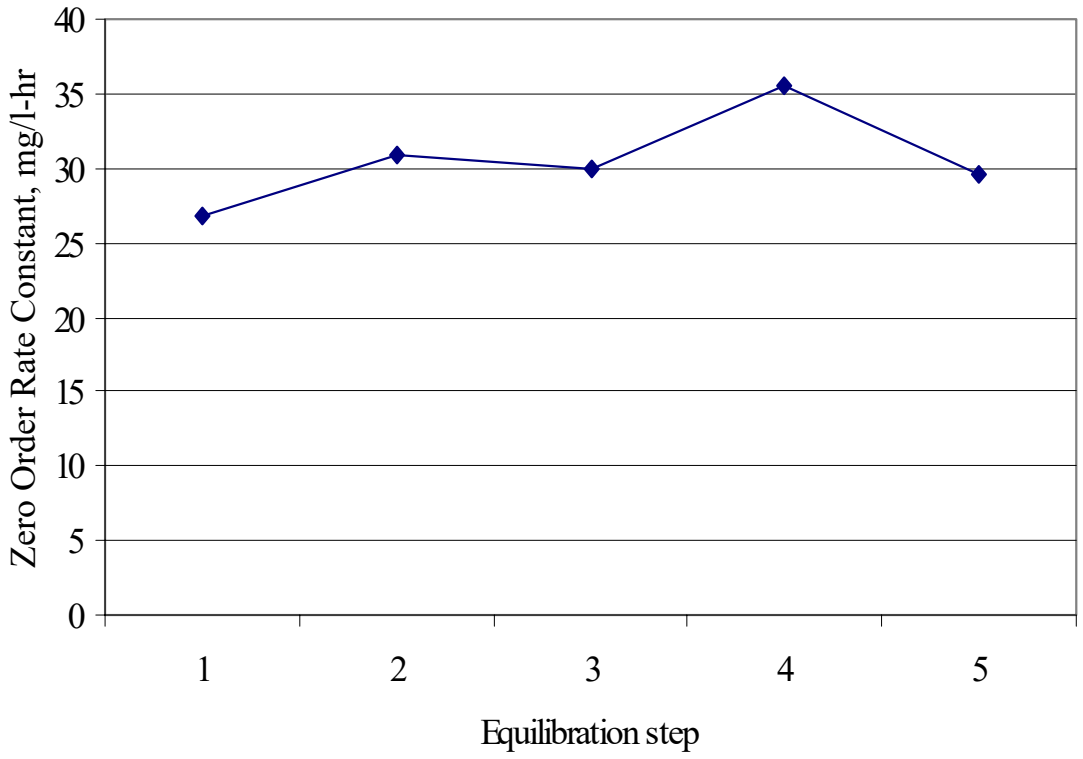


Figure 6.4. Zero Order Rate Constant Results for the Fate of Hydrogen Peroxide in Equilibrated Water Solutions Experiments (Not-autoclaved equilibrated water samples)

Note:
- These were conducted in two replicas

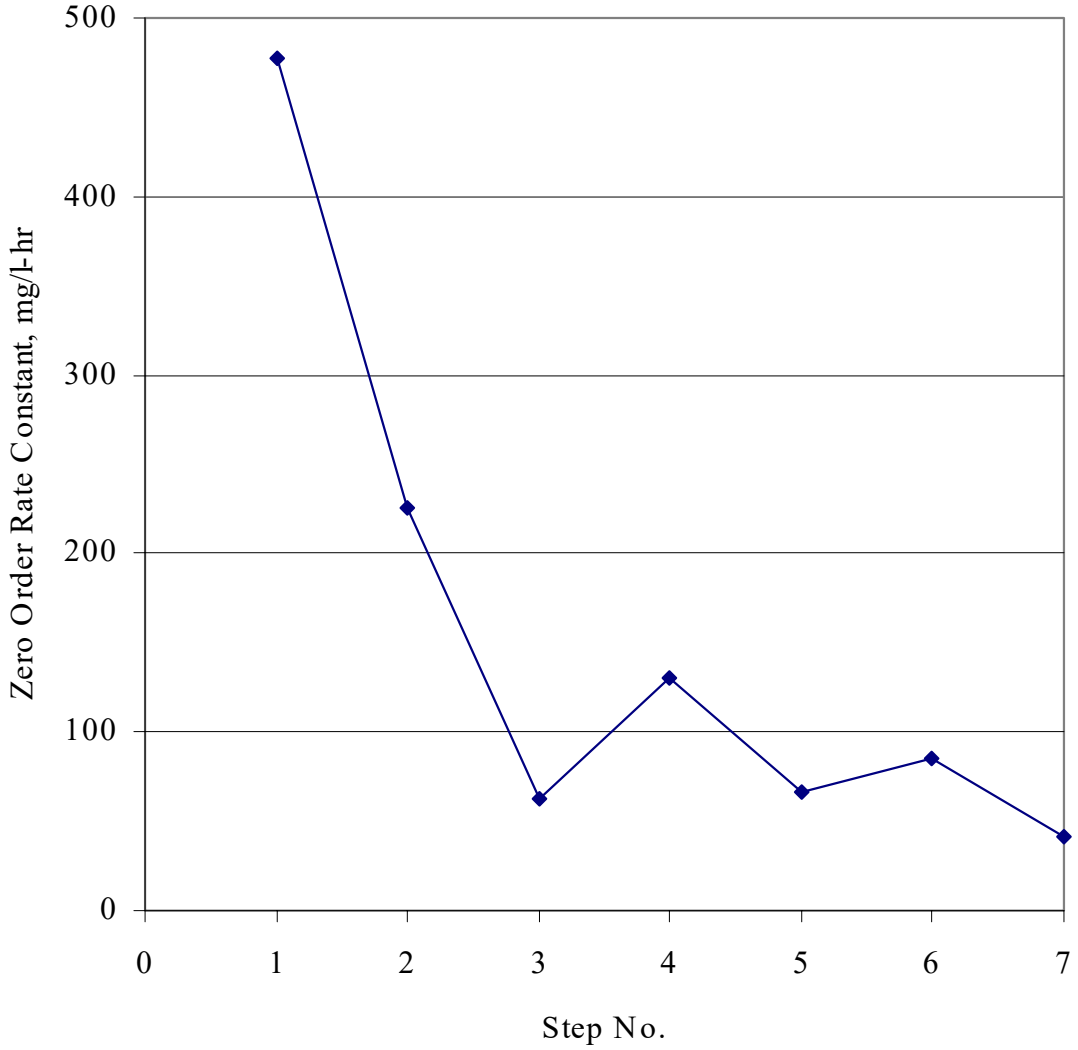


Figure 6.5. Hydrogen Peroxide Reactivity in the Lake Superior Sediment (1,000 mg/l)

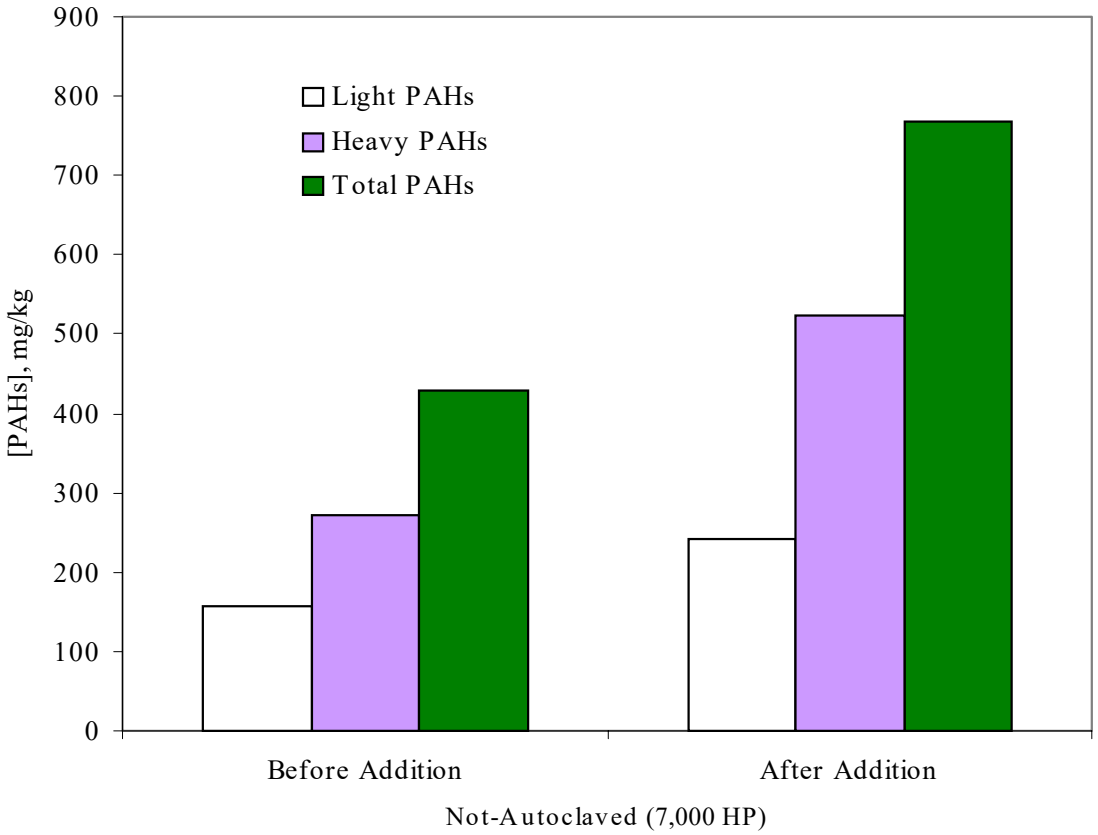


Figure 6.6. Fate of PAHs in the Lake Superior Sediment as a Function of Hydrogen Peroxide Dosing (1,000 HP dosing concentration)

Notes:
- HP denotes the amount of hydrogen peroxide added, mg/l
- These were conducted in two replicas

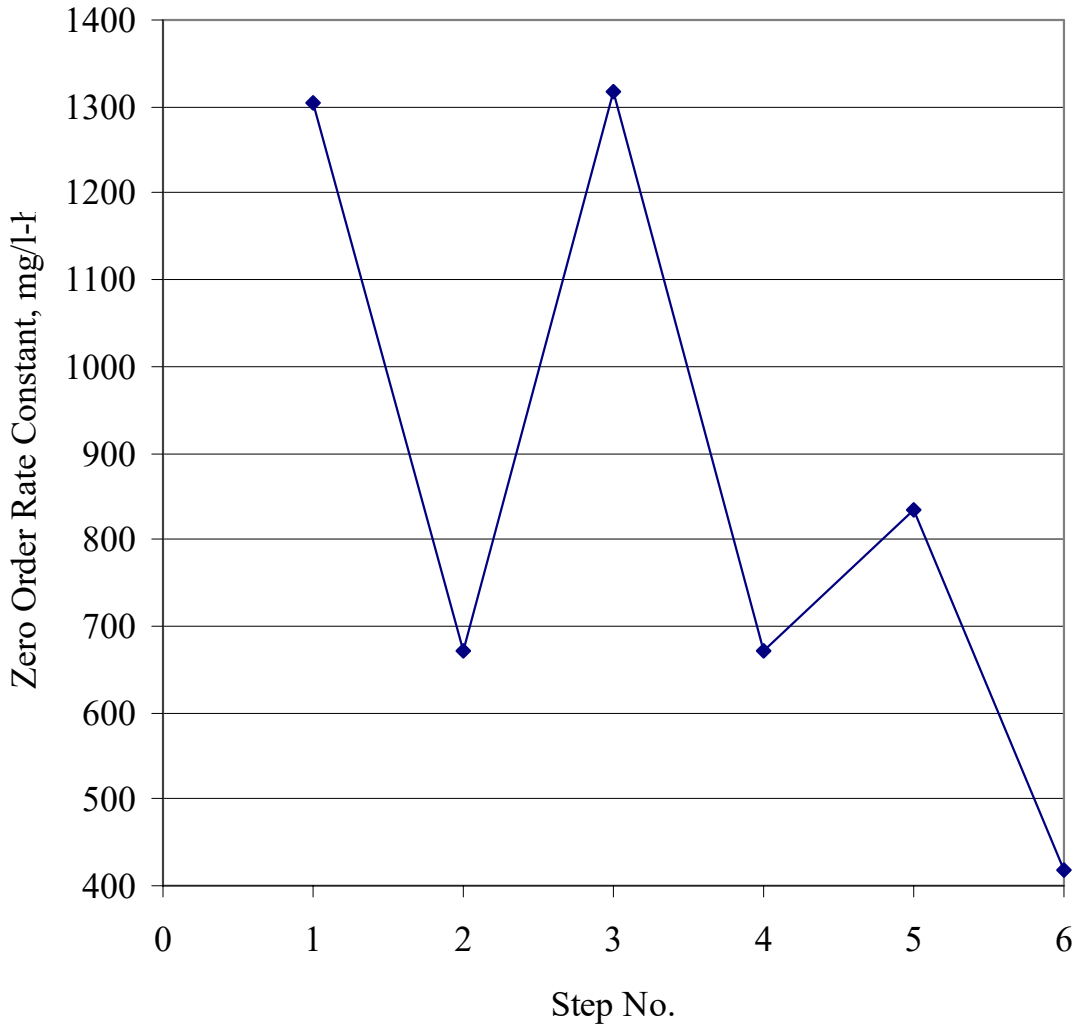


Figure 6.7. Hydrogen Peroxide Reactivity in the Lake Superior Sediment (10,000 mg/l)

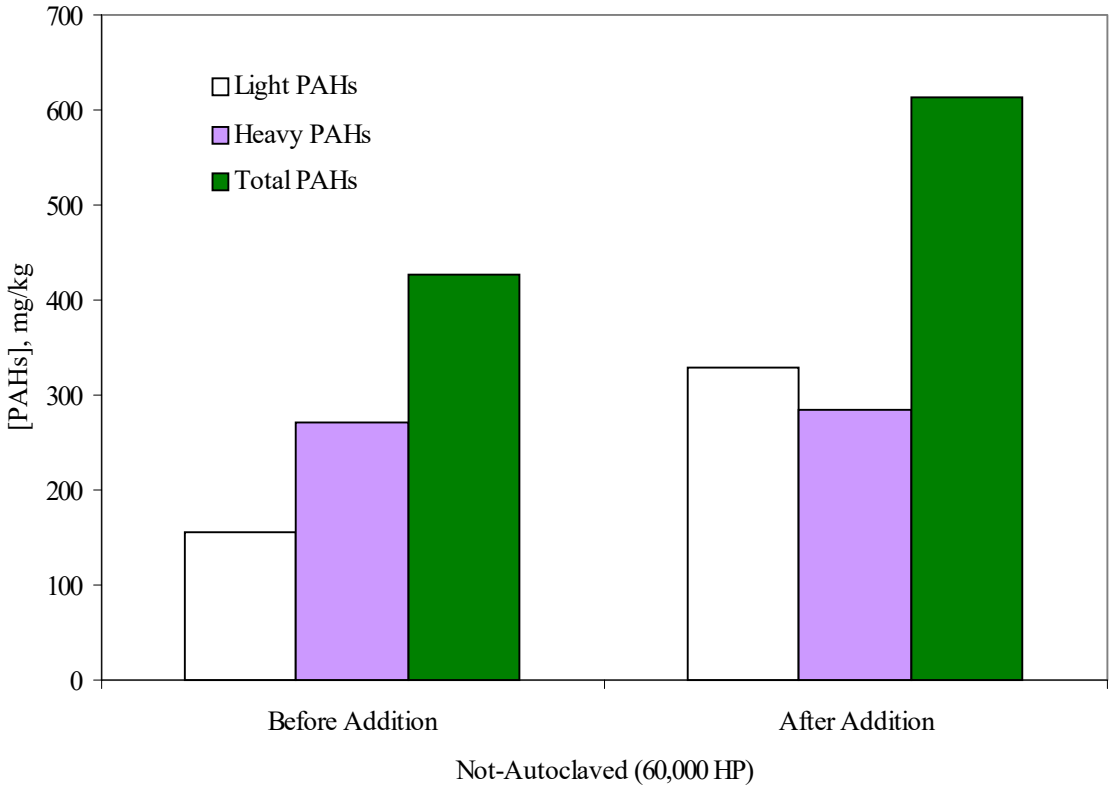


Figure 6.8. Fate of PAHs in the Lake Superior Sediment as a Function of Hydrogen Peroxide Dosing (10,000 HP dosing concentration)

Notes:
- HP denotes the amount of hydrogen peroxide added, mg/l
- These were conducted in two replicas

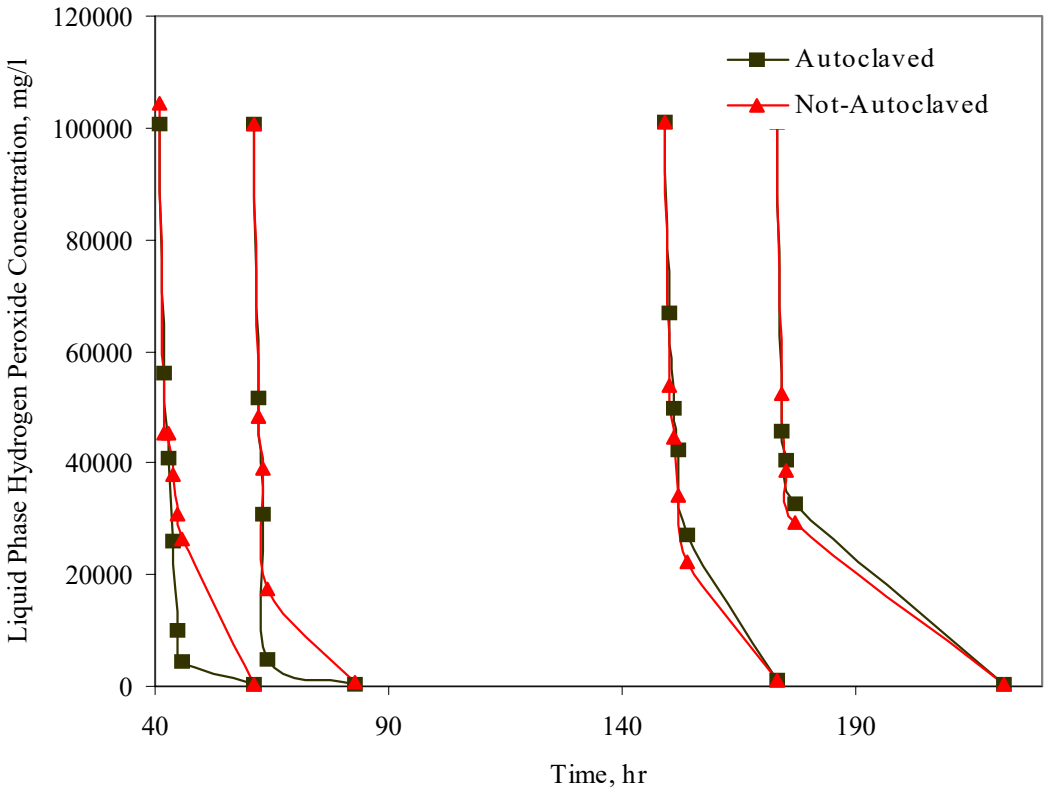


Figure 6.9. Hydrogen Peroxide Reactivity in the Lake Superior Sediment (Treatment hr 41-83 and hr 149-222)

Notes:
- Not-Autoclaved: Untreated Lake Superior Sediment
- Autoclaved: Lake Superior Sediment that was autoclaved at 121°C and 15 psi steam
- 100,000 mg/l hydrogen peroxide was dosed on hr-41, hr-61, hr-149, and hr-173

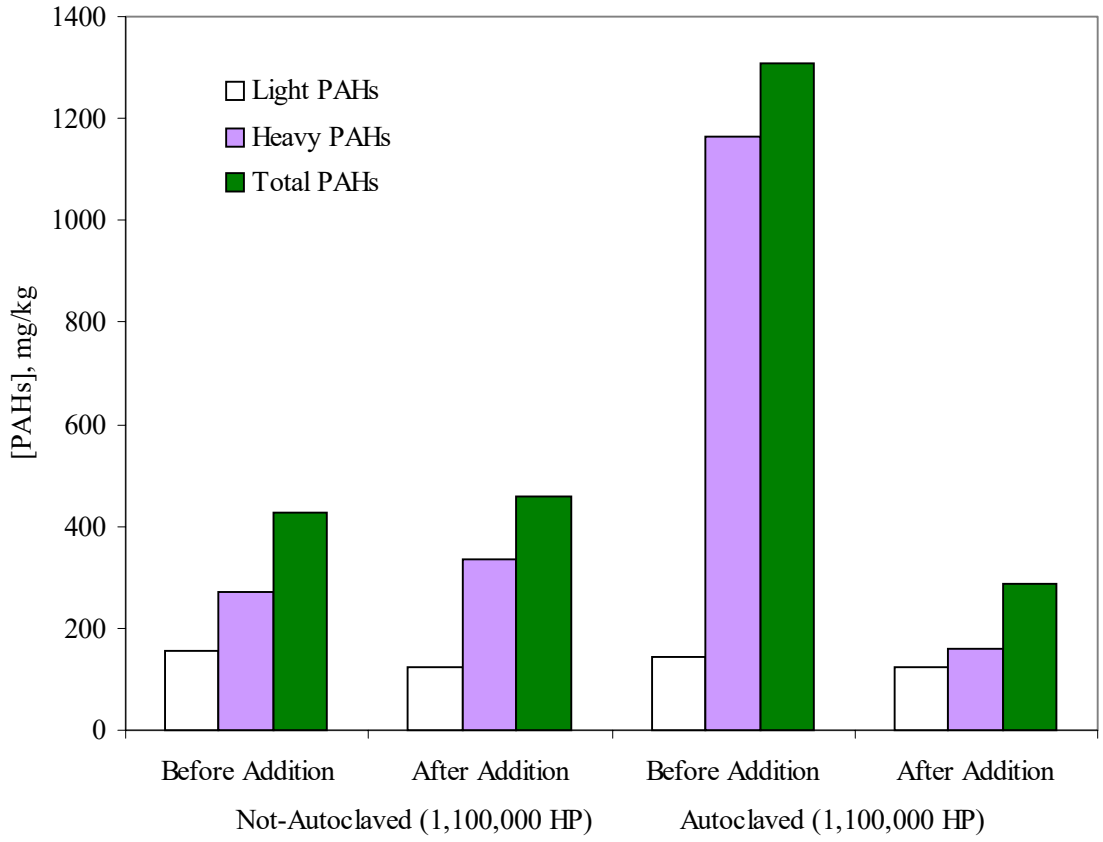


Figure 6.10. Fate of PAHs in the Lake Superior Sediment as a Function of Hydrogen Peroxide Dosing (100,000 HP dosing concentration)

Notes:
- Not-autoclaved: Untreated Lake Superior sediment
- Autoclaved: Lake Superior sediment that was autoclaved at 121°C and 15psi of steam
- HP denotes the amount of hydrogen peroxide added, mg/l
- These were conducted in two replicas

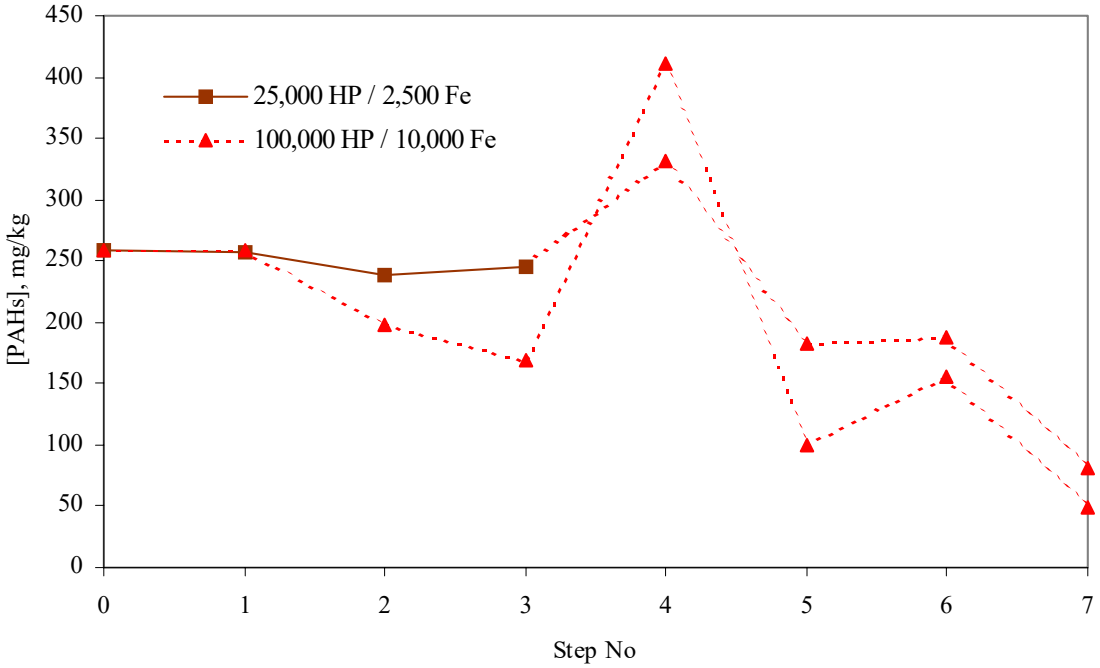


Figure 6.11. Fenton's Reagent Treatment of Total PAHs in the Lake Superior Sediment

Conditions:
- 25,000 HP/ 2,500 Fe and 100,000 HP/ 10,000 Fe indicate dosing steps to the slurry

Notes:
- HP: H_2O_2 in mg/l and Fe: Fe^{2+} in mg/l
- These were conducted in two replicas

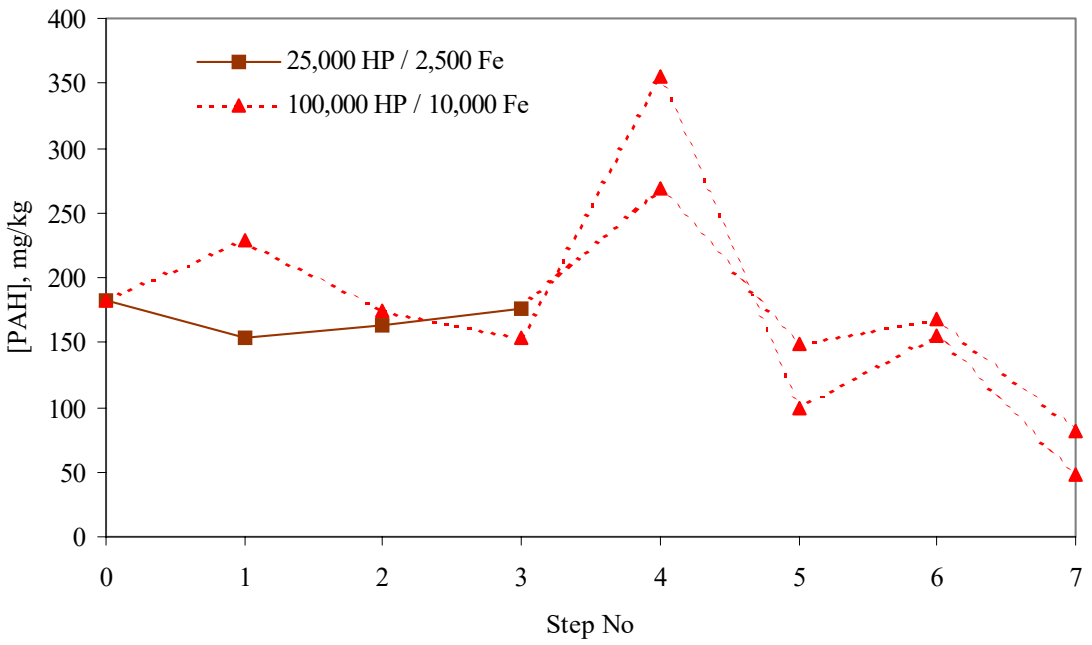


Figure 6.12. Fenton's Reagent Treatment of Light PAHs in the Lake Superior Sediment

Conditions:
- 25,000 HP/ 2,500 Fe and 100,000 HP/ 10,000 Fe indicate dosing steps to the slurry

Notes:
- HP: H_2O_2 in mg/l and Fe: Fe^{2+} in mg/l
- These were conducted in two replicas

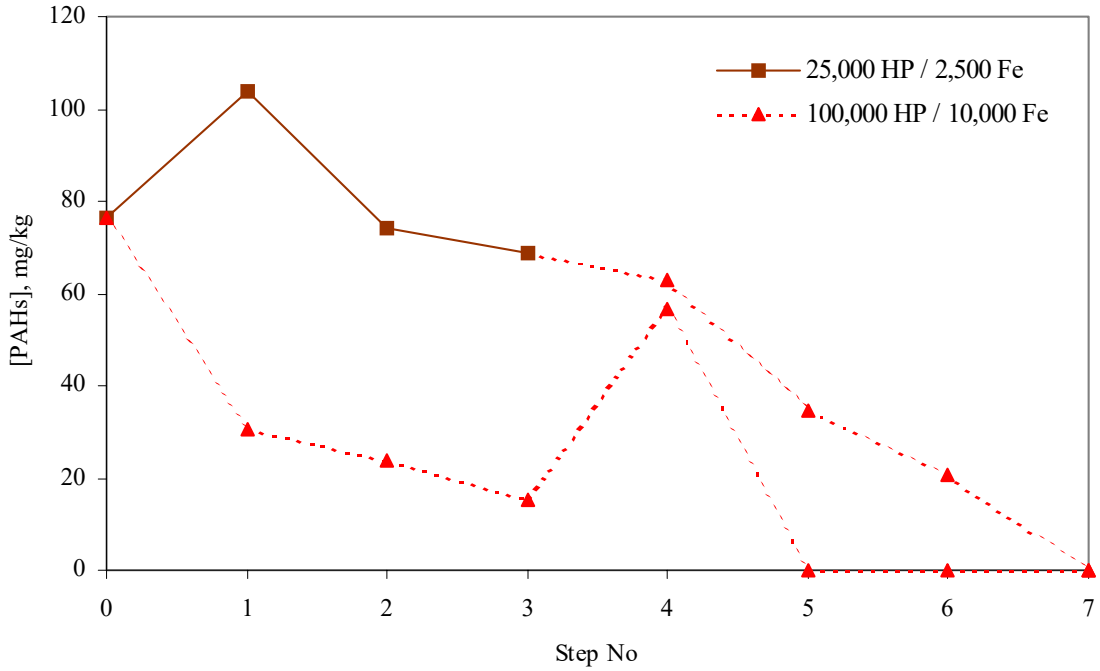


Figure 6.13. Fenton's Reagent Treatment of Heavy PAHs in the Lake Superior Sediment

Conditions:
- 25,000 HP/ 2,500 Fe and 100,000 HP/ 10,000 Fe indicate dosing steps to the slurry

Notes:
- HP: H_2O_2 in mg/l and Fe: Fe^{2+} in mg/l
- These were conducted in two replicas

CHAPTER VII

PHASE I: INTEGRATED EXPERIMENTS RESULTS

Wang (1999) successfully integrated biotreatment and chemical oxidation technologies for the removal of total petroleum hydrocarbons (TPHs) in soils. The author reported an enhancement in the degradation of TPHs in the chemical primed slurry systems over the biotic control. This finding indicates that the combination of both biotreatment and chemical oxidation technologies also can enhance the degradation of TPHs. For this reason, this next set of experiments was directed towards evaluating the enhancement that an oxidation step provides for the degradation of PAHs in previously biotreated sediment (Scioto River) using Fenton's Reagent. Note that the biotreatment results are presented and discussed in Chapter V (see Biotreatment Results of Scioto River Sediment). This set of experiments was conducted in shake-flask and not bioslurry units.

Integrated Experiments Results

The objective of this set of experiments was to determine the impact of Fenton's Reagent on PAH fate within the previously biotreated sediment. The applied Fenton's Reagent dosages were 20,000 mg/l H_2O_2/2,000 mg/l Fe^{2+}, 50,000 mg/l H_2O_2/5,000 mg/l Fe^{2+}, and 100,000 mg/l H_2O_2/10,000 mg/l Fe^{2+}. Note that the hydrogen peroxide to ferrous ion concentration ratio in all of these formulation was 10 to 1.

Foaming is a common phenomenon encountered during chemical oxidation treatments of soil containing elevated amounts of organic matter (i.e., bacteria and NOM) (Wang, 1999). Foaming problems usually result in the loss of soil and also reduce the contaminant-oxidizer contact time. Foaming problems were often encountered by Wang (1999) during the ozone, peroxone, and Fenton's Reagent treatment of TPH contaminated soils. In this study, foaming also was encountered during the ozone and peroxone experiments, especially during the first dosing application of hydrogen peroxide. Thus, to minimize foaming problems, which were expected to be encountered with adding high dosages of Fenton's Reagent, the applied strategies were formulated so as to dose the Fenton's Reagents in sequence and at increasing concentrations. In addition, it was discovered from an earlier Fenton's Reagent experiment (25K-10:1 ratio Experiments), that the application of Fenton's Reagent in this manner appeared to be more effective in removing PAHs. Note that these data represent an average of the duplicate sets. Appendix C presents the raw data along with the standard deviation associated with these data.

Figure 7.1 presents the Total PAHs degradation results achieved with the addition of Fenton's Reagent. After the initial dosing of Fenton's Reagent at 20,000 mg/l H_2O_2/2,000 mg/l Fe^{2+}, a slight increase in Total PAHs was observed for two of the sets (AS+100:20:5 and AS+100:20:5+T80). It is believed that this is due to the increase in the extraction efficiency caused by the oxidation of the NOM. This phenomenon also was reported by Kawahara et al. (1995), where the extractability for most of the PAHs was increased after the application of Fenton's Reagent. Further Fenton's Reagent dosing provided steady degradation of the PAHs in the sediment. The Total PAHs in most of the sets were not detected after seven applications. Of

particular note was the performance of the AS + 100:20:5 system which hit non-detect levels after only two applications.

From Figure 7.2, Light PAHs in the slurry for most of the sets were degraded within two dosing applications, except for the set involving Tween 80 addition. The addition of Fenton's Reagent at 20,000 mg/l H_2O_2/2,000 mg/l Fe^{2+} and 50,000 mg/l H_2O_2/5,000 mg/l Fe^{2+} provided steady improvement in the extraction efficiency of Light PAHs within the sediment due to the oxidation of the NOM. Despite this increase, further addition of Fenton's Reagent at 100,000 mg/l H_2O_2/10,000 mg/l Fe^{2+} resulted in significant degradation of Light PAHs. The Light PAHs in all slurry systems were not detected by the 8th dosing.

Figure 7.3 presents the phenanthrene degradation results achieved with Fenton's Reagent. Phenanthrene is a 3 ring PAH which is considered a Light PAH. The data show that the phenanthrene was only detected in the sets involving Tween 80 addition. Note that the amount of Light PAHs in the set involving Tween 80 addition was mainly phenanthrene. The first four dosing applications of Fenton's Reagent yielded a steady increase of phenanthrene in the sediment. These data strongly suggests that this increase was due to the increase in extraction efficiency caused by oxidation of the NOM. This phenomenon was observed in previous Fenton's Reagent Experiments (25K-10:1 ratio and 100K-10:1 ratio Experiments) and Kawahara et al. (1995) during the oxidation of PAH using Fenton's Reagent.

From Figure 7.4, the increase in the Total PAHs (see Figure 7.1) was mainly attributed to the increase in the concentration of the Heavy PAHs. Most of the Heavy PAHs were removed after six dosing applications. It is interesting to note that the amount of Light PAHs (see Figure 7.2)

in the slurry for the set involving Tween 80 was approximately half the amount of the Heavy PAHs to begin with and yet, the Light PAHs have persisted longer than the Heavy PAHs.

Figure 7.5 presents the selected PAHs (e.g., fluoranthene and benzo[a]anthracene) degradation results achieved with Fenton's Reagent. Note that the selected PAHs are 4 ring PAHs, which are known to be recalcitrant and have a low solubility in water; thus, resulting in poor biodegradation. These data show that the addition of Fenton's Reagent resulted in an initial increase in these PAHs in the sediment. This increase is also observed with the phenanthrene in the set involving Tween 80 addition; thus, it is believed that the steady increase in the amount of these PAHs in the sediment was due to the oxidation of the sorption bonds afforded by Fenton's Reagent. The extent of desorption for these selected PAHs provided by Fenton's Reagent varied within the various slurry sets. The rate of degradation for the selected PAHs also varied by slurry sets. The degradation for the selected PAHs was observed right after the initial dosing application of Fenton's Reagent. The selected PAHs were not detected in any of the systems, after six dosing applications of Fenton's Reagent. In general, the results show an increase in the amount of PAHs detected prior to total eventual removal.

Figure 7.6 presents the results of combined biotreatment and chemical oxidation treatment of the PAHs in Scioto River Sediment. The results clearly show that the addition of Fenton's Reagent resulted in improved degradation of the PAHs within the sediment.

In general, the addition of Fenton's Reagent enhanced the PAH removal in the Scioto River sediment. Total PAHs were not detected in any of the systems by eight dosing applications. The Tween 80 amending generally did not results in improved treatment based on the analytical

technique used. However, the addition of the surfactant does appear to remove more contaminant mass possibly resulting in a better remediation in the key run, in spite of the obvious limitation presented by current analytical techniques. A final note must be made in that Alexander et al. (1997) suggest that pollutant fractions not easily extracted do represent a contaminant mass likely not worthy of aggressive remediation because it is not available to pose an environment threat.

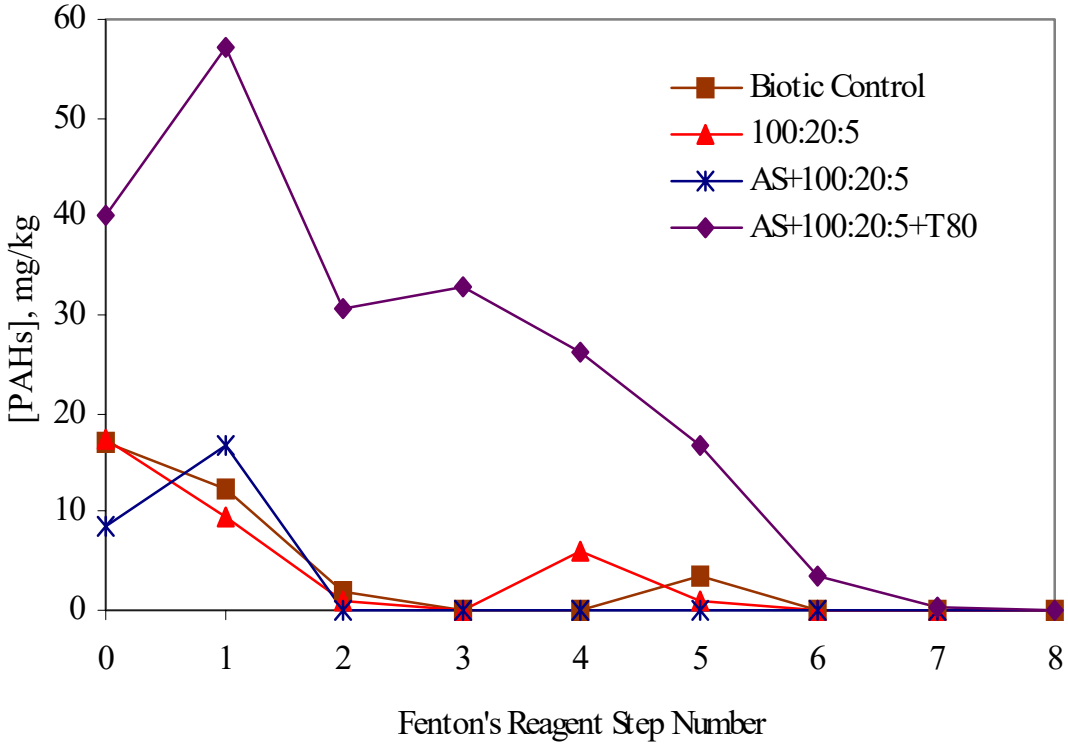


Figure 7.1. Fenton's Reagent Treatment of Total PAHs for the Scioto River Sediment

Conditions:
- Step no. 1: 20,000 HP + 2,000 Fe
- Step no. 2-3: 50,000 HP + 5,000 Fe
- Step no. 4-8: 100,000 HP + 10,000 Fe

Notes:
- AS: Bioaugmentation with activated sludge from the return line of a local wastewater treatment plant
- 100:20:5 represents PAH:N:P ratio
- T80: Tween 80 addition at 0.5% (w/w) the first week and 0.25% (w/w) the following weeks
- HP: Hydrogen peroxide concentration in mg/l
- Fe: Ferrous sulfate concentration in mg/l

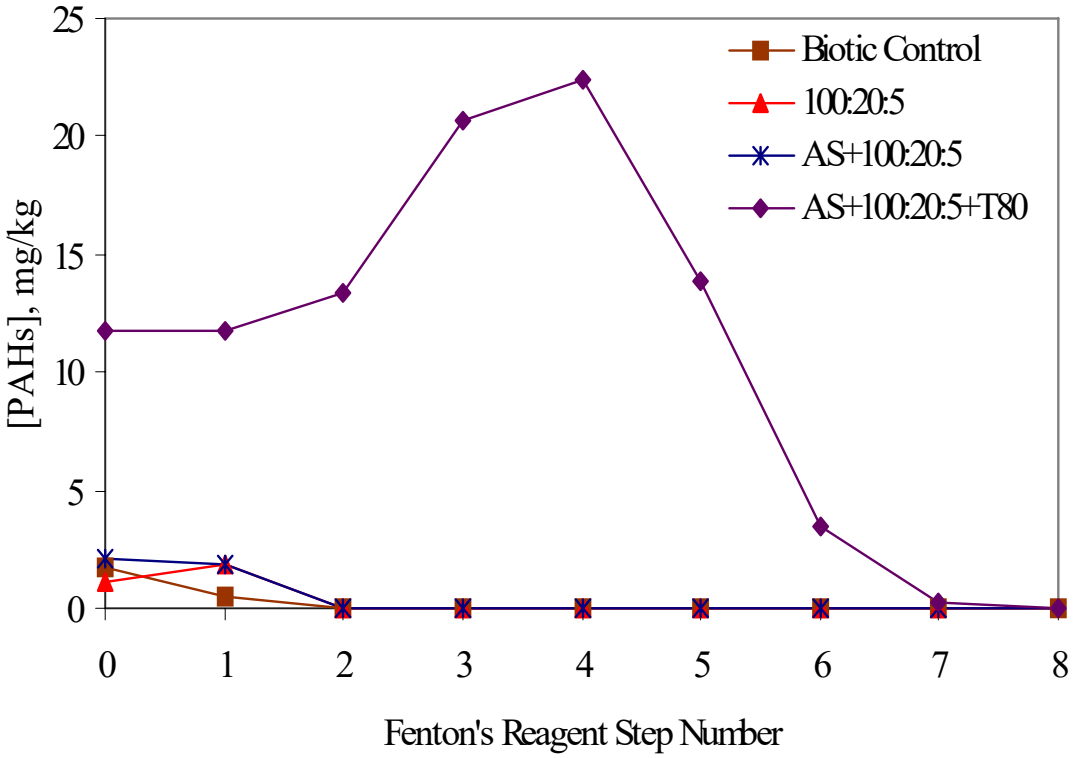


Figure 7.2. Fenton's Reagent Treatment of Light PAHs for the Scioto River Sediment

Conditions:
- Step no. 1: 20,000 HP + 2,000 Fe
- Step no. 2-3: 50,000 HP + 5,000 Fe
- Step no. 4-8: 100,000 HP + 10,000 Fe

Notes:
- AS: Bioaugmentation with activated sludge from the return line of a local wastewater treatment plant
- 100:20:5 represents PAH:N:P ratio
- T80: Tween 80 addition at 0.5% (w/w) the first week and 0.25% (w/w) the following weeks
- HP: Hydrogen peroxide concentration in mg/l
- Fe: Ferrous sulfate concentration in mg/l

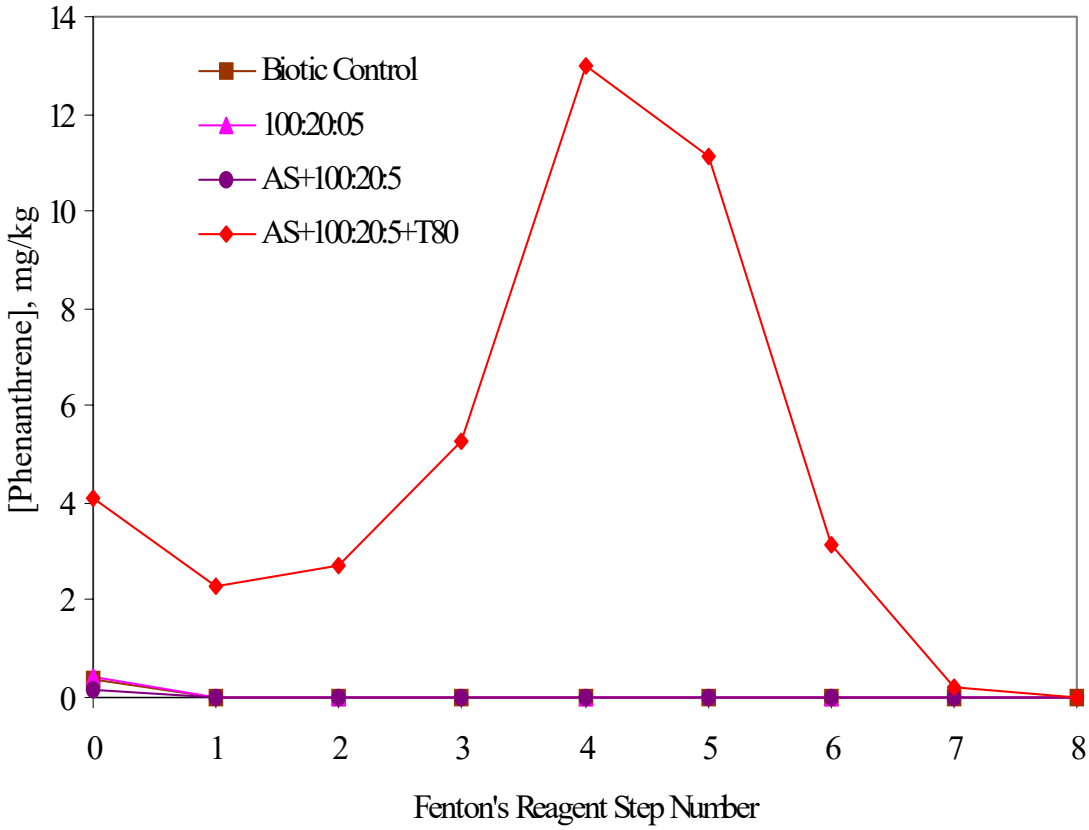


Figure 7.3. Fenton's Reagent Treatment of Phenanthrene for the Scioto River Sediment

Conditions:
- Step no. 1: 20,000 HP + 2,000 Fe
- Step no. 2-3: 50,000 HP + 5,000 Fe
- Step no. 4-8: 100,000 HP + 10,000 Fe

Notes:
- AS: Bioaugmentation with activated sludge from the return line of a local wastewater treatment plant
- 100:20:5 represents PAH:N:P ratio
- T80: Tween 80 addition at 0.5% (w/w) the first week and 0.25% (w/w) the following weeks
- HP: Hydrogen peroxide concentration in mg/l
- Fe: Ferrous sulfate concentration in mg/l

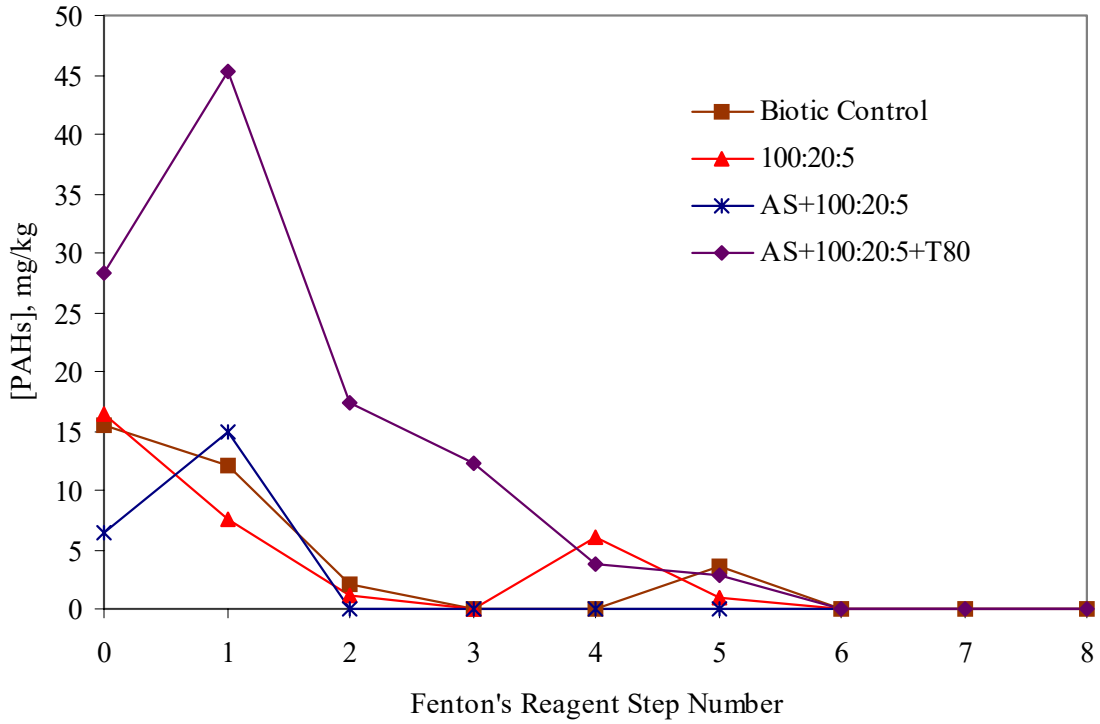


Figure 7.4. Fenton's Reagent Treatment of Heavy PAHs for the Scioto River Sediment

Conditions:
- Step no. 1:20,000 HP + 2,000 Fe
- Step no. 2-3:50,000 HP + 5,000 Fe
- Step no. 4-8: 100,000 HP + 10,000 Fe

Notes:
- AS: Bioaugmentation with activated sludge from the return line of a local wastewater treatment plant
- 100:20:5 represents PAH:N:P ratio
- T80: Tween 80 addition at 0.5% (w/w) the first week and 0.25% (w/w) the following weeks
- HP: Hydrogen peroxide concentration in mg/l
- Fe: Ferrous sulfate concentration in mg/l

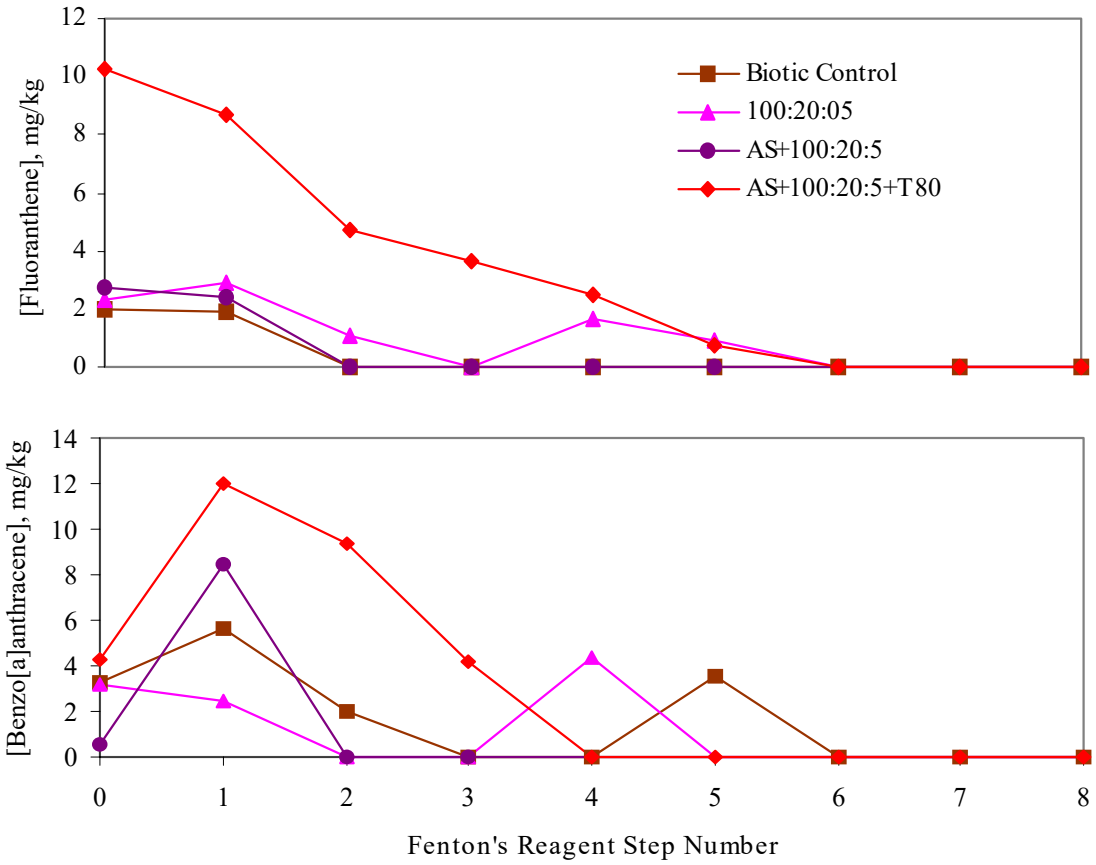


Figure 7.5. Fenton's Reagent Treatment of Selected PAHs for the Scioto River Sediment

Conditions:
- Step no. 1:20,000 HP + 2,000 Fe
- Step no. 2-3:50,000 HP + 5,000 Fe
- Step no. 4-8: 100,000 HP + 10,000 Fe

Notes:
- AS: Bioaugmentation with activated sludge from the return line of a local wastewater treatment plant
- 100:20:5 represents PAH:N:P ratio
- T80: Tween 80 addition at 0.5% (w/w) the first week and 0.25% (w/w) the following weeks
- HP: Hydrogen peroxide concentration in mg/l
- Fe: Ferrous sulfate concentration in mg/l

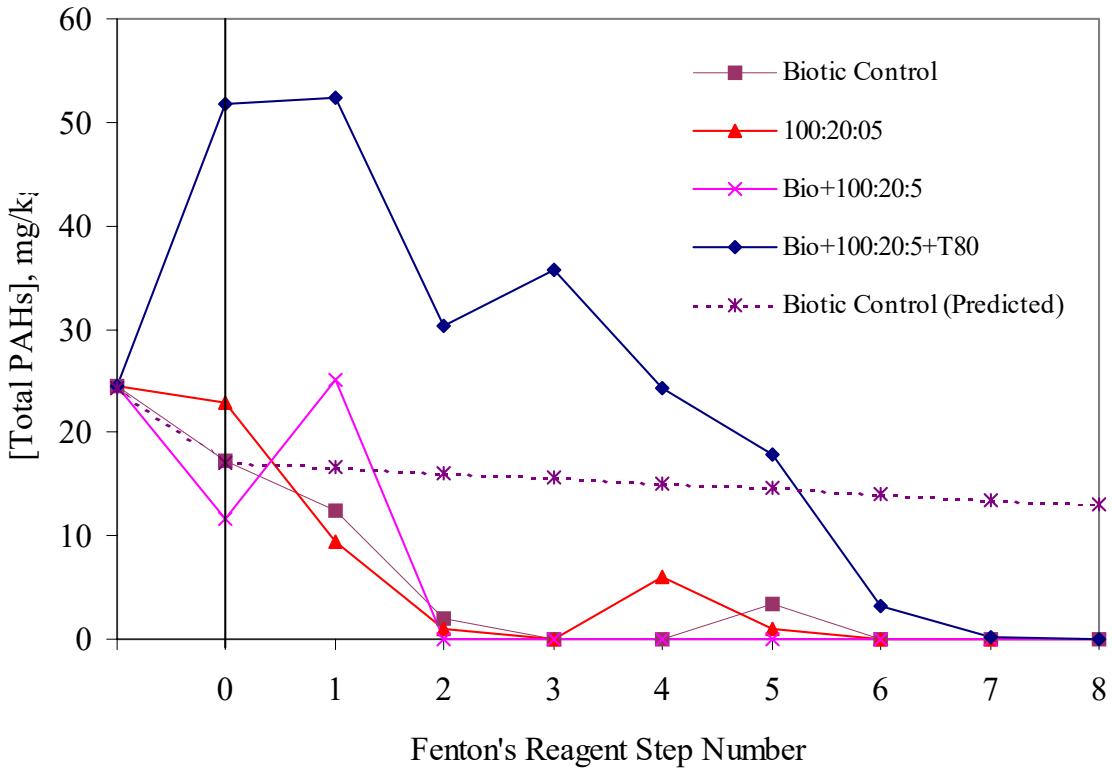


Figure 7.6. Results of Chemical Primed Bioremediation of PAHs for the Scioto River Sediment

Notes:
- AS: Bioaugmentation with activated sludge from the return line of a local wastewater treatment plant
- 100:20:5 represents PAH:N:P ratio
- T80: Tween 80 addition at 0.5% (w/w) the first week and 0.25% (w/w) the following weeks
- HP: Hydrogen peroxide concentration in mg/l
- Fe: Ferrous sulfate concentration in mg/l

CHAPTER VIII

PHASE II: RESULTS OF THE BIOTREATMENT AND INTEGRATED EXPERIMENTS WITHIN THE BIOSLURRY REACTORS

Phase II: Bioslurry Experiments

The bioslurry experiments were designed to demonstrate the feasability of chemical oxidation enhanced bioremediation of PAHs under more realistic reactor conditions (i.e., 5-L reactors). The objectives of this experimental phase were to determine the optimum chemical priming conditions to achieve the best enhancement results and evaluate the net results on the reestablished bioremediation stage in terms of PAH removal using engineered reactor units that closely mimic actual expected large-scale bioreactor designs. The sediment utilized in these experiments was the Lake Superior sediment. Four different treatment conditions were conducted in duplicate bioslurry reactors (a total of eight units). Appendix D presents the raw data along with the standard deviation associated with these data.

Table 8.1. presents the oxygen content within the headspace of the bioreactors measured over the course of the experiment. The results show that the oxygen content in the head space in all reactors was relatively stable around 20.9% (common oxygen level in air) over the course of this test. The set involving the addition of external carbon sources (e.g., glucose, sodium acetate,

and Tween 80) showed two points at the end of the test that were relatively low likely indicating activity toward the higher levels of free carbon added of that time. These data indicate relatively normal headspace air quality.

Table 8.2 presents the carbon dioxide content within the headspace of the bioreactors utilized in the bioslurry experiments. Note that the carbon dioxide detection level for the gas analyzer was 0.1 ppm. The results show that the carbon dioxide was detected in the headspace of the bioreactors within the first week of the test. The presence of carbon dioxide in the headspace in all the reactors indicates accelerated biological activity within the sediment. After the first week, carbon dioxide was not detected for the next ten weeks or so in all reactors. Carbon dioxide was observed again in the headspace of the bioreactor involving external carbon addition at Week 11 (Day 77). The presence of carbon dioxide in the headspace corresponded to the addition of the Tween 80 on Day 74 of the experiments; thus, it is believed that carbon dioxide was a by-product of Tween 80 degradation. Note that the details of the Tween 80 dosing strategy are discussed in a later segment.

Table 8.3 lists the volatile organic carbon content within the headspace of the bioreactors measured over the course of the experiment. The results show that volatile organic carbons concentration in the head space increase until the quarter-point of the experiment then started decreasing from that point on. This trend generally follows that of the trend observed within the slurries (discussed later).

Table 8.4 lists the results of adding nitrate to the bioslurry. The results show that the nitrate levels in the biotic control increased during the first week of bioremediation. Note that nitrate was

not added to the biotic control system. This increase could be attributable to the heterogenous distribution of nitrate within this sediment. The nutrients levels for other sets involving nutrients addition were higher than the control, as expected because of weekly additions. In general, the addition of nitrate in this study (1,000 mg/l) was higher than the addition of nitrate used in other studies, such as Wang (1999) and Zappi et al (1993). The amount of nitrate added for this study was based on a C:N:P ratio of 100:20:5 (i.e., less than 100 mg/l). The reasoning behind the elevated nitrate dosage is to support the high demand for nitrate that was considered to be associated with the PAHs value alone. Obviously, this demand was not as high as expected.

Table 8.5 presents the results of adding ortho-phosphate (o-p) to the bioslurry. The results show that ortho-phosphate levels in the sets involving o-p addition (e.g., 400 mg/l o-p) were slightly higher than the o-p level in the control set (no o-p was added) over the course of this test. Given that phosphate salt was added weekly, a relatively low buildup is observed indicating an appreciable utilization by the bacteria.

Table 8.6 presents the results of adding ammonia to the bioslurry. The results show that the ammonia levels in the control set were relatively the same as other sets involving nutrients addition. Ammonia was added in the form of ammonium nitrate. These low levels of ammonia indicate significant biological uptake by the microbes present in the sediment and in fact, these levels indicate possibly slightly reproducible levels due to the low ammonia levels measured over this test. This trend also was reported by Banerji et al. (1995) during the bioremediation of TPH, PAHs, and VOCs contaminated sediments, where the authors observed that the ammonia levels

dropped to below 1 mg/l despite the ammonium chloride addition (e.g, 40 mg/l) over the course of the bioremediation.

Figure 8.1 presents the results for tracking dissolved oxygen (DO) levels within the slurries over the course of this test phase. The DO levels in all of the reactors were low in the beginning of the experiment due to oxygen demand, but increased after being sparged with hydrocarbon filtered air through two of the three vents located at the bottom of the reactor. The increase in dissolved oxygen in the slurry systems on Days 9 and 53 of the experiments corresponded to the addition of distilled water to adjust the total solid to 30 % (w/w). From the results, the DO in the slurries was maintained above 2 mg/l which is sufficient levels to sustain a healthy aerobic environments. The addition of nutrients, naphthalene degraders, and co-metabolites to selected reactors did not affect the DO in the slurry. The significant drop in the DO for the set involving the addition of external carbon sources corresponded to the addition Tween 80 at 5 % (w/w) on Day 74 of the experiments. Foaming occurred right after the Tween 80 was added. The air supply volumetric flowrate was lowered from 10 scfh to 0.5 scfh after the addition of Tween 80 (till end of this experiment) to prevent excessive foaming which could result in loss of the sediment from the reactors. In order to be consistent, the volumetric flowrate for the other reactors not involving Tween 80 was also lowered to 0.5scfh. The DO for one of the reactors involving Tween 80 addition remained just below 2 mg/l after the Tween 80 addition. The significant drop in the DO on Day 77 of the experiments (after Tween 80 addition) is likely due attributable to the degradation of Tween 80.

Figure 8.2 presents the oxygen uptake rate (OUR) measurements for the bioslurry experiments. Initially, the OUR levels were high, but slowly decrease with times. However, there were occasional spikes in the OUR levels in all the reactors. The increase in the OUR correspond to addition of nutrients, co-metabolites, and surfactant which obviously stimulated increased biological activities. The OUR data track nicely with the expected outcomes of the various amending strategies in that the units with co-metabolites and nutrients had higher OURs than the others. Additionally, the reactors with no amendments (biotic controls) clearly had lower OURs indicating a lesser degree of biological activity. In general, the OUR levels observed in this study are lower in comparison to the OUR levels observed during the bioremediation of VOCs, TPH, and PAH contaminated soils reported by Banerji et al. (1995). The authors reported OUR levels of above 8 mg/l-hr for the sets that were biologically active versus the 1 mg/l-hr levels observed during this study.

Figure 8.3 presents the total suspended solids in the bioslurry experiments. The total suspended solids remained fairly constant, about 30% by weight, in the reactors over the course of this testing. The occasional increase in total suspended solids is attributed to loss of water from the reactors due to air sparging which were generally always followed by a decrease in the total solids attributable to the addition of fresh distilled water to maintain the total solid content around 30%.

Figure 8.4 presents the pH measurements for the bioreactor units. As can be seen upon review of the figure, the pH was maintained around 7.0 over the course of this test. This pH range is optimal for biological activity (Metcalf and Eddy, 1991). The results show that the pH for the

biotic control set remained relatively unchanged (around 7.1) over the course of the test. On the other hand, the pH for the amended sets fluctuated out of the optimum pH range. Thus, the pH was adjusted back to the optimal range (pH=7). The addition of nutrients and external carbon sources (e.g., glucose, naphthalene, sodium acetate, and Tween 80) appear to have an impact on pH depending on the nature of the amendment.

Figure 8.5 presents the Total Organic Carbon (TOC) results for the bioslurry experiments. Initially, the TOC was recorded around 100,000 mg/kg which is relatively higher than the TOC found in an average sediment (7,500 m/kg) (Zappi et al., 2000). Nonetheless, on Day 7 of the experiments, the average TOC values for all the reactors decreased to about 30,000 mg/kg and remained relatively constant over the course of the study. The significant drop in the TOC during the first week was partly attributed to the stripping of the volatile fraction of the organic sediment fractions. Additionally, the stimulated biological activity very likely degraded a large portion of the TOC.

Figures 8.6 and 8.7 present the Total PAHs degradation results and polynomial fitted (3rd order) Total PAHs degradation results for the bioslurry reactor experiments. Note that the initial PAHs values for the bioslurry reactors represent on average of duplicate sets (average per test condition). These results (both Figures 8.6 and 8.7) show that the addition of nutrients, naphthalene degraders, and external carbon sources (i.e., glucose, sodium acetate, and Tween 80) did not enhance the degradation of PAHs over the removal observed with the biotic controls.

The addition of co-metabolites was shown during Phase I to improve the biodegradation of recalcitrant Heavy PAHs through the process of co-metabolism (see Chapter V). Thus, the co-

metabolites (i.e., glucose, sodium acetate, and naphthalene) were added to enhance the degradation of the PAHs (especially Heavy PAHs). Since the removal of Heavy PAHs was enhanced during the previous experiments involving glucose addition (see Chapter V), 1,000 mg/l of glucose was added on Days 1, 11, and 23 of this experiment. The results (both Figures 8.6 and 8.7) show that addition of glucose did not appear to enhance the removal of the PAHs over the biotic control. Thus, the effect of different co-metabolites on the PAH degradation in the sediment was examined. One hundred mg/l of sodium acetate was added on Days 50 and 63 of the experiments; meanwhile, 1 liter of 25 mg/l naphthalene solution was added on Days 53 and 65 of the experiments. Again the results showed no improvement in the Total PAHs degradation over the biotic control. The results from previous bioavailability experiment (see Table 5.1) showed that naphthalene in the sediment remained unchanged over the course of the test, indicating that naphthalene degradation was hindered due to its low solubility in the aqueous phase. Thus, it is believed that the poor removal of PAHs in the sediment was attributable to low bioavailability. In order to increase the bioavailability, Tween 80 was added with the expectation of enhancing the PAH degradation. Five percent (w/w) of Tween 80 was added on Days 74 and 86 of this experiment; meanwhile, 2.5% (w/w) of Tween 80 was added on Days 107 and 116 of this experiment. The results show that the amount of Total PAHs decrease significantly after the addition of Tween 80 on Day 74 of this experiment prior to an increase on Day 98 of this experiment. Surfactant has been shown to increase the solubility of organic contaminants (i.e., TPH and PAHs) in the aqueous phase (Tiehm et al., 1997; Wang, 1999). This observation indicates that the decrease in the Total PAHs was likely attributable to the increase in the solubility of the

PAHs in the aqueous phase afforded by Tween 80. This trend was observed in the previous experiments involving Tween 80 (see Chapter V).

Figure 8.8 presents the Light PAHs degradation results of the bioslurry reactor experiments. The results show that the biodegradation of the Light PAHs also followed the trend observed with the Total PAHs (see Figure 8.6). Figure 8.9 presents the naphthalene results for the set involving nutrients and naphthalene degraders and the biotic control. Initially, 20 ml of naphthalene degraders was added on Days 1 and 11 of this experiment to improve the naphthalene degradation. The naphthalene degradation within the first 50 days did not improve over the biotic control. So on Day 50, 500 ml of naphthalene degraders (estimated population density of $1x10^8$ CFUs/ml) was added with the expectation being the increase in the population of the naphthalene degraders would later improve naphthalene degradation. The results of this effort show that naphthalene levels remained unchanged even with the addition of 500 ml of naphthalene degraders. This proves that the naphthalene degradation was inhibited due to limitations (i.e., low bioavailability) and not the lack of sufficient bacterial population.

Figure 8.10 presents the Heavy PAHs degradation results for the bioslurry experiments. The results show that the biodegradation of the Heavy PAHs also followed the trend observed with the Total PAHs (see Figure 8.6). Overall, the addition of the co-metabolites and Tween 80 did not enhance the removal of the Heavy PAHs.

Phase II: Chemical Oxidation Integrated Results

On the 49th day of the experiment, the slurry from the set involving nutrients addition only as oxidized using Fenton's Reagent, ozone and peroxone. Note that the raw data along with the standard deviation associated with these data are presented in Appendix D. Table 8.7 presents the summaries and selected results for the oxidation of the Lake Superior sediment for the set involving nutrients addition only. The heterotrophic counts for the slurry prior to oxidation was 1.4 x 10^7 CFUs/ml with no colonies found after chemical oxidation. The TOC were slightly reduced for all systems after oxidation. The pH values for the sediment were lower after the oxidation indicating the production of organic acids during the oxidation and/or due to the hydrolysis of ferric ions (Nebergall et al., 1976). A short experiments was conducted to measure the pH levels of the Fenton's Reagent and it was found that the pH of the ferrous sulfate and hydrogen peroxide dropped approximately from 3 to 1.5, indicating that hydrolysis of ferric ions (see Table 8.8). No significant changes in DO, ammonia, o-p, and nitrate levels were noticed after the oxidation, with the exception of the significant drop in the nitrate level for the set involving Fenton's Reagent dosing, where 61% of the nitrate disappeared. This change is not believed to be of any particular significance.

Figure 8.11 presents the ozonation results for the Light, Heavy, and Total PAHs in Lake Superior sediment for set involving nutrients addition only (Reactors 3 and 4). Note that these data represent an average of the data from the duplicate sets. After four hours of ozonation, approximately 67.7% of the Total PAHs was oxidized. The degradation of the Light and Heavy PAH fractions were 65 % and 69 %, respectively. When the ozone contact time was increased

from 4 to 8 hours, the PAH levels increased within the sediment. The increase in the PAHs amount is likely due to the additional degradation of the sorption bonds caused by the oxidation of NOM and erosion of soil agglomerates due to scouring affect by the foaming and agitation. Both of these act upon the extraction efficiency of the analytical process.

Figure 8.12 presents the peroxone results for the Light, Heavy, and Total PAHs in Lake Superior sediment for the set involving nutrients addition only (Reactors 3 and 4). Note that these data represent an average of the data from the duplicate sets. The data for the peroxone treatment followed the same degradation trend observed with the ozone experiments. Degradation of PAHs was observed within the first four hours of the treatment. The removal of Total PAHs was approximately 57.2%, with the Light and Heavy PAHs removals of 57.4% and 57%, respectively. However, when the hydrogen peroxide dosing concentration was increased from 100 mg/l to 500 mg/l, an increase in the extractable PAHs was observed. This trend also was observed in the previous peroxone treatment tests where increase in the extractable PAHs were observed after the hydrogen peroxide was increased from 62.5 mg/l to 500 mg/l (see Chapter VI). These data do show that the greater aggressiveness of the peroxone process did yield a more dramatic impact on PAH extractability.

Figure 8.13 presents the Fenton's Reagent results for the Light, Heavy, and Total PAHs in Lake Superior sediment for the set involving nutrients addition only (Reactors 3 and 4). Note that these data represent an average of the data from the duplicate sets. The tested Fenton's Reagent concentrations were 25,000 mg/l hydrogen peroxide/ 2,500 mg/l ferrous sulfate, 50,000 mg/l hydrogen peroxide/ 5,000 mg/l ferrous sulfate, and 100,000 mg/l hydrogen peroxide/ 10,000

mg/l ferrous sulfate. The results show degradation of Total PAHs after the initial dosing of Fenton's Reagent at 25,000 mg/l hydrogen peroxide/ 2,500 mg/l ferrous sulfate. The second Fenton's Reagent dosing at the same concentration did not appear to further improve the degradation of Total PAHs. Additionally, the further addition of Fenton's Reagent dosing concentrations at 50,000 mg/l hydrogen peroxide/ 5,000 mg/l ferrous sulfate did not appear to improve the degradation of the PAHs. However, when the Fenton's Reagent dosing concentrations were increased to 100,000 mg/l hydrogen peroxide/ 10,000 mg/l ferrous sulfate, the degradation of the Total PAHs is improve. After six consecutive additions of Fenton's Reagent at increasing concentrations, 74% of the Total PAHs was degraded. In terms of Light PAHs, the degradation trend followed the same trend observed with the Total PAHs. The removal of the Light PAHs in the sediment after six consecutive addition was 57%. In terms of the removal of Heavy PAHs, the significant degradation of Total PAHs during the fourth dosing (100,000 mg/l hydrogen peroxide/ 10,000 mg/l ferrous sulfate) was mainly attributed to Heavy PAHs. The removal of the Heavy PAHs after six repetitive additions of Fenton's Reagent was 91%. Overall, the extent of degradation noted with the Light PAHs was less in comparison to the Heavy PAHs. This was also observed in the previous Fenton's Reagent experiments (see Chapter VI). This trend appears to be attributable to the reactivity of these chemicals toward Fenton's Reagent oxidation.

Table 8.9 presents the summary of selected results for the oxidation of the Lake Superior sediment for the set involving naphthalene degraders and nutrients additions (Reactors 5 and 6). The heterotrophic counts for this slurry system was approximately 1 x 10^8 CFUs/ml. Additionally, about 61 CFUs/ml were found after Fenton's Reagent oxidation. Both nitrate and ortho-

phosphate were significantly reduced in the sediments. The pH value for the slurry system decreased from 6.6 to 4.4 after oxidation. This trend was also observed in the previous Fenton's Reagent experiment (see Table 8.7). Again, these data suggest the decrease in pH was attributable to the production of organic acids as by-products of organics degradation. Note also the pH drop in this set of experiments is lower in comparison to the pH drop observed with the previous Fenton's Reagent experiments (see Table 8.7). No significant changes to DO level was observed after the oxidation. The ammonia level in the sediment increased significantly after Fenton's Reagent oxidation. This trend was not observed in the previous Fenton's Reagent experiments (see Table 8.7).

Figure 8.14 presents the Fenton's Reagent results for the Light, Heavy, and Total PAHs in Lake Superior sediment for the set involving naphthalene degraders and nutrients addition (Reactors 5 and 6). Note that these data represent an average of the data from the duplicate sets. The tested Fenton's Reagent concentrations were 25,000 mg/l hydrogen peroxide/ 2,500 mg/l ferrous sulfate and 100,000 mg/l hydrogen peroxide/ 10,000 mg/l ferrous sulfate. The results show degradation of Total PAHs after the initial dosing of Fenton's Reagent at 25,000 mg/l hydrogen peroxide/ 2,500 mg/l ferrous sulfate. Further addition of Fenton's Reagent at 100,000 mg/l hydrogen peroxide/ 10,000 mg/l ferrous sulfate yielded only a slight improvement in the degradation of the Total PAHs. The removal of Total PAHs achieved with Fenton's Reagent was 31.9%. In terms of Light PAHs removal, the results (see Figure 8.14) show that the degradation followed the same trend observed with the Total PAHs. The removal of Light PAHs achieved after six repetitive additions of Fenton's Reagent was 46%. In terms of Heavy PAHs removal, the addition

of Fenton's Reagent provided a steady, but slight degradation of Heavy PAHs in the sediment. The removal of the Heavy PAHs was 15.1%. Overall, the treatment effectiveness of this oxidation step was much less than those observed with the other bioslurry set. This suggests that higher biomass dosed into these reactors reacted with the oxidizers via the catalase which in turn scavenged the oxidizers preventing their reaction with the PAHs.

Phase II: Post-Oxidation Results

On Day 84 of the experiments, slurry systems that were oxidized using ozone, peroxone, and Fenton's Reagent treatment were all composited and poured into Reactors 3 and 4 and biological activity in the sediment was reestablished via addition of naphthalene degraders. The pH was adjusted back to around 7.0 and nutrients also were added at 1,000 ppm nitrate and 400 ppm phosphate. After restarting biotreatment, the oxygen and carbon dioxide headspace levels were similar to those previously observed prior to oxidation steps (see Tables 8.1 and 8.2). On the other hand, headspace VOCs was not detected after the oxidation step. This was likely due to the oxidation of the VOCs during the chemical priming steps. The nitrate levels after oxidation was relatively higher in comparison to biotic control (Table 8.4). Note that naphthalene degraders were inoculated and the demand for nitrate was expected to be high. Thus, 1,000 ppm of nitrate was added, on top of the nitrate that was already present in the sediment, to support microbial growth.

In terms of ortho-phosphate (o-p), the o-p was low after the chemical priming stage (see Table 8.5); thus, as stated before, 400 pm of o-p was added also to support microbial growth. After a week of reestablishing biological activity, the o-p dropped two orders of magnitude. This

high demands of o-p indicates biological uptake by the microbes present in the sediment. This high demand of o-p was not observed with Wang (1999) or Zappi et al. (1993).

Again, ammonia was added to the slurry systems in the form of ammonium nitrate. On Day 91 of the experiments, the ammonia level was still higher in comparison to biotic control (see Table 8.6). The DO levels within the sediment remained comparatively unchanged after oxidation (see Figure 8.1). This indicates that the systems remained aerobic after biological activity was reestablished. The OUR levels were also about the same after oxidation (prior to oxidation) (see Figure 8.2). This level of OUR indicates the biological activity was effectively restored. The results show that pH increased significantly (pH of 8) after biological activity was reestablished in the sediment (see Figure 8.4).

Figure 8.15 presents the post-oxidation PAH analytical results for the bioremediation of the bioslurry experiments for the set involving nutrients addition only. These results show an increase in the Total PAHs after bioremediation had been reestablished. Despite this increase, a slight degradation of the Total PAHs was observed between Days 98 and 105 of the experiments prior to an increase in by Day 127. This increase in extractable PAHs is likely due to natural biosurfactants produced from the increased levels of bacterial activity. The degradation of PAHs within the sediment (after chemical oxidation) is a step sequence of the degradation of PAHs within the sediment before the oxidation step. This is based on the fact the trends of PAHs degradation (before and after oxidation) are similar. In general, no further degradation of PAHs was observed after the chemical oxidation. This phenomenon was not observed by Wang (1999) during the reestablished biotreatment of TPH contaminated soils. The results in Figure 8.15 also show that

the trend observed with the biodegradation of the Light and Heavy fractions also followed the trend observed with the Total PAHs.

Summary of Biotreatment and Integrated Results

In the bioslurry experiments, the objective was to bioremediate PAH contaminated sediment under conditions that better simulated real reactor conditions. Numerous bioremediation strategies were performed to find the optimal approach to decontaminating PAH in contaminated sediment. The additions of nutrients, naphthalene degraders, and co-metabolites did not provide significant improvement of PAH degradation over the biotic control. It was believed that the poor degradation was largely due to the limited bioavailability of the PAHs. Thus, Tween 80 was added to one of the slurry system with the expectation of increasing the bioavailability of the PAHs and later improve the biodegradation rate. The results show that the addition of Tween 80 on Day 74 of the experiments yielded a very slight improvement over the biotic control. Further addition of the Tween 80 ended up improving the extractability of the PAH in the aqueous phase, but not the extent of removal.

Ozone was found to have resulted in the degradation of PAH by 47% after 8 hours of contact time. The degradation of the Light and Heavy PAH fractions were 37.3% and 45.6%, respectively. On the other hand, peroxone treatment increased the extractability of PAHs via destabilization and/or oxidation of the PAH-adsorption bonds.

For the Fenton's Reagent experiments, there were two sets of bioreactors tested: the set involving nutrients addition alone (Reactors 3 and 4) and set involving naphthalene degraders

inoculation and nutrients addition (Reactors 5 and 6). After six repetitive applications of Fenton's Reagent, the removal of the Total PAHs was 74% for the nutrients amended sets. The removals of Light and Heavy PAHs were 57% and 91%, respectively. The degradation of Heavy PAH was significantly greater because of the availability of these chemicals in the aqueous phase for chemical oxidation. As stated before, Fenton's Reagent also was applied to the set involving the naphthalene degraders inoculation and nutrients addition. Clearly, the microbial density for this set is higher in comparison to the other set that was treated with Fenton's Reagent because of the inoculation of the naphthalene degraders on Day 50 of the experiments. The results show that the addition of Fenton's Reagent in sequence and in increasing dosing concentration provided 31.9% removal of Total PAHs. The removals of Light and Heavy PAHs were 46% and 15.1%, respectively. This level of PAHs degradation was lower in comparison to the degradation observed with the nutrients amended sets. It is believed that the degradation of the Heavy PAHs was hindered due to the reactivity of these chemicals towards Fenton's Reagent oxidation. However, it is also speculated that the addition of the naphthalene degraders might have contributed to this phenomenon.

The objective of the post oxidation step was to further degrade the remaining PAHs including the oxidation by-products in the sediment. The degradation of PAHs did appear to improve slightly after the biological activity was reestablished into the nutrients amended sets. Despite this improvement, the bioavailability of the PAHs in the sediment increased slightly over the next 40 days. Additionally, the degradation of the PAHs within the sediment (after chemical oxidation) is a step sequence of the degradation of PAHs within the sediment before the oxidation

step. The trends of PAHs degradation (before and after chemical oxidation) were similar in a sense indicating that the poor degradation of PAHs was due to limited bioavailability. The introduction of chemical oxidizers improved the extractability and degradability of the PAHs within the sediment, but did not improve the degradation of PAHs during the subsequent biotreatment step. Overall, no degradation of PAHs was observed in the post oxidation step. This conclusion is based on the fact that the final amount of Total PAHs towards the end of the experiments (Day 144) was higher than the amount when the biological activity was reestablished (Day 84).

Table 8.1. Bioreactor Headspace Oxygen Content Results for the Bioslurry Experiments

Condition / Day	Biotic control	Nutrients	Bio.+Nutrients	Bio.+Nutrients+Ext.C.
0	20.9	20.9	20.90	20.9
14	20.9	20.9	20.90	20.9
21	20.7	20.7	20.7	20.8
28	20.9	20.9	20.9	20.9
35	20.9	20.9	20.9	20.9
42	20.8	20.9	20.9	20.9
49	20.5	20.8	20.7	20.5
59	20.9	N/A	20.9	20.9
77	20.8	N/A	20.9	15.5
84	20.9	20.9	20.9	20.0

Notes:
- Oxygen content is represented as %
- Nutrients: Indicates 1,000 mg/l nitrate and 400 mg/l phosphate additions
- Bio.: Indicates naphthalene degraders addition
- Ext. C.: Indicates 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% Tween 80 additions
- N/A: Indicates not available

Table 8.2. Bioreactor Headspace Carbon Dioxide Results for the Bioslurry Experiments

Condition Day	Biotic control	Nutrients	Bio.+Nutrients	Bio.+Nutrients+Ext.C.
0	0.3	0.1	0.2	0.0
7	0.2	0.2	0.2	0.2
14	0.0	0.0	0.0	0.0
21	0.0	0.0	0.0	0.0
28	0.0	0.0	0.0	0.0
35	0.0	0.0	0.0	0.0
42	0.0	0.0	0.0	0.0
49	0.0	0.0	0.0	0.0
59	0.0	N/A	0.0	0.0
77	0.0	N/A	0.0	3.8
84	0.0	0.0	0.0	0.3

Notes:
- Carbon dioxide is represented as %
- Nutrients: Indicates 1,000 mg/l nitrate and 400 mg/l phosphate additions weekly
- Bio.: Indicates naphthalene degraders addition
- Ext. C.: Indicates 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% Tween 80 additions
- N/A: Indicates not available

Table 8.3. Bioreactor Headspace Volatile Organic Carbon Levels for the Bioslurry Experiments

Condition / Day	Biotic control	Nutrients	Bio.+Nutrients	Bio.+Nutrients+Ext.C.
0	350	330	360	330
7	380	340	320	400
14	1580	1580	1530	1490
21	2550	2660	2850	3230
28	340	130	740	500
35	700	430	130	170
42	1460	1130	1060	1050
49	1520	1410	1730	1420
59	30	N/A	10	360
77	830	N/A	1010	1180
84	520	0	30	400

Notes:
- Volatile organic carbon is represented as ppm
- Nutrients: Indicates 1,000 mg/l nitrate and 400 mg/l phosphate additions weekly
- Bio.: Indicates naphthalene degraders addition
- Ext. C.: Indicates 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% Tween 80 additions
- N/A: Indicates not available

Table 8.4. Nitrate Results in the Bioslurry Reactors for Phase II: Bioslurry Experiments

Day	Biotic control	Nutrients	Bio.+Nutrients	Bio.+Nutrients+Ext.C.
0	8.68	8.68	8.68	8.68
7	356.5	310	610.7	452.6
14	204.6	1922	1829	1457
21	368.9	3100	3069	2480
35	198.4	2356	2356	1860
42	443.3	3348	3286	2325
49	241.8	2542	2480	2046
56	291.4	N/A	2635	1705
63	269.7	N/A	2139	1829
91	344.1	N/A	2883	23.87
98	272.4	1643	2263	940.54
109	356.5	2449	2976	2883
116	713	5270	5332	3143.4
123	930	6820	7130	4708.9
130	647.9	6665	N/A	4056.97
137	806	7750	7440	805.38
151	2604	10850	8060	2111.1

Notes:
- Nitrate is represented as mg/l
- Nutrients: Indicates 1,000 mg/l nitrate and 400 mg/l phosphate additions weekly
- Bio.: Indicates naphthalene degraders addition
- Ext. C.: Indicates 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% Tween 80 additions
- N/A: Indicates not available

Table 8.5. Ortho-Phosphate Results in the Bioslurry Reactors for Phase II: Bioslurry Experiments

Day	Biotic control	Nutrients	Bio.+Nutrients	Bio.+Nutrients+Ext.C.
0	0.21	0.46	0.44	0.36
7	0.09	0.20	0.18	0.16
14	0.11	0.51	0.62	0.35
21	0.21	0.46	0.44	0.36
35	0.09	0.20	0.18	0.16
42	0.09	0.21	0.21	0.23
49	0.08	0.15	0.12	0.16
56	0.08	N/A	12.65	6.98
63	0.10	N/A	5.38	4.38
77	0.06	N/A	12.40	4.33
91	0.11	0.96	40.75	12.00
98	0.17	0.45	22.38	2.48
109	0.15	0.51	18.75	3.19
116	0.18	0.54	14.63	3.84
123	0.19	0.49	0.00	3.51
130	0.16	10.70	7.50	3.18
137	0.14	8.63	4.88	3.78
151	0.17	5.25	4.25	3.53

Notes:
- Ortho-phosphate is represented as mg/l
- Nutrients: Indicates 1,000 mg/l nitrate and 400 mg/l phosphate additions weekly
- Bio.: Indicates naphthalene degraders addition
- Ext. C.: Indicates 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% Tween 80 additions
- N/A: Indicates not available

Table 8.6. Ammonia Results in the Bioslurry Reactors for Phase II: Bioslurry Experiments

Day	Biotic control	Nutrients	Bio.+Nutrients	Bio.+Nutrients+Ext.C.
0	0.36	0.36	0.36	0.36
7	0.18	0.11	0.15	0.05
14	0.43	0.42	0.45	0.40
21	0.15	0.49	0.55	0.37
35	0.20	0.13	0.11	0.09
42	0.06	0.07	0.06	0.05
49	0.06	0.05	0.05	0.05
56	0.06	N/A	0.05	0.05
63	0.06	N/A	0.05	0.05
77	0.06	N/A	0.05	0.04
91	0.16	5.19	0.06	15.58
98	0.16	0.07	0.06	3.59
109	0.06	0.06	0.05	1.99
116	0.39	0.06	0.04	2.15
123	0.09	0.03	0.00	3.50
130	0.09	0.05	0.16	1.03
151	0.04	0.01	0.01	0.10

Notes:
- Ammonia is represented as mg/l
- Nutrients: Indicates 1,000 mg/l nitrate and 400 mg/l phosphate additions weekly
- Bio.: Indicates naphthalene degraders addition
- Ext. C.: Indicates 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% Tween 80 additions
- N/A: Indicates not available

Table 8.7. Summary of the Chemical Priming Conditions and Selected Results for the Nutrients Sets (Reactors 3 and 4)

Condition:		Fenton's Reagent	Ozone	Peroxone
Ozone Flow Rate, scfh		N/A	2.5	2.5
Percent Ozone (by wt)		N/A	4	4
• $[H_2O_2]$, mg/l		350,000	-	2,400
• $[FeSO_4]$, mg/l		35,000	-	-
H_2O_2/Fe^{2+} ratio		10:1	-	-
Total Heterotrophic Count, CFUs/	Before / After	$1.4x10^7$ / 0	$1.4x10^7$ / 0	$1.4x10^7$ / 0
pH	Before / After	6.7 / 2.5	6.7 / 5.3	6.7 / 5.4
DO, mg/l	Before / After	5.2 / 5.5	5.2 / 3.5	5.2 / 5.0
Ammonia, mg/l	Before / After	0.05 / 0.03	0.05 / 0.02	0.05 / 0.02
Nitrate, mg/l	Before / After	2542 / 992	2542 / 2387	2542 / 2511
O-P, mg/l	Before / After	0.15 / 0.32	0.15 / 0.38	0.15 / 0.1
TOC, mg/kg	Before / After	34115 / 30858	34115 / 30330	34115 / 32228

Note:
- Nutrients: Indicates 1,000 mg/l nitrate and 400 mg/l phosphate additions weekly
- N/A: Indicates not applicable

Table 8.8. pH Levels of Ferrous Sulfate and Hydrogen Peroxide

pH \ Compounds	Before Addition		After Addition
	Ferrous Sulfate[1]	Hydrogen Peroxide[2]	Ferrous Sulfate + Hydrogen Peroxide
Average	3.16	3.54	1.68
Standard Deviation	0.03	0.24	0.04

Notes:
[1]25,000 mg/l Ferrous sulfate solution
[2]150,000 mg/l hydrogen peroxide solution

Table 8.9. Summary of the Chemical Priming Conditions and Selected Results for the Bio.+Nutrients (Reactors 5 and 6)

Condition:		Fenton's Reagent
• $[H_2O_2]$, mg/l		450,000
• $[FeSO_4]$, mg/l		45,000
H_2O_2/Fe^{2+} ratio		10:1
Total Heterotrophic Count, CFUs/ml	Before / After	1×10^8 / 61
pH	Before / After	6.6 / 4.4
DO, mg/l	Before / After	5.2 / 5.7
Ammonia, mg/l	Before / After	0.04 / 255.00
Nitrate, mg/l	Before / After	6820 / 2294
O-P, mg/l	Before / After	14.60 / 0.25

Notes:
- Nutrients: Indicates 1,000 mg/l nitrate and 400 mg/l phosphate additions weekly
- Bio.: Indicates naphthalene degraders addition
- N/A: Indicates not applicable

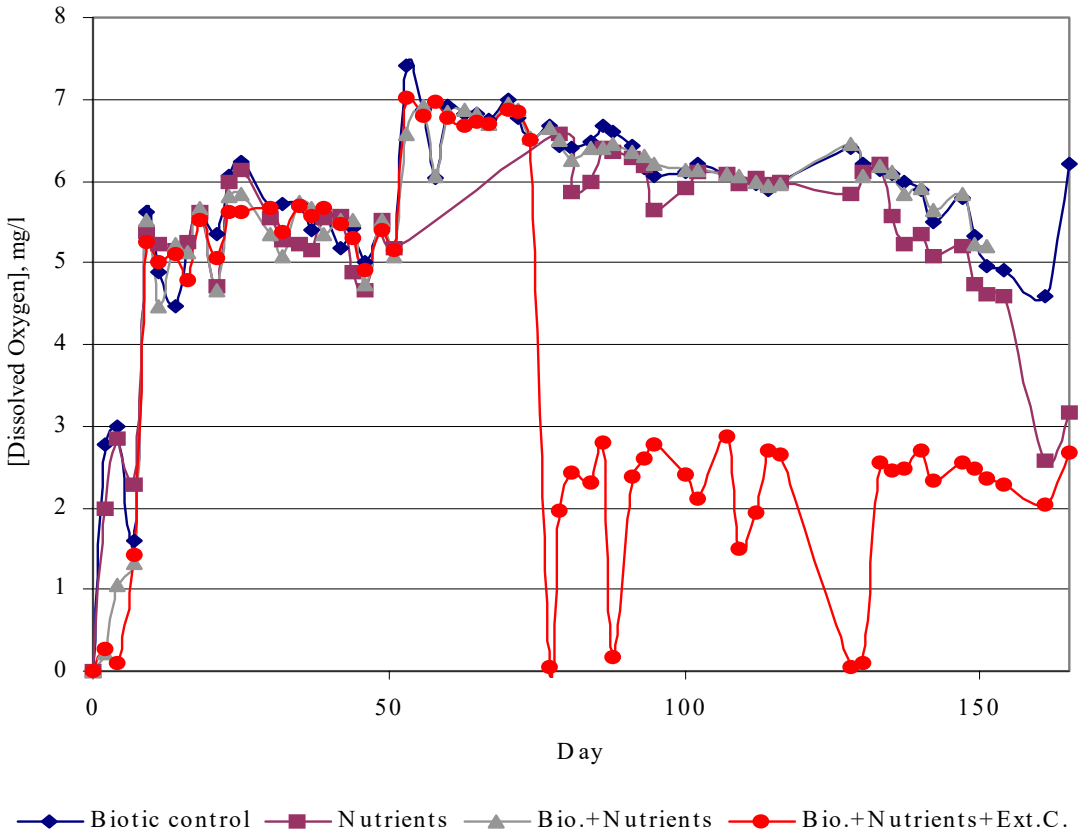


Figure 8.1. Dissolved Oxygen Readings for Phase II: Bioslurry Experiments

Notes:
- Nutrients: Indicates 1,000 mg/l nitrate and 400 mg/l phosphate additions weekly
- Bio.: Indicates naphthalene degraders addition
- Ext.C.: Indicates 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene, and 5% and 2.5% Tween 80 additions

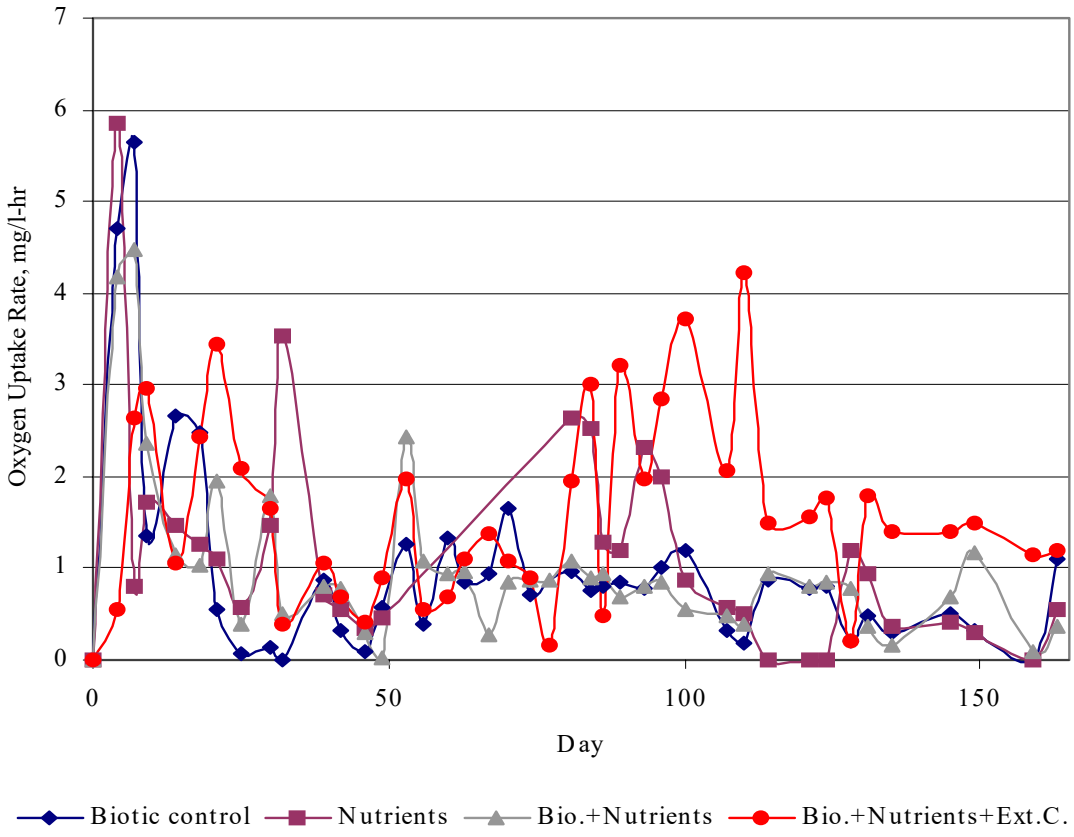


Figure 8.2. Oxygen Uptake Rate Results for Phase II: Bioslurry Experiments

Notes:
- Nutrients: Indicates 1,000 mg/l nitrate and 400 mg/l phosphate additions weekly
- Bio.: Indicates naphthalene degraders addition
- Ext.C.: Indicates 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene, and 5% and 2.5% Tween 80 additions

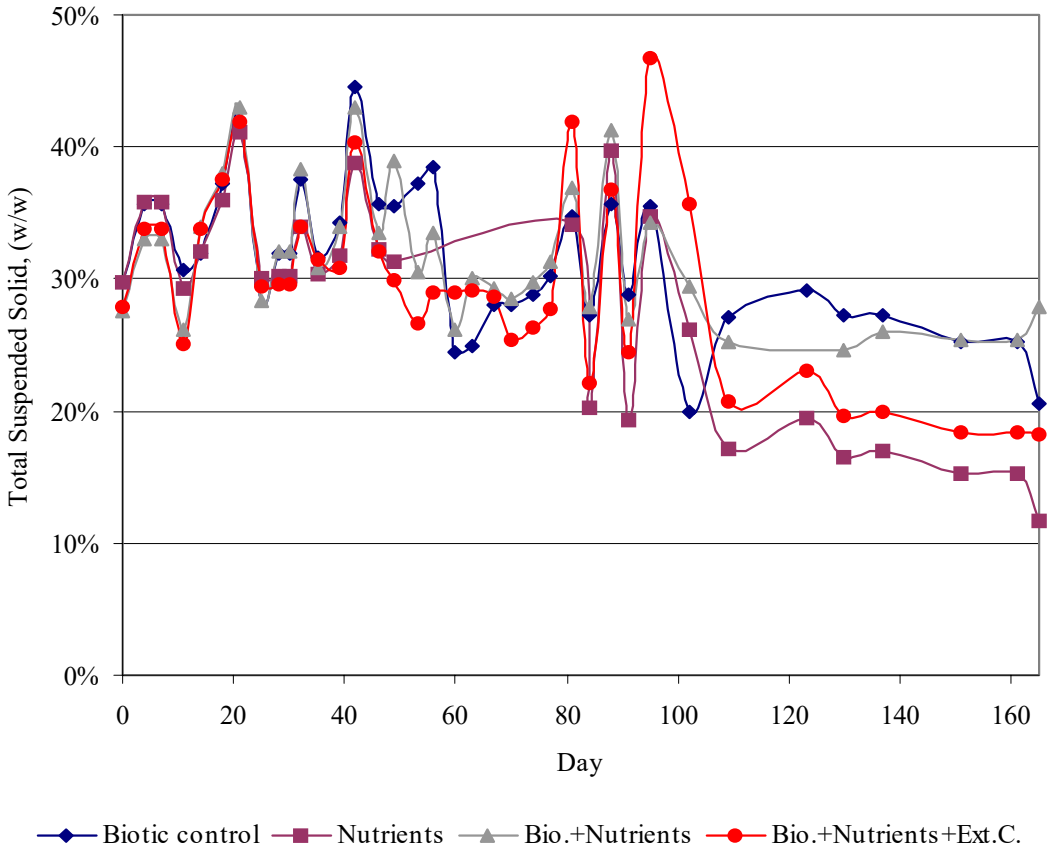


Figure 8.3. Total Suspended Solid Results for Phase II: Bioslurry Experiments

Notes:
- Nutrients: Indicates 1,000 mg/l nitrate and 400 mg/l phosphate additions weekly
- Bio.: Indicates naphthalene degraders addition
- Ext.C.: Indicates 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene, and 5% and 2.5% Tween 80 additions

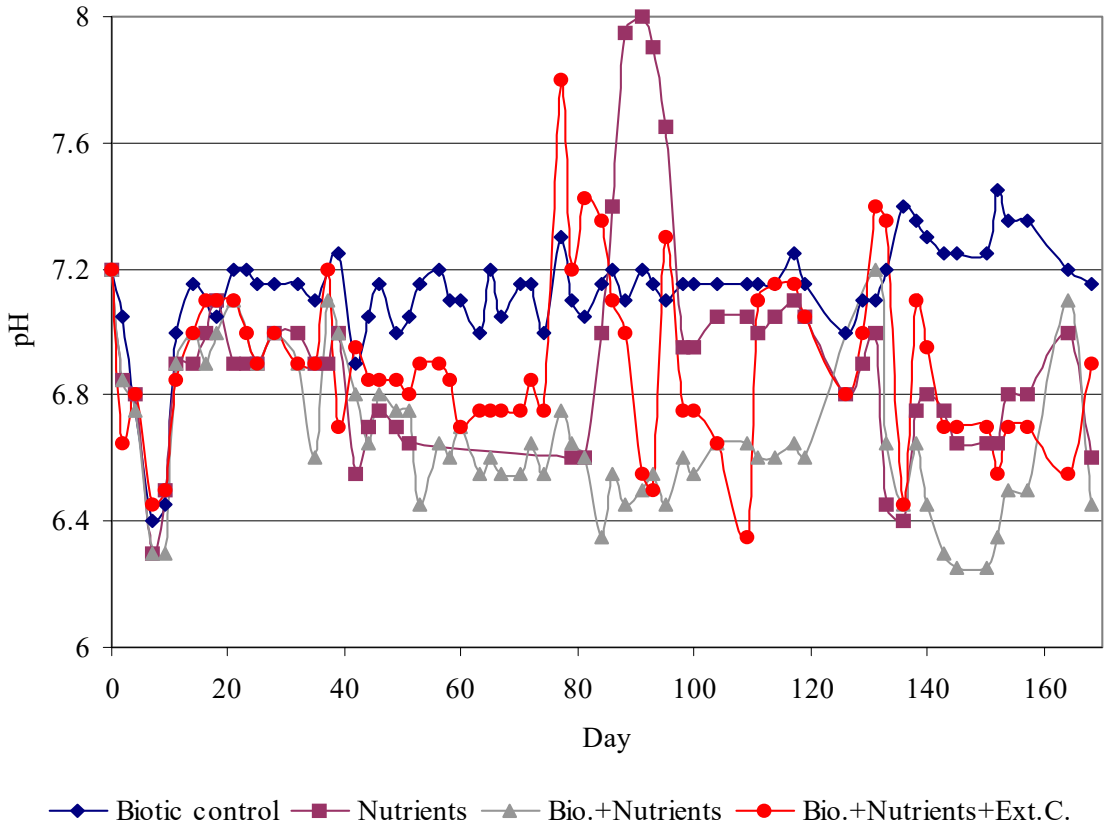


Figure 8.4. pH Readings for Phase II: Bioslurry Experiments

Notes:
- Nutrients: Indicates 1,000 mg/l nitrate and 400 mg/l phosphate additions weekly
- Bio.: Indicates naphthalene degraders addition
- Ext.C.: Indicates 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene, and 5% and 2.5% Tween 80 additions

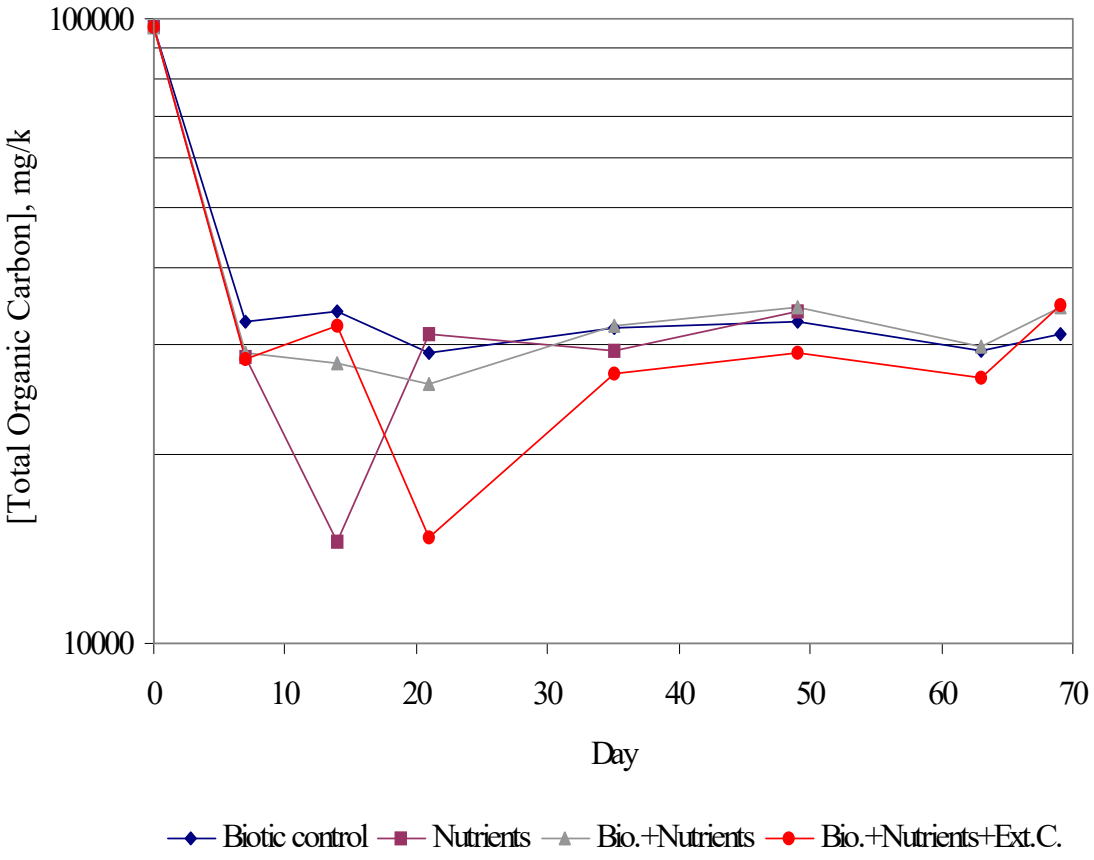


Figure 8.5. Total Organic Carbon in Sediment Results for Phase II: Bioslurry Experiments

Notes:
- Nutrients: Indicates 1,000 mg/l nitrate and 400 mg/l phosphate additions weekly
- Bio.: Indicates naphthalene degraders addition
- Ext.C.: Indicates 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene, and 5% and 2.5% Tween 80 additions

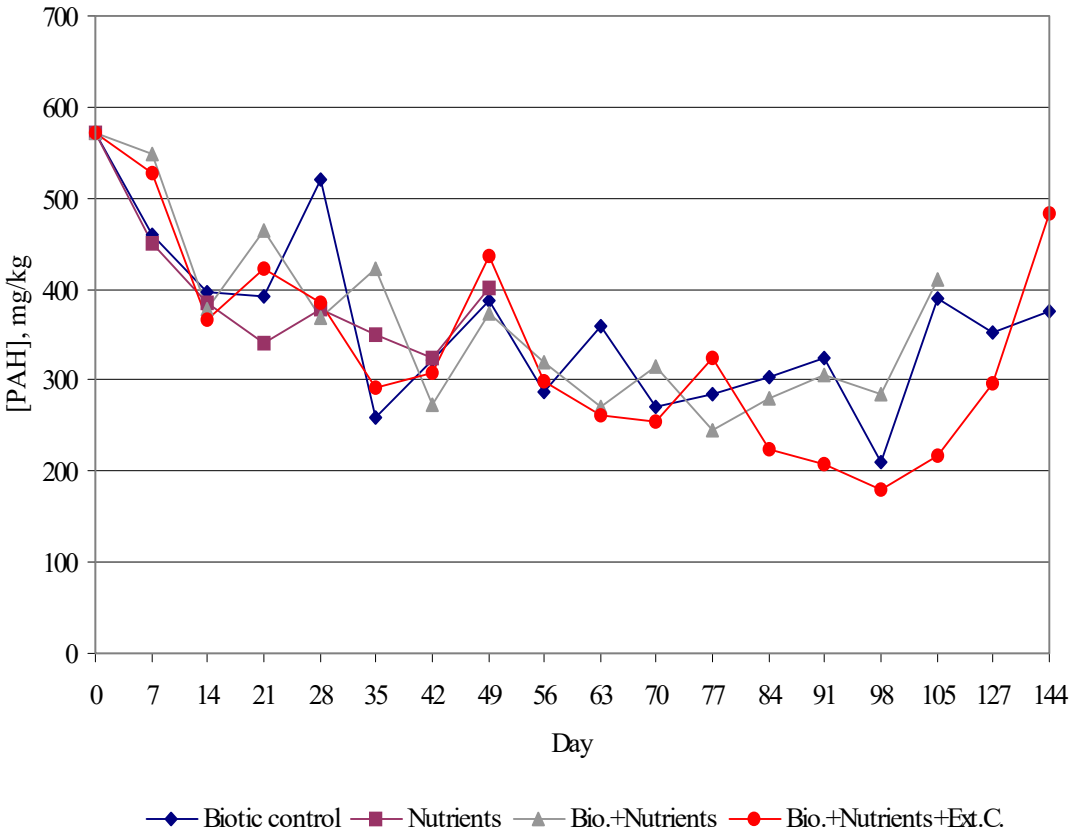


Figure 8.6. Bioremediation Results for Total PAHs in the Lake Superior Sediment

Notes:
- Nutrients: Indicates 1,000 mg/l nitrate and 400 mg/l phosphate additions weekly
- Bio.: Indicates naphthalene degraders addition
- Ext.C.: Indicates 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene, and 5% and 2.5% Tween 80 additions

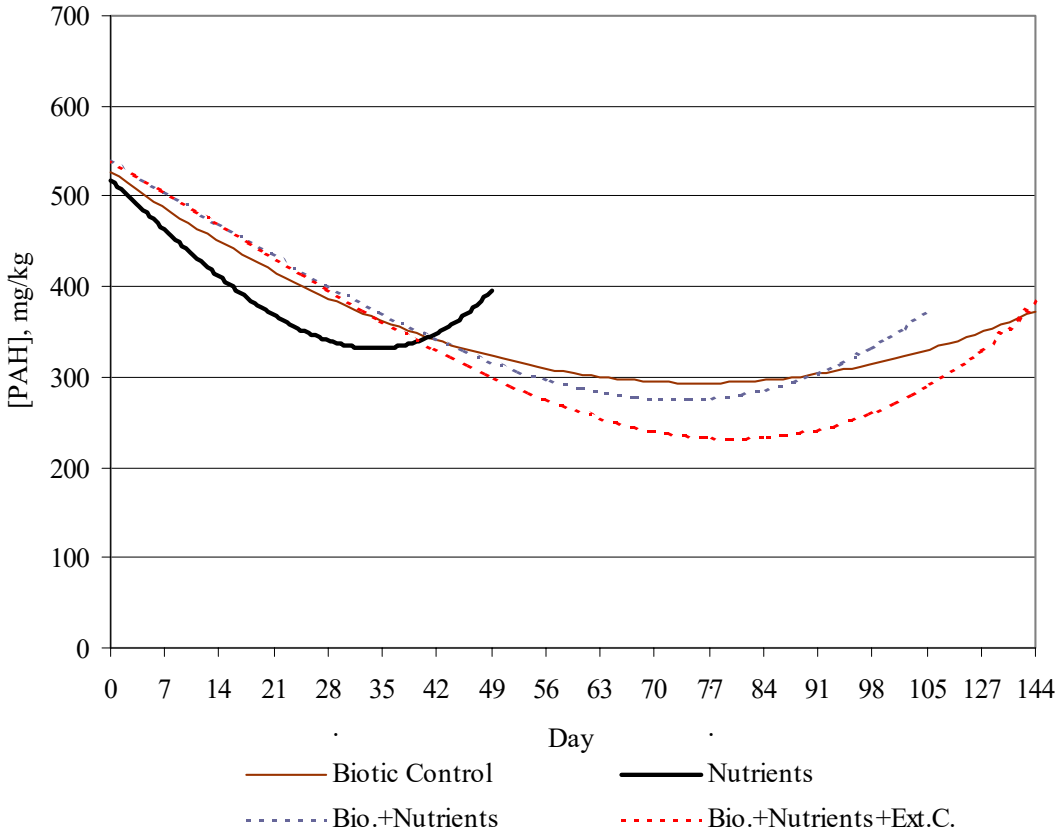


Figure 8.7. Polynomial Fit of the Bioremediation Results for Total PAHs in the Lake Superior Sediment

Notes:
- Nutrients: Indicates 1,000 mg/l nitrate and 400 mg/l phosphate additions weekly
- Bio.: Indicates naphthalene degraders addition
- Ext.C.: Indicates 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene, and 5% and 2.5% Tween 80 additions

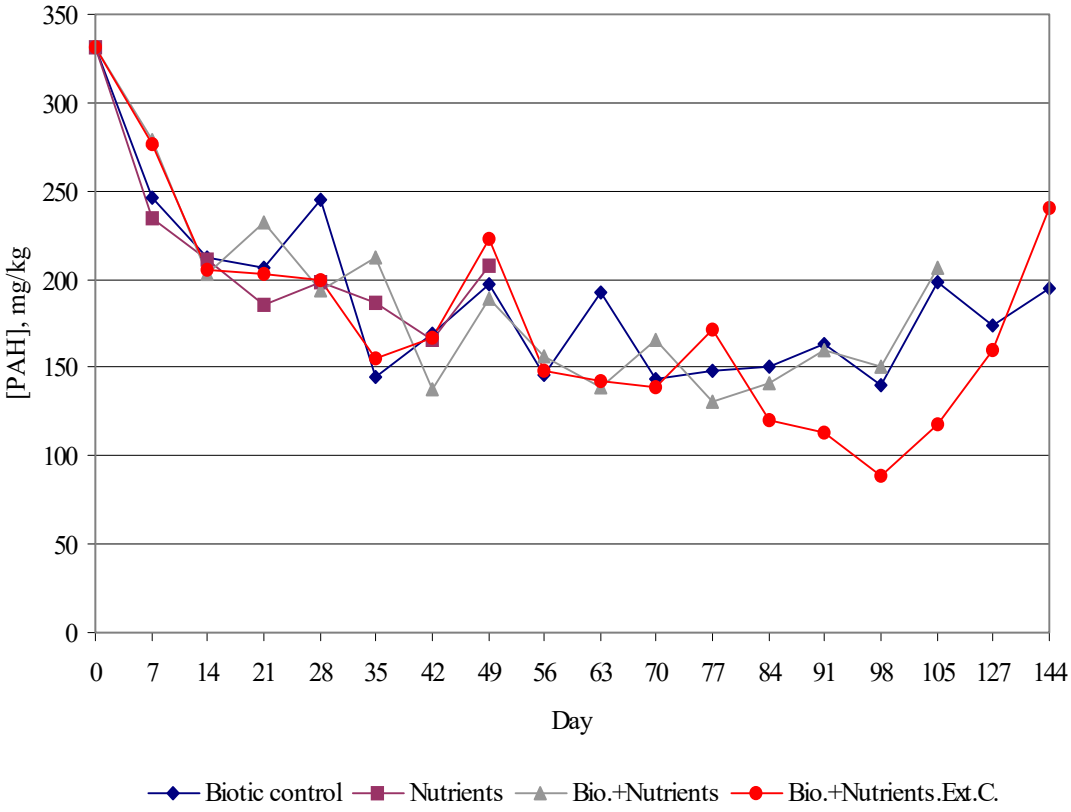


Figure 8.8. Bioremediation Results for Light PAHs in the Lake Superior Sediment

Notes:
- Nutrients: Indicates 1,000 mg/l nitrate and 400 mg/l phosphate additions weekly
- Bio.: Indicates naphthalene degraders addition
- Ext.C.: Indicates 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene, and 5% and 2.5% Tween 80 additions

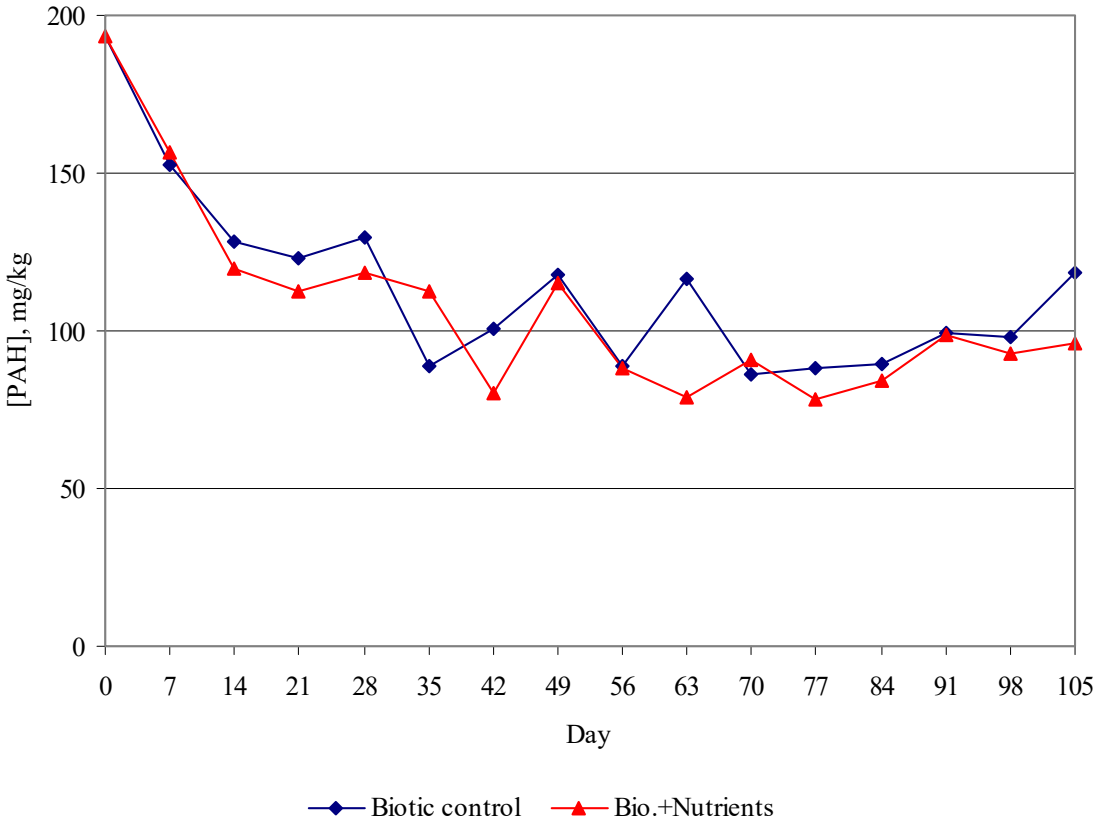


Figure 8.9. Bioremediation Results for Naphthalene in the Lake Superior Sediment

Notes:
- Nutrients: Indicates 1,000 mg/l nitrate and 400 mg/l phosphate additions weekly
- Bio.: Indicates naphthalene degraders addition

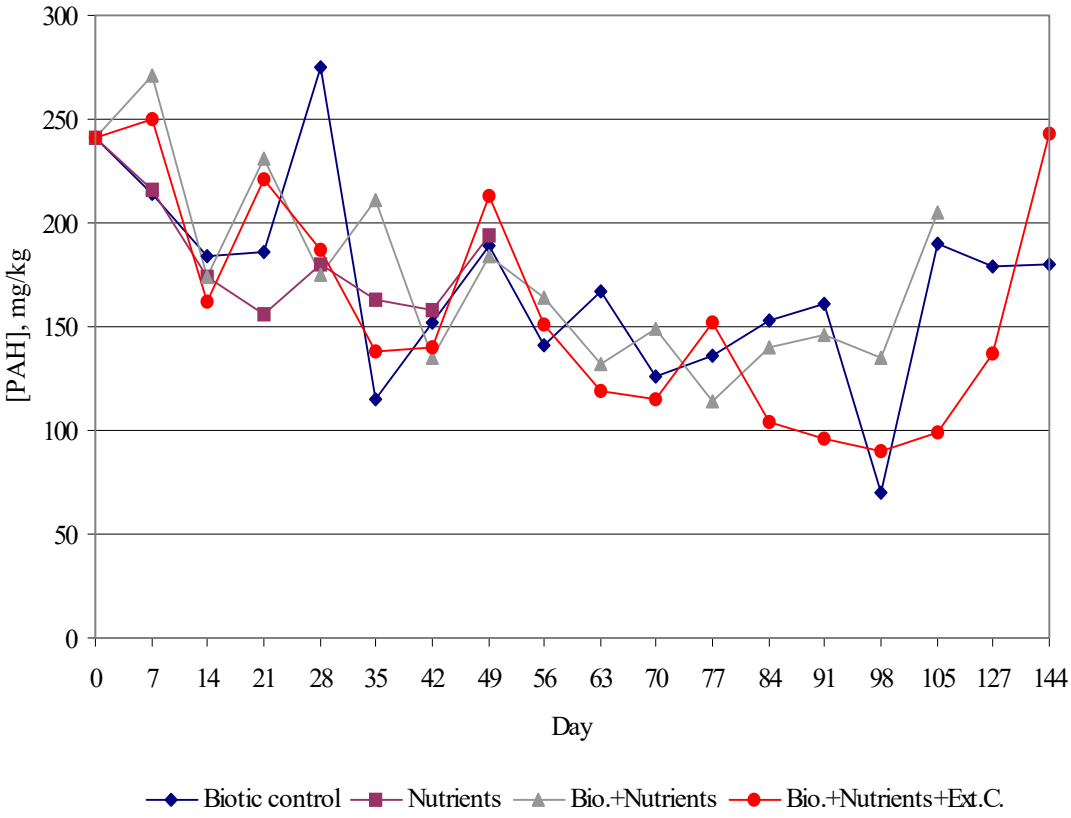


Figure 8.10. Bioremediation Results for Heavy PAHs Results in the Lake Superior Sediment

Notes:
- Nutrients: Indicates 1,000 mg/l nitrate and 400 mg/l phosphate additions weekly
- Bio.: Indicates naphthalene degraders addition
- Ext.C.: Indicates 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene, and 5% and 2.5% Tween 80 additions

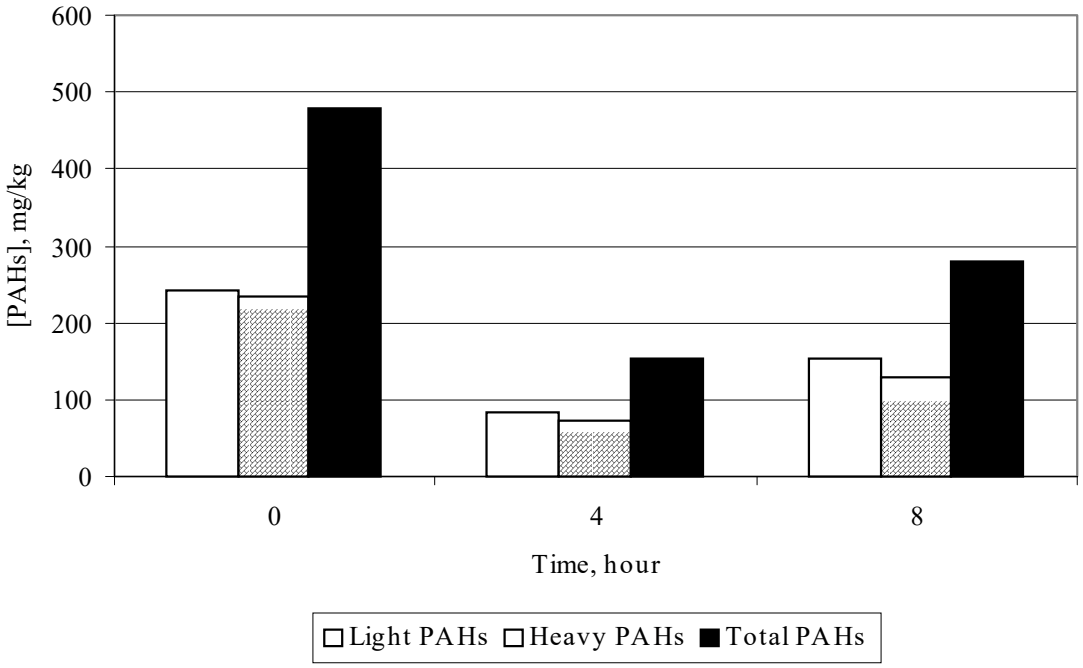


Figure 8.11. Integrated Ozonation Results of Lake Superior Sediment
(Nutrients set- Reactors 3 and 4)

Note:
- 3% (w/w) ozone at 2.5 scfh
- Nutrients: Indicates 1,000 mg/l nitrate and 400 mg/l phosphate additions weekly

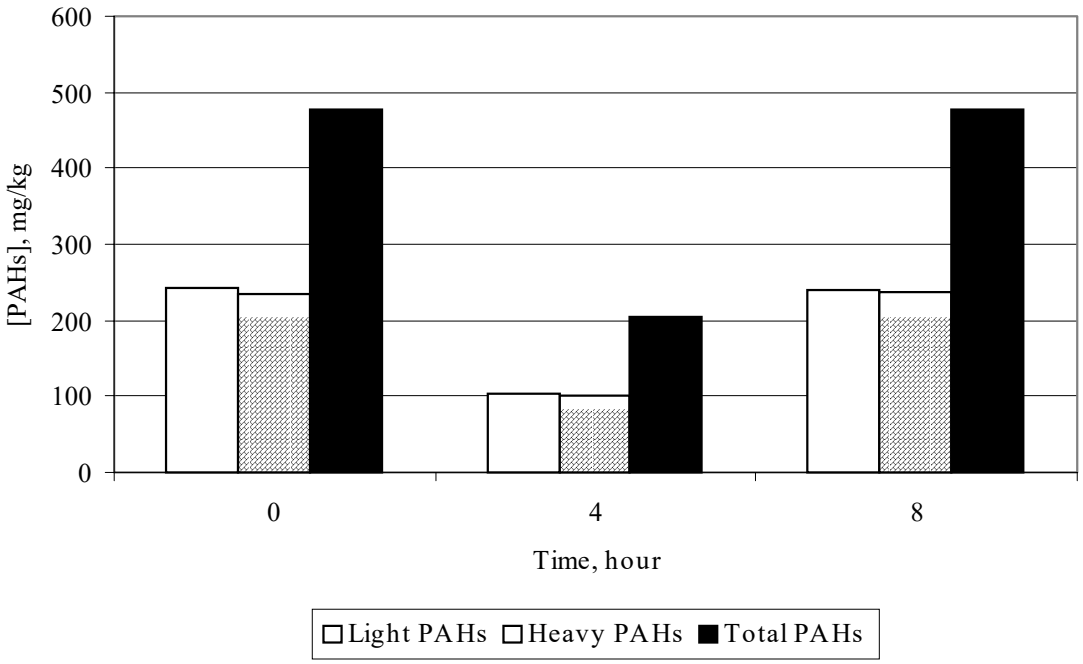


Figure 8.12. Integrated Peroxone Treatment Results of Lake Superior Sediment (Nutrients set- Reactors 3 and 4)

Notes:
- 3%wt Ozone at 2.5 scfh
- 100 mg/l H_2O_2 every hour for the first 4 hours and 500 mg/l H_2O_2 dosing every hour for the next 4 hours
- Nutrients: Indicates 1,000 mg/l nitrate and 400 mg/l phosphate additions weekly

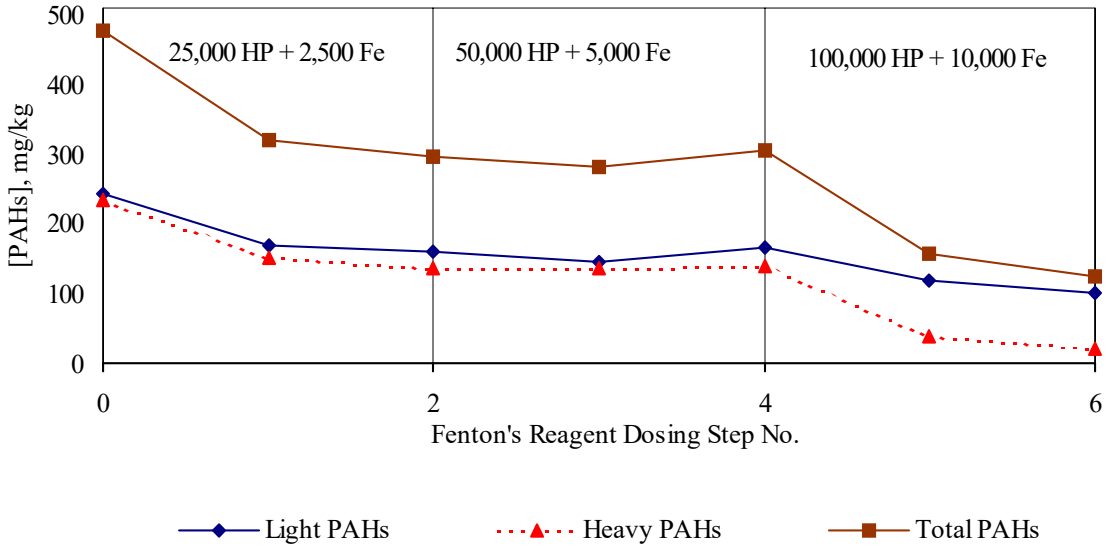


Figure 8.13. Integrated Fenton's Reagent Treatment Results of Lake Superior Sediment (Nutrients set-Reactors 3 and 4)

Notes:
- Nutrients: Indicates 1,000 mg/l nitrate and 400 mg/l phosphate additions weekly
- 25,000 HP/2,500 Fe, 50,000 HP/5,000 Fe, and 100,000 HP/10,00 Fe indicate the hydrogen peroxide and ferrous sulfate dosing step applied at increasing concentrations
- HP: Indicates H_2O_2 in mg/l
- Fe: Indicates Fe^{2+} in mg/l

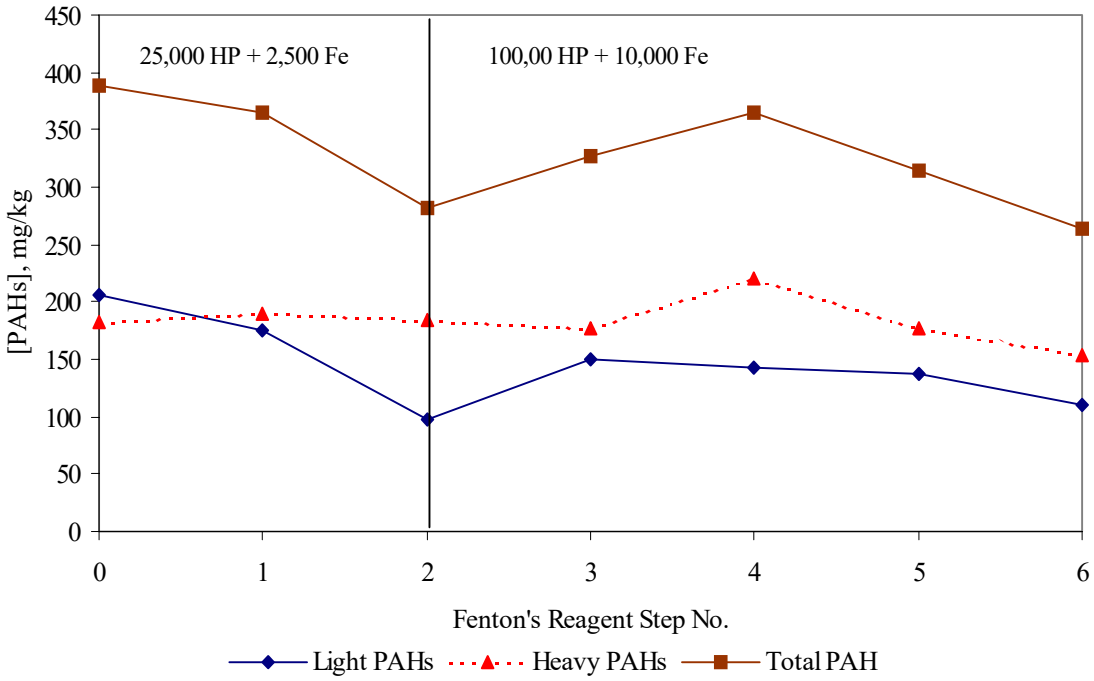


Figure 8.14. Integrated Fenton's Reagent Results of PAH in Lake Superior Sediment (Bio.+Nutrients set-Reactors 5 and 6)

Notes:
- Nutrients: Indicates 1,000 mg/l nitrate and 400 mg/l phosphate additions weekly
- Bio.: Indicates naphthalene degraders addition
- 25,000 HP/2,500 Fe and 100,000 HP/10,00 Fe indicate the hydrogen peroxide and ferrous sulfate dosing step applied at increasing concentrations
- HP: Indicates H_2O_2 in mg/l
- Fe: Indicates Fe^{2+} in mg/l

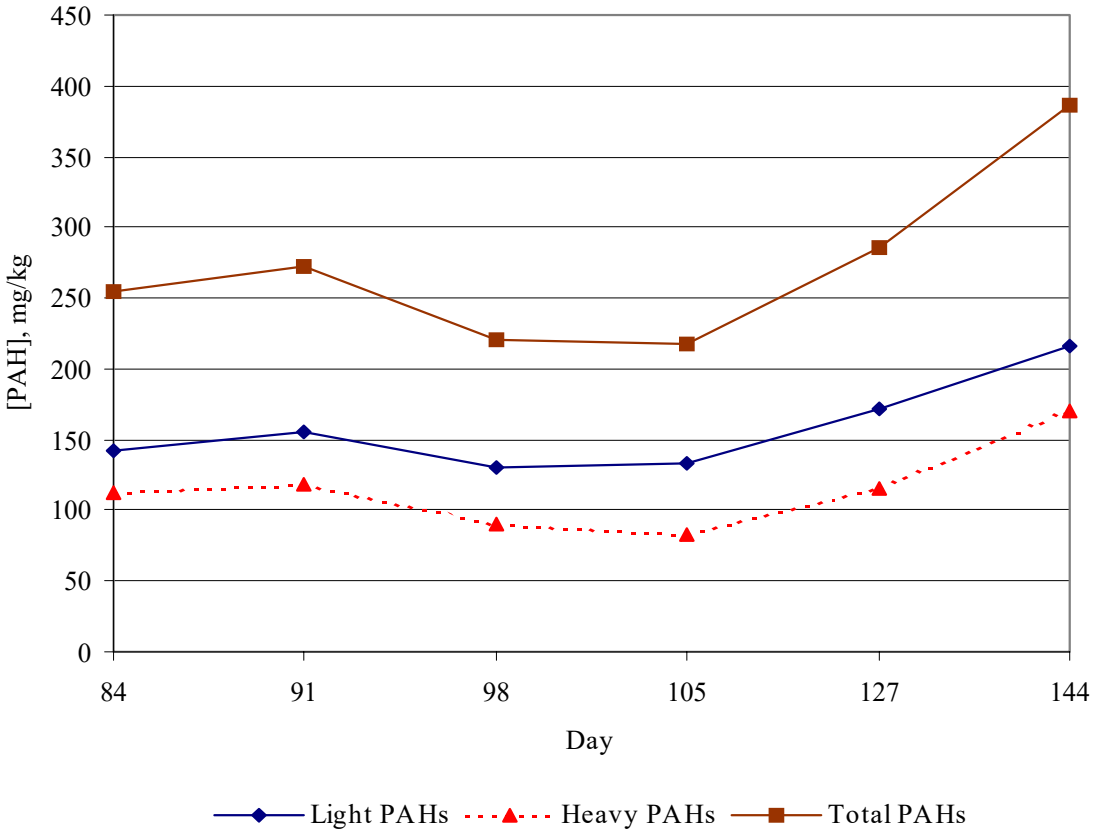


Figure 8.15. Post-Oxidation PAH Results in the Lake Superior Sediment (Nutrients Set- Reactors 3 and 4)

Notes:
- Nutrients: Indicates 1,000 mg/l nitrate and 400 mg/l phosphate additions weekly

CHAPTER IX

CONCLUSIONS AND IMPLICATIONS

Conclusions

The following primary conclusions were made from this study:

a. Poor degradation associated with biotreatment of the naphthalene was due to limited bioavailability and not the enzymatic capability of the microorganisms.

b. An increase in amount of extractable PAHs was observed after a short period of decreasing levels during all of the biotreatment steps.

c. The lesser aggressive oxidation process (Fenton's Reagent) resulted in a 50% Total PAH removal, while the more aggressive oxidation process (peroxone) dramatically increased the level of extractable Total PAHs (probably due to the oxidation of the organic adsorption site).

d. The proposed combination of both biotreatment and chemical oxidation was deemed ineffective for the higher contaminated sediment (Lake Superior). It was speculated that the presence of high biomass densities within the bioslurry reactors and a complex chemical matrix scavenged the oxidizers.

e. The integration of biotreatment and chemical oxidation was deemed successful for the lesser contaminated sediment (Scioto River), likely due to reduced stimulated biomass levels and a much simpler chemical matrix.

The following secondary conclusions were made based from the results of the individual experiments:

Lake Superior Sediment

a. The addition of nutrients at a PAH:N:P concentration ratio of 1:32:13 provided slow but steady degradation of PAHs within sediment as opposed to the set involving PAH:N:P concentration ratio of 100:20:5, which provided limited degradation. This increased nutrient dosage was considered a better dosing ratio when taking into account the total organic carbon present in the sediment.

b. The slurry systems involving addition of Tween 80 exhibited an 80% increase in the amount of extractable Total PAHs within the sediment as compared to the initial Total PAHs.

c. The addition of Tween 80 and glucose improved the degradation of the PAHs over the course of 20 weeks. Heavy PAHs were not detected within the sediment (glucose amended set) after 15 weeks of biotreatment.

d. The amendments of both Tween 80 and glucose hindered the degradation of Light PAHs as compared to the degradation of the Heavy PAHs. This effect was believed to be caused by substrate competition.

e. Ozonation of the sediment provided a 26% removal of the Total PAHs in the sediment slurry within 2 hours of treatment.

f. Peroxone treatment provided a 43.3% removal of the Total PAHs in the sediment within the first six hours of treatment. However, further treatment of peroxone resulted in a 70% increase in the amount of extractable PAHs within the sediment. The oxidation of the adsorption link was speculated to be the cause of this increase.

g. On average, 67% of added 1000 mg/l H_2O_2 was consumed in the equilibrated water samples within a 24-hour period. Reaction with the dissolved constituents from the sediments was believed to be the cause of these reactions.

h. The addition of hydrogen peroxide at 1,000 mg/l, 10,000 mg/l, and 100,000 mg/l provided an 80%, 40%, and 7% increase in the extractable Total PAHs, respectively, within the sediment as compared to the initial extractable Total PAHs.

i. All systems exhibited over 90% hydrogen peroxide degradation in the sediment within 20 hours of treatment time. The hydrogen peroxide removal was believed to be due to both abiotic reactions (oxidation with natural organic matter and dissolved cations) and biotic reactions (reaction with catalase).

j. Heavy PAHs within all slurry systems were not detected after seven dosing applications of Fenton's Reagent (25,000 mg/l H_2O_2 + 2,500 mg/l Fe^{2+} and 100,000 mg/l H_2O_2 + 10,000 mg/l Fe^{2+}).

k. The addition of Fenton's Reagent using a lower cumulative amount of H_2O_2 and Fe^{2+} was an effective and comparably a more economical treatment condition compared to the higher dosed Fenton's Reagent system in terms of PAH removal from the sediment.

l. The addition of Tween 80 into the bioslurry reactors after Day 98 of the experiments resulted in a 169% increase in the amount of extractable PAHs within the sediment.

m. After eight hours of treatment, ozonation provided a 41% removal of extractable PAHs from the sediment that was previously bioslurry treated.

n. Peroxone treatment provided 57% removal of the total extractable PAHs in the previously bioslurry treated sediment within the first four hours of treatment. However, further treatment of the sediment sample with peroxone resulted in a 57% increase in the amount of extractable PAHs over the initial starting concentration.

o. The subsequent biotreatment step after the chemical oxidation provided a 51% increase in the amount of extractable PAHs within the sediment in 60 days. This trend was observed each time a biotreatment step was applied (pre-post oxidation).

Scioto River Sediment

a. The addition of nutrients (N and P), activated sludge, and Tween 80 resulted in a 100% increase in the amount of extractable PAHs in the sediment within four weeks of biotreatment as compared to the initial Total PAHs.

b. The systems involving the addition of nutrients and/or activated sludge achieved at least an 80% removal of PAHs by the third week of biotreatment prior to an increase in the amount of extractable PAHs (approximately 30% of the original concentration) by the fourth week (an overall net 70% reduction).

c. All slurry systems exhibited the same complete removal of PAH after seven dosing applications of Fenton's Reagent. This effect was not observed within the Lake

Superior Sediment, proving a high potential for treating this sample using this proposed process.

Study Implications

This study indicates mixed results in terms of the viability of the proposed process for treating PAH-contaminated sediments. The highly contaminated and chemically more complex sediment (Lake Superior) proved too challenging for the integrated process. However, the less chemically complex sediment (Scioto River) appears to be conducive toward the proposed integrated treatment process. The application of the integrated process is likely best performed early into the biotreatment step once the total extractable PAHs are partly removed (less than 50% of the initial concentration). This will allow for the natural sediment oxygen demand to be overcome, without dramatically disturbing the adsorption equilibria. After the biotreatment step, chemical oxidation appears to be capable of rapidly degrading the remaining fractions of PAHs. However, given that the process worked with one sediment and not the other, additional research is needed to determine what mechanisms are controlling treatment within these sediment systems.

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APPENDIX A

SUMMARY OF EXPERIMENTAL DATA FOR PHASE I:

BIOTREATMENT SCREENING EXPERIMENTS

Notes:

2-ring PAH: Naphthalene
3-ring PAHs: Acenaphthylene, Acenaphthene, Fluorene, Anthracene, and Phenanthrene
4-ring PAHs: Fluoranthene, Pyrene, Benzo[a]anthracene, and Chrysene
5-ring PAHs: Benzo[k]fluoranthene, Benzo[b]fluoranthene, Benzo[a]pyrene, and Dibenz[a,h]anthracene
6-ring PAHs: Benzo[g,h,i] perylene and Indeno[1,2,3-cd]perylene
Ave: Average
Stdev: Standard deviation

Table A.1. PAH Results for the Bioavailability Experiments

Condition	Naphthalene Degraders + 25 mg/l Naphthalene Solution Addition				Naphthalene Degraders + PAH Contaminated Sediment			
Treatment Time, Hour	Liquid Phase Naphthalene Analysis, mg/l							
	Replica		Ave	Stdev	Replica		Ave	Stdev
	1	2			1	2		
0	11.64	22.55	17.10	7.72	3.24	2.39	2.81	0.60
1.6	2.25	2.63	2.44	.27	0	0	0	0
70.1	0	0	0	0	0	0	0	0

Treatment Time, Hour	Soil Phase Naphthalene Analysis, mg/kg			
	Replica		Ave	Stdev
	1	2		
0	314.87	254.60	284.73	42.62
1.6	193.67	244.67	219.17	36.06
70.1	311.11	177.23	244.17	94.67

Table A.2. pH Results for the Biotreatment of the Scioto River Sediment

			Week				
			0	1	2	3	4
Biotic Control	Replica	1	7.58	7.46	7.75	7.39	7.59
		2	7.58	7.25	7.60	7.38	7.48
	Average		7.58	7.36	7.68	7.39	7.54
	Stdev		0.00	0.15	0.11	0.01	0.08
Nutrients	Replica	1	7.58	6.79	7.40	7.20	7.32
		2	7.58	6.59	7.36	7.16	7.32
	Average		7.58	6.69	7.38	7.18	7.32
	Stdev		0.00	0.14	0.03	0.03	0.00
AS.+100:20:5	Replica	1	7.58	6.63	7.40	7.15	7.31
		2	7.58	6.64	7.38	7.11	7.27
	Average		7.58	6.64	7.39	7.13	7.29
	Stdev		0.00	0.01	0.01	0.03	0.03
AS.+100:20:5 + T80	Replica	1	7.58	6.06	6.05	5.84	5.48
		2	7.58	6.08	6.05	5.83	6.00
	Average		7.58	6.07	6.05	5.84	5.74
	Stdev		0.00	0.01	0.00	0.01	0.37

Notes:
- PAH represented as mg/kg
- AS.: Bioaugmentation with activated sludge from the return line of a local wastewater
- 100:20:5 represent PAH:N:P ratio
- T80: Tween 80 addition at 0.5% (w/w) the first week and 0.25% (w/w) the following weeks

Table A.3. PAH Results for Phase I: Bioremediation Screening Test (Scioto River Sediment)

Condition	Week	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
Biotic Control	0	Replica	1	1.44	6.44	7.88	14.09	4.46	4.30	22.86	30.74
			2	2.42	1.15	3.57	8.48	2.28	3.76	14.52	18.09
		Average		1.93	3.79	5.72	11.29	3.37	4.03	18.69	24.41
		Stdev		0.69	3.75	3.05	3.97	1.55	0.38	5.89	8.95
	1	Replica	1	1.17	6.36	7.53	16.95	8.97	6.57	32.50	40.02
			2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Average		0.59	3.18	3.76	8.48	4.49	3.29	16.25	20.01
		Stdev		0.83	4.49	5.32	11.99	6.34	4.65	22.98	28.30
	2	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	0.00	6.45	6.45	15.95	13.54	5.46	34.94	41.39
		Average		0.00	3.23	3.23	7.97	6.77	2.73	17.47	20.70
		Stdev		0.00	4.56	4.56	11.28	9.57	3.86	24.71	29.27
	3	Replica	1	0.00	1.43	1.43	6.67	5.00	4.39	16.06	17.49
			2	0.00	10.97	10.97	18.02	14.39	9.19	41.59	52.56
		Average		0.00	6.20	6.20	12.34	9.69	6.79	28.83	35.03
		Stdev		0.00	6.74	6.74	8.03	6.64	3.39	18.06	24.80
	4	Replica	1	0.00	1.13	1.13	3.81	1.18	2.61	7.60	8.73
			2	0.00	2.33	2.33	10.63	6.65	6.01	23.29	25.62
		Average		0.00	1.73	1.73	7.22	3.91	4.31	15.44	17.17
		Stdev		0.00	0.85	0.85	4.82	3.87	2.41	11.10	11.94

Note:
- PAH represented as mg/kg

Table A.3. (Continued)

Condition	Week	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
100:20:5	0	Replica	1	1.44	6.44	7.88	14.09	4.46	4.30	22.86	30.74
			2	2.42	1.15	3.57	8.48	2.28	3.76	14.52	18.09
		Average		1.93	3.79	5.72	11.29	3.37	4.03	18.69	24.41
		Stdev		0.69	3.75	3.05	3.97	1.55	0.38	5.89	8.95
	1	Replica	1	0.00	6.49	6.49	4.82	0.45	0.76	6.04	12.53
			2	0.00	0.60	0.60	6.50	4.01	3.77	14.28	14.88
		Average		0.00	3.54	3.54	5.66	2.23	2.27	10.16	13.70
		Stdev		0.00	4.16	4.16	1.18	2.51	2.13	5.83	1.66
	2	Replica	1	0.00	0.00	0.00	1.87	0.79	1.26	3.92	3.92
			2	0.00	0.00	0.00	0.59	0.00	1.93	2.52	2.52
		Average		0.00	0.00	0.00	1.23	0.40	1.59	3.22	3.22
		Stdev		0.00	0.00	0.00	0.91	0.56	0.48	0.99	0.99
	3	Replica	1	0.00	0.00	0.00	1.49	2.63	3.09	7.21	7.21
			2	0.00	0.00	0.00	0.00	0.00	1.10	1.10	1.10
		Average		0.00	0.00	0.00	0.74	1.32	2.10	4.16	4.16
		Stdev		0.00	0.00	0.00	1.05	1.86	1.41	4.32	4.32
	4	Replica	1	0.00	1.96	1.96	8.79	8.44	7.44	24.68	26.64
			2	0.00	1.04	1.04	6.67	5.16	6.15	17.98	19.02
		Average		0.00	1.50	1.50	7.73	6.80	6.80	21.33	22.83
		Stdev		0.00	0.65	0.65	1.50	2.32	0.91	4.74	5.39

Notes:
- PAH represented as mg/kg
- 100:20:5 represents PAH:N:P ratio

Table A.3. (Continued)

Condition	Week	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
AS. + 100:20:5	0	Replica	1	1.44	6.44	7.88	14.09	4.46	4.30	22.86	30.74
			2	2.42	1.15	3.57	8.48	2.28	3.76	14.52	18.09
		Average		1.93	3.79	5.72	11.29	3.37	4.03	18.69	24.41
		Stdev		0.69	3.75	3.05	3.97	1.55	0.38	5.89	8.95
	1	Replica	1	0.00	1.48	1.48	7.59	5.03	5.34	17.95	19.43
			2	0.00	0.53	0.53	3.48	1.36	2.61	7.45	7.99
		Average		0.00	1.00	1.00	5.54	3.19	3.98	12.70	13.71
		Stdev		0.00	0.67	0.67	2.90	2.59	1.93	7.42	8.09
	2	Replica	1	0.00	0.06	0.06	2.89	0.00	3.31	6.20	6.26
			2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Average		0.00	0.03	0.03	1.45	0.00	1.65	3.10	3.13
		Stdev		0.00	0.04	0.04	2.04	0.00	2.34	4.38	4.42
	3	Replica	1	0.00	0.00	0.00	0.00	0.00	0.81	0.81	0.81
			2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Average		0.00	0.00	0.00	0.00	0.00	0.41	0.41	0.41
		Stdev		0.00	0.00	0.00	0.00	0.00	0.58	0.58	0.58
	4	Replica	1	0.00	0.01	0.01	1.54	0.00	1.96	3.50	3.51
			2	0.00	5.62	5.62	10.92	0.00	3.30	14.23	19.84
		Average		0.00	2.81	2.81	6.23	0.00	2.63	8.86	11.68
		Stdev		0.00	3.97	3.97	6.63	0.00	0.95	7.58	11.55

Notes:
- PAH represented as mg/kg
- AS.: Bioaugmentation with activated sludge from the return line of a local wastewater
- 100:20:5 represent PAH:N:P ratio

Table A.3. (Continued)

Condition	Week	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
AS. + 100:20:5 + T80	0	Replica	1	1.44	6.44	7.88	14.09	4.46	4.30	22.86	30.74
			2	2.42	1.15	3.57	8.48	2.28	3.76	14.52	18.09
		Average		1.93	3.79	5.72	11.29	3.37	4.03	18.69	24.41
		Stdev		0.69	3.75	3.05	3.97	1.55	0.38	5.89	8.95
	1	Replica	1	0.00	7.15	7.15	19.14	3.88	3.12	26.15	33.30
			2	0.00	0.55	0.55	3.21	18.08	0.00	21.29	21.84
		Average		0.00	3.85	3.85	11.18	10.98	1.56	23.72	27.57
		Stdev		0.00	4.67	4.67	11.26	10.04	2.21	3.43	8.10
	2	Replica	1	0.00	3.95	3.95	8.11	34.23	0.00	42.34	46.29
			2	0.00	6.14	6.14	15.36	1.97	0.00	17.32	23.46
		Average		0.00	5.05	5.05	11.73	18.10	0.00	29.83	34.88
		Stdev		0.00	1.55	1.55	5.13	22.81	0.00	17.69	16.14
	3	Replica	1	0.00	4.14	4.14	9.92	8.95	0.00	18.87	23.01
			2	0.00	4.79	4.79	9.91	22.00	7.65	39.56	44.35
		Average		0.00	4.46	4.46	9.92	15.48	3.83	29.22	33.68
		Stdev		0.00	0.46	0.46	0.01	9.23	5.41	14.63	15.09
	4	Replica	1	0.71	6.29	7.00	11.34	0.88	0.99	13.21	20.21
			2	0.00	23.19	23.19	38.00	17.40	4.60	60.00	83.20
		Average		0.36	14.74	15.10	24.67	9.14	2.80	36.61	51.70
		Stdev		0.50	11.96	11.45	18.85	11.68	2.56	33.09	44.54

Notes:
- PAH represented as mg/kg
- AS.: Bioaugmentation with activated sludge from the return line of a local wastewater
- 100:20:5 represent PAH:N:P ratio
- T80: Tween 80 addition at 0.5% (w/w) the first week and 0.25% (w/w) the following weeks

Table A.4. PAH Results for Phase I: Bioremediation Screening Test (Lake Superior Sediment)

Condition	Week	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
Biotic Control	0	Replica	1	81.40	63.34	144.74	83.58	29.31	21.73	83.58	228.32
			2	114.59	63.85	178.45	88.07	29.75	27.10	88.07	266.52
		Average		98.00	63.60	161.59	85.83	29.53	24.42	85.83	247.42
		Stdev		23.47	0.37	23.84	3.18	0.32	3.80	3.18	27.01
	1	Replica	1	109.36	54.65	164.01	116.50	48.15	34.46	82.61	246.63
			2	110.36	49.61	159.97	80.06	24.50	29.91	54.41	214.38
		Average		109.86	52.13	161.99	98.28	36.33	32.19	68.51	230.50
		Stdev		0.71	3.57	2.86	25.76	16.72	3.22	19.94	22.80
	2	Replica	1	77.15	46.03	123.17	38.62	25.82	19.49	45.32	168.49
			2	92.89	42.42	135.31	41.19	24.98	37.56	62.54	197.85
		Average		85.02	44.23	129.24	39.90	25.40	28.52	53.93	183.17
		Stdev		11.13	2.55	8.59	1.82	0.59	12.77	12.18	20.76
	3	Replica	1	95.28	46.84	142.12	43.49	36.15	83.12	119.27	261.40
			2	73.44	43.08	116.52	32.12	23.57	34.32	57.89	174.41
		Average		84.36	44.96	129.32	37.81	29.86	58.72	88.58	217.90
		Stdev		15.45	2.66	18.10	8.04	8.90	34.51	43.40	61.51
	4	Replica	1	62.78	42.42	105.20	33.93	23.84	31.15	54.99	160.19
			2	67.85	41.22	109.07	29.52	17.01	34.98	51.99	161.06
		Average		65.31	41.82	107.14	31.73	20.43	33.06	53.49	160.63
		Stdev		3.59	0.85	2.74	3.12	4.83	2.71	2.12	0.62

Note:
- PAH represented as mg/kg

Table A.4. (Continued)

Condition	Week	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
100:20:5	0	Replica	1	81.40	63.34	144.74	83.58	29.31	21.73	83.58	228.32
			2	114.59	63.85	178.45	88.07	29.75	27.10	88.07	266.52
		Average		98.00	63.60	161.59	85.83	29.53	24.42	85.83	247.42
		Stdev		23.47	0.37	23.84	3.18	0.32	3.80	3.18	27.01
	1	Replica	1	26.02	27.64	53.66	128.50	39.12	25.24	128.50	182.15
			2	21.67	25.18	46.86	139.50	27.28	28.67	139.50	186.36
		Average		23.85	26.41	50.26	134.00	33.20	26.95	134.00	184.26
		Stdev		3.08	1.73	4.81	7.78	8.37	2.42	7.78	2.97
	2	Replica	1	84.02	42.36	126.38	73.81	30.75	19.90	73.81	200.19
			2	95.62	49.70	145.33	40.56	46.48	26.07	40.56	185.89
		Average		89.82	46.03	135.85	57.19	38.61	22.98	57.19	193.04
		Stdev		8.20	5.19	13.40	23.51	11.13	4.37	23.51	10.11
	3	Replica	1	112.24	54.53	166.78	92.82	57.05	29.76	92.82	259.59
			2	117.34	84.79	202.13	139.50	81.24	47.03	139.50	341.63
		Average		114.79	69.66	184.45	116.16	69.15	38.39	116.16	300.61
		Stdev		3.60	21.40	25.00	33.01	17.11	12.21	33.01	58.01
	4	Replica	1	74.11	55.73	129.85	73.81	43.82	25.94	73.81	203.66
			2	76.81	39.57	116.38	40.56	35.92	24.17	40.56	156.94
		Average		75.46	47.65	123.11	57.19	39.87	25.05	57.19	180.30
		Stdev		1.91	11.43	9.52	23.51	5.58	1.25	23.51	33.03

Notes:
- PAH represented as mg/kg
- 100:20:5 represents PAH:N:P ratio

Table A.4. (Continued)

Condition	Week	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
1:32:13	0	Replica	1	81.40	63.34	144.74	83.58	29.31	21.73	83.58	228.32
			2	114.59	63.85	178.45	88.07	29.75	27.10	88.07	266.52
		Average		98.00	63.60	161.59	85.83	29.53	24.42	85.83	247.42
		Stdev		23.47	0.37	23.84	3.18	0.32	3.80	3.18	27.01
	1	Replica	1	86.22	42.64	128.86	66.29	20.78	25.65	66.29	195.15
			2	129.95	54.63	184.58	97.75	31.37	35.06	97.75	282.33
		Average		108.09	48.63	156.72	82.02	26.08	30.35	82.02	238.74
		Stdev		30.92	8.47	39.40	22.25	7.49	6.66	22.25	61.64
	2	Replica	1	74.49	41.86	116.36	42.95	15.13	8.30	42.95	159.30
			2	73.86	42.60	116.46	32.82	15.50	13.15	32.82	149.28
		Average		74.18	42.23	116.41	37.88	15.32	10.72	37.88	154.29
		Stdev		0.45	0.52	0.07	7.16	0.26	3.43	7.16	7.09
	3	Replica	1	62.44	42.64	105.08	35.40	23.27	41.75	35.40	140.48
			2	59.33	41.92	101.25	32.14	19.90	40.41	32.14	133.39
		Average		60.88	42.28	103.16	33.77	21.59	41.08	33.77	136.93
		Stdev		2.20	0.51	2.71	2.30	2.38	0.95	2.30	5.01
	4	Replica	1	55.17	40.89	96.06	25.88	11.88	7.06	25.88	121.93
			2	83.92	42.75	126.67	50.55	23.15	30.82	50.55	177.22
		Average		69.54	41.82	111.36	38.21	17.51	18.94	38.21	149.58
		Stdev		20.33	1.32	21.64	17.45	7.97	16.80	17.45	39.09

Notes:
- PAH represented as mg/kg
- 1:32:13 represent PAH:N:P ratio

Table A.4. (Continued)

Condition	Week	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
AS. + 100:20:5	0	Replica	1	81.40	63.34	144.74	83.58	29.31	21.73	83.58	228.32
			2	114.59	63.85	178.45	88.07	29.75	27.10	88.07	266.52
		Average		98.00	63.60	161.59	85.83	29.53	24.42	85.83	247.42
		Stdev		23.47	0.37	23.84	3.18	0.32	3.80	3.18	27.01
	1	Replica	1	26.83	28.00	54.83	84.08	31.85	24.49	84.08	138.91
			2	18.44	25.10	43.54	119.77	33.74	21.58	119.77	163.31
		Average		22.64	26.55	49.19	101.93	32.79	23.03	101.93	151.11
		Stdev		5.94	2.05	7.98	25.24	1.33	2.05	25.24	17.25
	2	Replica	1	98.49	45.93	144.42	89.39	36.72	22.59	89.39	233.81
			2	101.21	51.21	152.43	77.46	58.80	32.09	77.46	229.89
		Average		99.85	48.57	148.43	83.43	47.76	27.34	83.43	231.85
		Stdev		1.92	3.74	5.66	8.44	15.61	6.72	8.44	2.78
	3	Replica	1	118.83	52.62	171.45	84.08	58.30	37.48	84.08	255.53
			2	127.80	55.54	183.35	88.64	61.09	30.88	88.64	271.98
		Average		123.32	54.08	177.40	86.36	59.69	34.18	86.36	263.76
		Stdev		6.34	2.07	8.41	3.22	1.97	4.67	3.22	11.63
	4	Replica	1	114.90	55.38	170.28	89.39	49.55	30.50	89.39	259.67
			2	73.85	49.47	123.33	77.46	37.19	17.59	77.46	200.78
		Average		94.38	52.43	146.80	83.43	43.37	24.05	83.43	230.23
		Stdev		29.02	4.18	33.20	8.44	8.74	9.13	8.44	41.64

Notes:
- PAH represented as mg/kg
- AS.: Bioaugmentation with activated sludge from the return line of a local wastewater treatment plant
- 100:20:5 represents PAH:N:P ratio

Table A.4. (Continued)

Condition	Week	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
AS1 + 100:20:5 + T80	0	Replica	1	81.40	63.34	144.74	83.58	29.31	21.73	83.58	228.32
			2	114.59	63.85	178.45	88.07	29.75	27.10	88.07	266.52
		Average		98.00	63.60	161.59	85.83	29.53	24.42	85.83	247.42
		Stdev		23.47	0.37	23.84	3.18	0.32	3.80	3.18	27.01
	1	Replica	1	11.06	112.98	124.04	196.90	133.13	256.99	196.90	320.95
			2	11.43	116.63	128.06	258.32	200.33	418.45	258.32	386.39
		Average		11.25	114.81	126.05	227.61	166.73	337.72	227.61	353.67
		Stdev		0.26	2.58	2.84	43.43	47.52	114.17	43.43	46.27
	2	Replica	1	15.63	160.31	175.94	651.16	289.09	777.67	651.16	827.09
			2	16.65	160.22	176.87	419.69	261.77	728.75	419.69	596.56
		Average		16.14	160.27	176.40	535.42	275.43	753.21	535.42	711.82
		Stdev		0.72	0.06	0.66	163.67	19.32	34.60	163.67	163.01
	3	Replica	1	15.10	150.95	166.05	223.42	94.85	320.87	223.42	389.47
			2	15.73	177.23	192.95	449.89	278.17	951.67	449.89	642.84
		Average		15.41	164.09	179.50	336.65	186.51	636.27	336.65	516.15
		Stdev		0.44	18.58	19.02	160.14	129.63	446.04	160.14	179.16
	4	Replica	1	19.35	137.68	157.03	190.49	156.62	378.99	190.49	347.51
			2	18.64	142.55	161.19	402.03	323.66	961.21	402.03	563.22
		Average		18.99	140.12	159.11	296.26	240.14	670.10	296.26	455.37
		Stdev		0.50	3.44	2.94	149.58	118.11	411.69	149.58	152.53

Notes:
- PAH represented as mg/kg
- AS1: Bioaugmentation with activated sludge from the return line of a swine waste project
- 100:20:5 represent PAH:N:P ratio
- T80: Tween 80 addition at 0.5% (w/w) the first week and 0.25% (w/w) the following weeks

Table A.5. pH Measurements for Phase I: Biotreatment Experiments involving Glucose and Tween 80 Amendments

Week	Glucose				Tween 80			
	Replica		Average	Stdev	Replica		Average	Stdev
	1	2			1	2		
0	6.91	7.08	6.99	0.12	6.91	7.08	6.99	0.12
1	6.33	6.43	6.38	0.07	6.64	6.63	6.64	0.01
2	6.54	6.48	6.51	0.04	6.61	6.84	6.73	0.16
3	6.78	6.82	6.80	0.03	6.51	6.56	6.54	0.04
4	7.08	6.98	7.03	0.07	6.66	6.71	6.69	0.04
5	7.22	7.21	7.22	0.01	6.98	7.10	7.04	0.08
6	7.38	7.31	7.35	0.05	6.95	7.07	7.01	0.08
7	6.98	7.03	7.01	0.04	6.89	6.91	6.90	0.01
8	6.77	7.20	6.99	0.30	6.54	6.65	6.60	0.08
9	7.37	7.50	7.44	0.09	6.96	6.87	6.92	0.06
10	7.15	7.11	7.13	0.03	6.65	6.63	6.64	0.01
11	7.10	7.20	7.15	0.07	6.70	6.70	6.70	0.00
12	7.10	7.30	7.20	0.14	6.80	6.90	6.85	0.07
13	6.90	7.10	7.00	0.14	5.90	6.60	6.25	0.49
14	7.30	7.40	7.35	0.07	6.90	6.70	6.80	0.14
15	7.30	7.20	7.25	0.07	6.40	6.20	6.30	0.14
16	7.00	7.10	7.05	0.07	6.10	5.80	5.95	0.21
17	7.11	6.87	6.99	0.17	6.00	5.32	5.66	0.48
18	6.90	7.00	6.95	0.07	6.40	5.20	5.80	0.85
19	6.60	6.60	6.60	0.00	5.70	4.90	5.30	0.57
20	7.10	6.80	6.95	0.21	5.60	4.70	5.15	0.64

Notes:
- Glucose: 1,000 mg/l glucose addition weekly
- Tween 80: 3% (w/w) Tween addition weekly

Table A.6. Dissolved Oxygen Readings for Phase I: Biotreatment Experiments involving Glucose and Tween 80 Amendments

Week	Glucose				Tween80			
	Replica		Average	Stdev	Replica		Average	Stdev
	1	2			1	2		
0	3.46	3.66	3.56	0.14	3.46	3.66	3.56	0.14
1	5.90	4.70	5.30	0.85	2.01	3.12	2.57	0.78
2	3.23	3.50	3.37	0.19	3.62	3.11	3.37	0.36
3	9.31	9.41	9.36	0.07	7.28	8.25	7.77	0.69
4	5.88	6.27	6.08	0.28	7.01	6.31	6.66	0.49
5	6.78	6.81	6.80	0.02	3.28	4.51	3.90	0.87
6	4.29	4.01	4.15	0.20	1.37	1.70	1.54	0.23
7	4.84	4.18	4.51	0.47	3.97	3.29	3.63	0.48
8	4.24	4.54	4.39	0.21	3.22	2.98	3.10	0.17
9	4.38	4.28	4.33	0.07	3.06	2.79	2.93	0.19
10	3.39	3.53	3.46	0.10	2.94	2.80	2.87	0.10
11	6.31	6.10	6.21	0.15	3.62	3.16	3.39	0.33
12	2.98	2.89	2.94	0.06	2.13	1.94	2.04	0.13
13	4.42	4.61	4.52	0.13	2.71	3.03	2.87	0.23
14	3.42	3.63	3.53	0.15	1.50	1.08	1.29	0.30
15	8.31	8.35	8.33	0.03	6.74	6.83	6.79	0.06
16	2.91	2.98	2.95	0.05	1.67	2.41	2.04	0.52
17	5.42	5.22	5.32	0.14	4.02	5.11	4.57	0.77
18	4.05	4.50	4.28	0.32	4.86	5.07	4.97	0.15
19	3.71	3.63	3.67	0.06	1.51	2.21	1.86	0.49
20	3.71	3.64	3.68	0.05	1.32	1.05	1.19	0.19

Notes:
- DO represented as mg/l
- Glucose: 1,000 mg/l glucose addition weekly
- Tween 80: 3% (w/w) Tween addition weekly

Table A.7. PAH Results for Phase I: Biotreatment Experiments involving Tween 80 and Glucose Amending

Condition	Week	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
Glucose	0	Replica	1	81.40	63.34	144.74	83.58	29.31	21.73	83.58	228.32
			2	114.59	63.85	178.45	88.07	29.75	27.10	88.07	266.52
		Average		98.00	63.60	161.59	85.83	29.53	24.42	85.83	247.42
		Stdev		23.47	0.37	23.84	3.18	0.32	3.80	3.18	27.01
	1	Replica	1	44.94	13.56	58.50	16.56	5.17	0.91	22.64	81.14
			2	54.20	15.78	69.98	16.51	5.49	0.96	22.95	92.93
		Average		49.57	14.67	64.24	16.53	5.33	0.94	22.80	87.04
		Stdev		6.55	1.57	8.12	0.04	0.22	0.04	0.22	8.34
	2	Replica	1	51.58	6.77	58.36	7.54	0.00	3.41	10.94	69.30
			2	52.59	13.59	66.18	15.52	4.43	0.00	19.95	86.14
		Average		52.09	10.18	62.27	11.53	2.22	1.70	15.45	77.72
		Stdev		0.71	4.82	5.53	5.65	3.13	2.41	6.37	11.90
	3	Replica	1	39.86	6.57	46.43	8.77	1.80	0.00	10.57	56.99
			2	97.04	76.05	173.09	72.87	11.59	0.00	84.46	257.55
		Average		68.45	41.31	109.76	40.82	6.69	0.00	47.51	157.27
		Stdev		40.43	49.13	89.57	45.33	6.92	0.00	52.25	141.82
	4	Replica	1	117.76	96.77	214.54	70.84	0.00	0.00	70.84	285.37
			2	104.54	86.38	190.92	52.54	14.82	0.00	67.36	258.29
		Average		111.15	91.58	202.73	61.69	7.41	0.00	69.10	271.83
		Stdev		9.35	7.35	16.70	12.94	10.48	0.00	2.46	19.15
	5	Replica	1	105.50	80.62	186.12	75.09	14.21	0.00	89.30	275.42
			2	82.02	69.96	151.97	79.02	27.80	0.00	106.82	258.79
		Average		93.76	75.29	169.05	77.06	21.00	0.00	98.06	267.11
		Stdev		16.60	7.54	24.15	2.78	9.61	0.00	12.39	11.76
	6	Replica	1	88.80	73.88	162.68	45.03	0.00	0.00	45.03	207.71
			2	97.31	74.14	171.45	77.17	24.15	0.00	101.32	272.77
		Average		93.06	74.01	167.07	61.10	12.07	0.00	73.17	240.24
		Stdev		6.02	0.18	6.20	22.73	17.08	0.00	39.81	46.01

Notes:
- PAH represented as mg/kg
- Glucose: 1,000 mg/l glucose addition weekly
- Tween 80: 3% (w/w) Tween addition weekly

Table A.7. (Continued)

Condition	Week	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
Glucose	7	Replica	1	113.31	101.09	214.40	62.55	0.00	0.00	62.55	276.95
			2	122.77	91.71	214.47	102.54	37.15	11.52	151.22	365.69
		Average		118.04	96.40	214.44	82.55	18.58	5.76	106.89	321.32
		Stdev		6.69	6.63	0.05	28.28	26.27	8.15	62.70	62.75
	8	Replica	1	101.17	80.03	181.20	64.84	0.00	0.00	64.84	246.04
			2	314.10	253.04	567.14	254.43	39.54	0.00	293.97	861.11
		Average		207.64	166.54	374.17	159.64	19.77	0.00	179.41	553.58
		Stdev		150.56	122.33	272.90	134.06	27.96	0.00	162.02	434.92
	9	Replica	1	120.14	95.89	216.03	54.97	0.00	0.00	54.97	271.00
			2	119.69	72.44	192.14	24.80	0.00	0.00	24.80	216.94
		Average		119.92	84.17	204.08	39.88	0.00	0.00	39.88	243.97
		Stdev		0.32	16.58	16.90	21.33	0.00	0.00	21.33	38.22
	10	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	137.54	64.02	201.56	0.00	0.00	0.00	0.00	201.56
		Average		68.77	32.01	100.78	0.00	0.00	0.00	0.00	100.78
		Stdev		97.25	45.27	142.52	0.00	0.00	0.00	0.00	142.52
	11	Replica	1	218.81	204.59	423.40	130.57	0.00	0.00	130.57	553.97
			2	179.38	89.36	268.74	106.80	0.00	0.00	106.80	375.55
		Average		199.09	146.98	346.07	118.69	0.00	0.00	118.69	464.76
		Stdev		27.88	81.48	109.36	16.81	0.00	0.00	16.81	126.16
	12	Replica	1	150.04	139.19	289.22	88.12	51.56	0.00	139.68	428.90
			2	147.06	109.79	256.84	91.63	55.08	0.00	146.72	403.56
		Average		148.55	124.49	273.03	89.88	53.32	0.00	143.20	416.23
		Stdev		2.11	20.79	22.90	2.49	2.49	0.00	4.98	17.92
	13	Replica	1	149.69	82.23	231.91	96.19	0.00	0.00	96.19	328.11
			2	152.63	125.07	277.70	105.80	0.00	0.00	105.80	383.50
		Average		151.16	103.65	254.81	101.00	0.00	0.00	101.00	355.80
		Stdev		2.08	30.29	32.37	6.80	0.00	0.00	6.80	39.17

Notes:
- PAH represented as mg/kg
- Glucose: 1,000 mg/l glucose addition weekly
- Tween 80: 3% (w/w) Tween addition weekly

Table A.7. (Continued)

Condition	Week	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
Glucose	14	Replica	1	147.48	73.80	221.28	86.11	0.00	0.00	86.11	307.39
			2	140.95	87.95	228.90	58.08	0.00	0.00	58.08	286.98
		Average		144.22	80.87	225.09	72.10	0.00	0.00	72.10	297.19
		Stdev		4.62	10.01	5.39	19.82	0.00	0.00	19.82	14.43
	15	Replica	1	131.12	0.00	131.12	0.00	0.00	0.00	0.00	131.12
			2	119.30	0.00	119.30	0.00	0.00	0.00	0.00	119.30
		Average		125.21	0.00	125.21	0.00	0.00	0.00	0.00	125.21
		Stdev		8.36	0.00	8.36	0.00	0.00	0.00	0.00	8.36
	16	Replica	1	187.65	0.00	187.65	0.00	0.00	0.00	0.00	187.65
			2	177.90	0.00	177.90	0.00	0.00	0.00	0.00	177.90
		Average		182.77	0.00	182.77	0.00	0.00	0.00	0.00	182.77
		Stdev		6.89	0.00	6.89	0.00	0.00	0.00	0.00	6.89
	17	Replica	1	177.00	0.00	177.00	0.00	0.00	0.00	0.00	177.00
			2	156.88	0.00	156.88	0.00	0.00	0.00	0.00	156.88
		Average		166.94	0.00	166.94	0.00	0.00	0.00	0.00	166.94
		Stdev		14.23	0.00	14.23	0.00	0.00	0.00	0.00	14.23
	18	Replica	1	97.29	0.00	97.29	0.00	0.00	0.00	0.00	97.29
			2	153.26	0.00	153.26	0.00	0.00	0.00	0.00	153.26
		Average		125.28	0.00	125.28	0.00	0.00	0.00	0.00	125.28
		Stdev		39.58	0.00	39.58	0.00	0.00	0.00	0.00	39.58
	19	Replica	1	140.16	0.00	140.16	0.00	0.00	0.00	0.00	140.16
			2	120.85	0.00	120.85	0.00	0.00	0.00	0.00	120.85
		Average		130.51	0.00	130.51	0.00	0.00	0.00	0.00	130.51
		Stdev		13.65	0.00	13.65	0.00	0.00	0.00	0.00	13.65
	20	Replica	1	60.87	0.00	60.87	0.00	0.00	0.00	0.00	60.87
			2	42.52	0.00	42.52	0.00	0.00	0.00	0.00	42.52
		Average		51.70	0.00	51.70	0.00	0.00	0.00	0.00	51.70
		Stdev		12.97	0.00	12.97	0.00	0.00	0.00	0.00	12.97

Notes:
- PAH represented as mg/kg
- Glucose: 1,000 mg/l glucose addition weekly
- Tween 80: 3% (w/w) Tween addition weekly

Table A.7. (Continued)

Condition	Week	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
Tween 80	0	Replica	1	81.40	63.34	144.74	83.58	29.31	21.73	83.58	228.32
			2	114.59	63.85	178.45	88.07	29.75	27.10	88.07	266.52
		Average		98.00	63.60	161.59	85.83	29.53	24.42	85.83	247.42
		Stdev		23.47	0.37	23.84	3.18	0.32	3.80	3.18	27.01
	1	Replica	1	42.66	14.87	57.53	24.55	4.68	0.39	29.62	87.15
			2	55.73	19.86	75.59	29.97	4.02	0.00	33.99	109.58
		Average		49.20	17.36	66.56	27.26	4.35	0.19	31.81	98.37
		Stdev		9.24	3.53	12.77	3.83	0.46	0.28	3.09	15.86
	2	Replica	1	42.77	11.12	53.89	24.67	4.25	0.00	28.92	82.81
			2	43.77	9.70	53.47	20.89	2.87	0.00	23.76	77.23
		Average		43.27	10.41	53.68	22.78	3.56	0.00	26.34	80.02
		Stdev		0.71	1.00	0.30	2.67	0.98	0.00	3.65	3.95
	3	Replica	1	66.46	55.60	122.06	98.65	19.22	0.00	117.87	239.93
			2	78.07	55.09	133.16	86.17	16.15	0.00	102.32	235.48
		Average		72.27	55.34	127.61	92.41	17.68	0.00	110.09	237.70
		Stdev		8.21	0.36	7.85	8.82	2.17	0.00	10.99	3.14
	4	Replica	1	75.35	69.99	145.34	127.54	25.11	0.00	152.66	298.00
			2	69.86	54.25	124.11	96.65	18.66	0.00	115.31	239.42
		Average		72.61	62.12	134.73	112.10	21.89	0.00	133.99	268.71
		Stdev		3.88	11.13	15.01	21.84	4.56	0.00	26.41	41.42
	5	Replica	1	92.86	75.16	168.02	137.45	34.32	0.00	171.76	339.78
			2	79.89	59.65	139.54	105.17	19.99	0.00	125.16	264.70
		Average		86.38	67.41	153.78	121.31	27.15	0.00	148.46	302.24
		Stdev		9.17	10.97	20.14	22.82	10.13	0.00	32.96	53.09
	6	Replica	1	63.09	47.96	111.05	87.96	8.21	0.00	96.17	207.21
			2	59.65	43.42	103.08	88.45	17.90	0.00	106.35	209.43
		Average		61.37	45.69	107.06	88.21	13.05	0.00	101.26	208.32
		Stdev		2.43	3.21	5.64	0.35	6.85	0.00	7.20	1.57

Notes:
- PAH represented as mg/kg
- Glucose: 1,000 mg/l glucose addition weekly
- Tween 80: 3% (w/w) Tween addition weekly

Table A.7. (Continued)

Condition	Week	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
Tween 80	7	Replica	1	94.32	74.69	169.01	177.08	17.70	0.00	194.78	363.78
			2	81.10	54.65	135.75	108.56	20.22	0.00	128.78	264.53
		Average		87.71	64.67	152.38	142.82	18.96	0.00	161.78	314.16
		Stdev		9.34	14.17	23.51	48.45	1.79	0.00	46.66	70.18
	8	Replica	1	82.84	63.16	146.00	126.45	12.28	0.00	138.74	284.74
			2	77.92	49.85	127.76	108.77	13.10	0.00	121.87	249.63
		Average		80.38	56.50	136.88	117.61	12.69	0.00	130.30	267.18
		Stdev		3.48	9.41	12.90	12.50	0.57	0.00	11.93	24.82
	9	Replica	1	79.45	32.61	112.06	101.82	0.00	0.00	101.82	213.88
			2	69.36	28.97	98.33	69.22	0.00	0.00	69.22	167.54
		Average		74.40	30.79	105.19	85.52	0.00	0.00	85.52	190.71
		Stdev		7.14	2.58	9.71	23.05	0.00	0.00	23.05	32.77
	10	Replica	1	291.89	128.76	420.65	544.69	59.79	0.00	604.48	1025.13
			2	112.01	0.00	112.01	169.04	0.00	0.00	169.04	281.05
		Average		201.95	64.38	266.33	356.86	29.90	0.00	386.76	653.09
		Stdev		127.20	91.05	218.25	265.62	42.28	0.00	307.90	526.14
	11	Replica	1	108.57	39.69	148.26	159.70	34.53	0.00	194.23	342.49
			2	0.00	21.50	21.50	121.74	0.00	0.00	121.74	143.23
		Average		54.29	30.59	84.88	140.72	17.27	0.00	157.99	242.86
		Stdev		76.77	12.86	89.63	26.84	24.42	0.00	51.26	140.90
	12	Replica	1	103.23	41.20	144.43	170.11	37.65	0.00	207.76	352.19
			2	88.26	41.99	130.25	165.04	0.00	0.00	165.04	295.29
		Average		95.74	41.60	137.34	167.57	18.83	0.00	186.40	323.74
		Stdev		10.58	0.56	10.03	3.59	26.62	0.00	30.21	40.24
	13	Replica	1	135.83	69.69	205.52	186.42	0.00	0.00	186.42	391.94
			2	96.82	43.12	139.95	121.56	0.00	0.00	121.56	261.50
		Average		116.32	56.41	172.73	153.99	0.00	0.00	153.99	326.72
		Stdev		27.58	18.79	46.37	45.87	0.00	0.00	45.87	92.23

Notes:
- PAH represented as mg/kg
- Glucose: 1,000 mg/l glucose addition weekly
- Tween 80: 3% (w/w) Tween addition weekly

Table A.7. (Continued)

Condition	Week	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
Tween 80	14	Replica	1	124.81	42.74	167.55	159.79	0.00	0.00	159.79	327.34
			2	130.96	61.72	192.68	232.58	52.84	0.00	285.42	478.10
		Average		127.89	52.23	180.11	196.19	26.42	0.00	222.61	402.72
		Stdev		4.35	13.42	17.77	51.47	37.36	0.00	88.83	106.61
	15	Replica	1	254.14	0.00	254.14	219.68	0.00	0.00	219.68	473.82
			2	292.79	0.00	292.79	171.30	0.00	0.00	171.30	464.09
		Average		273.46	0.00	273.46	195.49	0.00	0.00	195.49	468.95
		Stdev		27.33	0.00	27.33	34.21	0.00	0.00	34.21	6.89
	16	Replica	1	149.27	0.00	149.27	136.72	0.00	0.00	136.72	285.98
			2	90.42	0.00	90.42	55.15	0.00	0.00	55.15	145.58
		Average		119.85	0.00	119.85	95.93	0.00	0.00	95.93	215.78
		Stdev		41.61	0.00	41.61	57.67	0.00	0.00	57.67	99.28
	17	Replica	1	86.55	0.00	86.55	49.74	0.00	0.00	49.74	136.30
			2	88.85	0.00	88.85	0.00	0.00	0.00	0.00	88.85
		Average		87.70	0.00	87.70	24.87	0.00	0.00	24.87	112.57
		Stdev		1.62	0.00	1.62	35.17	0.00	0.00	35.17	33.55
	18	Replica	1	133.09	0.00	133.09	116.44	0.00	0.00	116.44	249.53
			2	85.57	0.00	85.57	134.17	462.84	0.00	597.01	682.58
		Average		109.33	0.00	109.33	125.30	231.42	0.00	356.72	466.05
		Stdev		33.60	0.00	33.60	12.54	327.28	0.00	339.81	306.21
	19	Replica	1	68.60	0.00	68.60	0.00	0.00	0.00	0.00	68.60
			2	81.60	0.00	81.60	0.00	0.00	0.00	0.00	81.60
		Average		75.10	0.00	75.10	0.00	0.00	0.00	0.00	75.10
		Stdev		9.20	0.00	9.20	0.00	0.00	0.00	0.00	9.20
	20	Replica	1	48.83	0.00	48.83	29.07	0.00	0.00	29.07	77.90
			2	50.23	0.00	50.23	0.00	0.00	0.00	0.00	50.23
		Average		49.53	0.00	49.53	14.54	0.00	0.00	14.54	64.07
		Stdev		0.99	0.00	0.99	20.56	0.00	0.00	20.56	19.57

Notes:
- PAH represented as mg/kg
- Glucose: 1,000 mg/l glucose addition weekly
- Tween 80: 3% (w/w) Tween addition weekly

APPENDIX B

SUMMARY OF EXPERIMENTAL DATA FOR PHASE I: CHEMICAL OXIDATION SCREENING EXPERIMENTS

Notes:

2-ring PAH: Naphthalene
3-ring PAHs: Acenaphthylene, Acenaphthene, Fluorene, Anthracene, and Phenanthrene
4-ring PAHs: Fluoranthene, Pyrene, Benzo[a]anthracene, and Chrysene
5-ring PAHs: Benzo[k]fluoranthene, Benzo[b]fluoranthene, Benzo[a]pyrene, and Dibenz[a,h]anthracene
6-ring PAHs: Benzo[g,h,i]perylene and Indeno[1,2,3-cd]perylene
Ave: Average
Stdev: Standard deviation

Table B.1. PAH Results for Phase I: Ozonation of the Lake Superior Sediment

Treatment	Hour	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
Ozone	0	Replica	1	48.97	32.19	81.16	24.08	5.34	2.99	32.42	113.58
			2	49.96	32.45	82.42	25.41	9.97	3.30	38.68	121.10
		Average		49.46	32.32	81.79	24.74	7.66	3.15	35.55	117.34
		Stdev		0.70	0.19	0.89	0.93	3.27	0.22	4.43	5.32
	2	Replica	1	37.66	23.86	61.52	19.74	5.28	1.65	26.67	88.19
			2	35.65	21.78	57.43	19.33	6.13	2.28	27.73	85.16
		Average		36.65	22.82	59.47	19.53	5.70	1.97	27.20	86.68
		Stdev		1.42	1.47	2.89	0.29	0.60	0.44	0.75	2.14

Notes:
- PAH represented as mg/kg
- 3% (w/w) ozone concentration at 2.5 scfh

Table B.2. PAH Results for Phase I: Peroxone Treatment of the Lake Superior Sediment

Treatment	Hour	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
Peroxone	0	Replica	1	48.97	32.19	81.16	24.08	5.34	2.99	32.42	113.58
			2	49.96	32.45	82.42	25.41	9.97	3.30	38.68	121.10
		Average		49.46	32.32	81.79	24.74	7.66	3.15	35.55	117.34
		Stdev		0.70	0.19	0.89	0.93	3.27	0.22	4.43	5.32
	2	Replica	1	31.37	12.47	43.84	10.47	1.52	0.02	12.02	55.85
			2	24.98	10.23	35.21	10.79	0.88	0.00	11.68	46.88
		Average		28.17	11.35	39.52	10.63	1.20	0.01	11.85	51.37
		Stdev		4.52	1.58	6.10	0.23	0.45	0.01	0.24	6.34
	4	Replica	1	44.20	12.76	56.96	9.30	0.00	0.00	9.30	66.26
			2	39.23	11.27	50.50	9.05	0.00	0.00	9.05	59.55
		Average		41.72	12.01	53.73	9.17	0.00	0.00	9.17	62.90
		Stdev		3.52	1.06	4.57	0.18	0.00	0.00	0.18	4.75
	6	Replica	1	40.44	9.65	50.09	7.82	0.00	0.00	7.82	57.92
			2	50.19	13.42	63.61	11.38	0.00	0.00	11.38	75.00
		Average		45.32	11.54	56.85	9.60	0.00	0.00	9.60	66.46
		Stdev		6.90	2.66	9.56	2.52	0.00	0.00	2.52	12.08
	9	Replica	1	184.47	124.10	308.56	42.40	0.00	0.00	42.40	350.97
			2	182.11	114.55	296.66	58.48	0.00	36.13	94.61	391.27
		Average		183.29	119.32	302.61	50.44	0.00	18.06	68.50	371.12
		Stdev		1.66	6.75	8.42	11.37	0.00	25.55	36.91	28.50
	12	Replica	1	138.47	88.69	227.16	100.38	23.72	0.00	124.11	351.26
			2	95.78	77.48	173.26	50.00	0.00	0.00	50.00	223.26
		Average		117.12	83.09	200.21	75.19	11.86	0.00	87.05	287.26
		Stdev		30.19	7.93	38.11	35.63	16.77	0.00	52.40	90.51
	15	Replica	1	142.04	73.65	215.69	61.93	0.00	0.00	61.93	277.61
			2	115.08	48.61	163.69	56.59	0.00	0.00	56.59	220.28
		Average		128.56	61.13	189.69	59.26	0.00	0.00	59.26	248.94
		Stdev		19.07	17.70	36.77	3.78	0.00	0.00	3.78	40.54

Notes:
- PAH represented as mg/kg
- 3% (w/w) ozone concentration at 2.5 scfh

Table B.2. (Continued)

Treatment	Hour	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
Peroxone	18	Replica	1	183.95	118.54	302.49	116.65	35.38	0.00	152.03	454.52
			2	154.30	96.34	250.64	115.43	0.00	0.00	115.43	366.07
		Average		169.13	107.44	276.57	116.04	17.69	0.00	133.73	410.30
		Stdev		20.96	15.70	36.66	0.86	25.02	0.00	25.88	62.54
	21	Replica	1	81.33	62.96	144.29	60.90	0.00	0.00	60.90	205.19
			2	86.33	52.89	139.22	43.82	0.00	0.00	43.82	183.04
		Average		83.83	57.93	141.76	52.36	0.00	0.00	52.36	194.12
		Stdev		3.53	7.12	3.58	12.08	0.00	0.00	12.08	15.67

Notes:
- PAH represented as mg/kg
- 3% (w/w) ozone concentration at 2.5 scfh

Table B.3. Total Heterotrophic Counts for the Fate of Hydrogen Peroxide in Equilibrated Water Solutions

Equilibrated Water	Replica		Average	Stdev
	1	2		
Not-autoclaved	20	20	2	0

Note:
- Total heterotrophic counts represented as CFUs/ml

Table B.4. Hydrogen Peroxide Reactivity for the Fate of Hydrogen Peroxide in Equilibrated Water Solutions

Run	1					2				
Hour	Control	Replica				Control	Replica			
		1	2	Average	Stdev		1	2	Average	Stdev
0	1000	1000	1000	1000	0.00	1000	1000	1000	1000	0.00
0.5	1075	570	630	600	42.43	1030	485	500	493	10.61
1	1060	500	540	520	28.28	1045	460	475	468	10.61
2	1040	455	495	475	28.28	1055	395	400	398	3.54
4	1010	485	540	513	38.89	985	310	315	313	3.54
8	1025	470	485	478	10.61	1000	405	385	395	14.14
22	1005	400	435	418	24.75	1075	315	327.5	321	8.84
Run	3					4				
Hour	Control	Replica				Control	Replica			
		1	2	Average	Stdev		1	2	Average	Stdev
0	1000	1000	1000	1000	0.00	1000	1000	1000	1000	0.00
0.5	1090	425	437.5	431	8.84	1000	440	440	440	0.00
1	1035	360	357.5	359	1.77	945	455	435	445	14.14
2	1005	350	340	345	7.07	980	415	405	410	7.07
4	990	345	347.5	346	1.77	980	380	372.5	376	5.30
8	945	360	372.5	366	8.84	945	330	355	343	17.68
22	980	315	327.5	321	8.84	980	220	217.5	219	1.77
Run	5					6				
Hour	Control	Replica				Control	Replica			
		1	2	Average	Stdev		1	2	Average	Stdev
0	1000	1000	1000	1000	0.00	1000	1000	1000	1000	0.00
0.5	980	460	440	450	14.14	985	505	510	508	3.54
1	965	420	412.5	416	5.30	1005	460	530	495	49.50
2	950	405	400	403	3.54	1000	485	510	498	17.68
4	975	385	392.5	389	5.30	995	510	495	503	10.61
8	965	355	362.5	359	5.30	990	500	480	490	14.14
22	975	350	350	350	0.00	995	500	490	495	7.07

Notes:
- Run 1-5 water samples were not autoclaved
- Run 6 water samples were autoclaved
- Hydrogen peroxide concentration represented as mg/l

Table B.5. Hydrogen Peroxide Reactivity Results for the Fate of Hydrogen Peroxide in Sediment Experiments (1,000 ppm H_2O_2 Experiments)

	Replica				
Hour	1	2	3	Average	Stdev
0	1000	1000	1000	1000	0
2	45	25	65	45	20
4	490	370	435	431.7	60.07
6	175	90	160	141.7	45.37
24	15	10	10	11.7	2.89
26	750	760	925	811.7	98.28
28	340	330	570	413.3	135.77
30	205	165	330	233.3	86.07
48	10	70	10	30	34.64
60	5	5	10	6.7	2.89
84	10	15	15	13.3	2.89

Note:
- Hydrogen peroxide concentration represented as mg/l

Table B.6. PAHs Results for the Fate of Hydrogen Peroxide in Sediment (1,000 ppm H_2O_2 Experiments)

Treatment		PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
1,000 ppm H_2O_2	Before HP	Replica	1	98.00	63.60	161.59	85.83	29.53	24.42	139.78	301.37
			2	14.79	136.60	151.39	80.73	49.62	272.28	402.62	554.01
		Average		56.39	100.10	156.49	83.28	39.57	148.35	271.20	427.69
		Stdev		58.83	51.62	7.22	3.6	14.20	175.26	185.86	178.65
	After HP	Replica	1	26.27	215.09	241.36	106.42	101.05	401.83	609.30	850.66
			2	25.44	218.41	243.85	218.51	96.61	124.93	440.05	683.90
		Average		25.85	216.75	242.61	162.46	98.83	263.38	524.67	767.28
		Stdev		0.59	2.35	1.76	79.26	3.14	195.80	119.68	117.92

Notes:
-HP: Indicates the addition of hydrogen peroxide
- PAH represented as mg/kg

Table B.7. Hydrogen Peroxide Reactivity Results for the Fate of Hydrogen Peroxide in Sediment Experiments (10,000 ppm H_2O_2 Experiments)

	Replica				
Hour	1	2	3	Average	Stdev
0	10000	10000	10000	10000	0.00
2	6800	7100	7150	7016.7	189.30
4	4700	3850	4300	4283.3	425.25
6	2350	1950	2200	2166.7	202.07
24	0	200	0	66.7	115.47
26	7150	8000	7250	7466.7	464.58
28	3250	4100	3500	3616.7	436.84
30	1900	2750	1850	2166.7	505.80
48	50	100	100	83.3	28.87
60	100	100	50	83.3	28.87
84	100	50	50	66.7	28.87

Note:
- Hydrogen peroxide concentration represented as mg/l

Table B.8. PAHs Results for the Fate of Hydrogen Peroxide in Sediment (10,000 ppm H_2O_2 Experiments)

Treatment		PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
10,000 ppm H_2O_2	Before HP	Replica	1	98.00	63.60	161.59	85.83	29.53	24.42	139.78	301.37
			2	14.79	136.60	151.39	80.73	49.62	272.28	402.62	554.01
		Average		56.39	100.10	156.49	83.28	39.57	148.35	271.20	427.69
		Stdev		58.83	51.62	7.22	3.6	14.20	175.26	185.86	178.65
	After HP	Replica	1	0.00	455.60	455.60	221.10	192.79	22.84	436.73	892.32
			2	0.00	201.38	201.38	100.63	0.00	32.30	132.93	334.31
		Average		0.00	328.49	328.49	160.87	96.40	27.57	284.83	613.32
		Stdev		0.00	179.76	179.76	85.18	136.33	6.69	214.81	394.57

Notes:
- PAH represented as mg/kg
- HP: Indicates the addition of hydrogen peroxide

Table B.9. Total Heterotrophic Counts for the Fate of Hydrogen Peroxide in Sediment Experiments (100,000 ppm H_2O_2 Experiments)

Sediment	Replica		Ave	Stdev
	1	2		
Not-autoclaved	1.4e7	2.5e6	8.3e6	8.1e6

Note:
- Total heterotrophic counts represented as CFUs/ml

Table B.10. Hydrogen Peroxide Reactivity Results for the Fate of Hydrogen Peroxide in Sediment Experiments (100,000 ppm H_2O_2 Experiments)

	Autoclaved					Not Autoclaved				
	Replica					Replica				
Hour	1	2	3	Average	Stdev	1	2	3	Average	Stdev
1	94000	95500	92500	94000	1500	71500	71500	54000	65666.7	10103.6
20	6500	5000	6000	5833.33	763.763	9000	7000	8500	8166.67	1040.83
21	79000	76000	71500	75500	3774.92	101500	54500	51000	69000	28200.2
23	51000	42000	40500	44500	5678.91	48000	42000	38500	42833.3	4804.51
41	500	500	500	500	0	7000	3000	3500	4500	2179.45
42	56000	60000	52000	56000	4000	48000	44000	43500	45166.7	2466.44
43	43500	41000	38500	41000	2500	48500	43000	45000	45500	2783.88
44	28000	24000	26500	26166.7	2020.73	42500	35000	36000	37833.3	4072.26
45	12000	8000	10500	10166.7	2020.73	37000	26500	29500	31000	5408.33
46	6000	3500	4000	4500	1322.88	36000	17500	26000	26500	9260.13
61	500	500	500	500	0	500	500	500	500	0
62	55500	48500	50500	51500	3605.55	58000	44000	42500	48166.7	8548.88
63	34000	26500	32000	30833.3	3883.73	47000	36000	33500	38833.3	7182.15
64	7500	2500	4000	4666.67	2565.8	29000	10000	13000	17333.3	10214.4
83	500	500	500	500	0	1000	500	1000	833.333	288.675
87	13500	8000	9000	10166.7	2929.73	26000	12000	13000	17000	7810.25
91	75000	71000	79000	75000	4000	75000	76000	59500	70166.7	9251.13
92	58500	37000	40500	45333.3	11536.2	52500	28500	36500	39166.7	12220.2
105	42500	39500	44500	42166.7	2516.61	50500	32000	39000	40500	9340.77
106	35500	21500	31000	29333.3	7147.26	39500	14500	19500	24500	13228.8
127	500	500	500	500	0	500	500	500	500	0
130	54000	51500	51000	52166.7	1607.28	51500	47000	44000	47500	3774.92
132	35500	29500	31000	32000	3122.5	31500	21500	15500	22833.3	8082.9
135	20000	7000	8000	11666.7	7234.18	14500	4000	4000	7500	6062.18

Note:
- Hydrogen peroxide concentration represented as mg/l

Table B.10. (Continued)

	Autoclaved					Not Autoclaved				
	Replica					Replica				
Hour	1	2	3	Average	Stdev	1	2	3	Average	Stdev
149	1500	1000	1000	1166.67	288.675	1500	1000	1000	1166.67	288.675
150	62000	51500	87500	67000	18513.5	46000	66500	49000	53833.3	11071.7
151	53000	49500	47000	49833.3	3013.86	47000	41000	46000	44666.7	3214.55
152	43500	38000	45500	42333.3	3883.73	37000	32500	33500	34333.3	2362.91
154	32500	23500	25500	27166.7	4725.82	30000	18000	19000	22333.3	6658.33
173	1000	1000	1500	1166.67	288.675	1000	1000	1000	1000	0
174	44500	46000	47000	45833.3	1258.31	51000	55500	50500	52333.3	2753.79
175	39500	38000	44000	40500	3122.5	42500	38500	35000	38666.7	3752.78
177	34500	30000	33500	32666.7	2362.91	33000	27500	28000	29500	3041.38
222	500	500	500	500	0	500	500	500	0.5	0

Note:
- Hydrogen peroxide concentration represented as mg/l

Table B.11. PAH Results for the Fate of Hydrogen Peroxide in Sediment Experiments (100,000 ppm H_2O_2 Experiments)

Not Autoclaved											
Treatment		PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
100,000 ppm H_2O_2	Before HP	Replica	1	98.00	63.60	161.59	85.83	29.53	24.42	139.78	301.37
			2	14.79	136.60	151.39	80.73	49.62	272.28	402.62	554.01
		Average		56.39	100.10	156.49	83.28	39.57	148.35	271.20	427.69
		Stdev		58.83	51.62	7.22	3.6	14.20	175.26	185.86	178.65
	After HP	Replica	1	0.00	129.65	129.65	82.29	70.51	224.78	377.58	507.23
			2	0.00	119.01	119.01	69.77	53.16	171.56	294.49	413.50
		Average		0.00	122.44	122.44	74.63	58.10	196.64	329.38	451.81
		Stdev		0.00	6.25	6.25	6.71	10.82	26.74	43.11	49.14
Autoclaved											
100,000 ppm H_2O_2	Before HP	Replica	1	0.00	150.96	150.96	125.87	1019.27	329.28	1474.42	1625.37
			2	14.62	123.93	138.54	93.06	407.34	353.74	854.14	992.69
			3	0.00	150.27	150.27	119.54	948.93	405.36	1473.82	1624.09
		Average		4.87	141.72	146.59	112.82	791.85	362.79	1267.46	1414.05
		Stdev		8.44	15.41	6.98	17.40	334.84	38.84	357.94	364.91
	After HP	Replica	1	0.00	120.42	120.42	75.78	40.80	38.56	155.15	275.57
			2	0.00	127.64	127.64	64.28	53.75	49.28	167.31	294.95
			3	0.00	121.14	121.14	77.43	45.66	41.01	164.11	285.25
		Average		0.00	123.07	123.07	72.50	46.74	42.95	162.19	285.26
		Stdev		0.00	3.97	3.97	7.16	6.54	5.62	6.31	9.69

Notes:
- PAH represented as mg/kg
- HP: Indicates the addition of hydrogen peroxide

Table B.12. PAH Results for Fenton's Reagent Treatment of the Lake Superior Sediment (25,000 mg/l H_2O_2 + 2,500 mg/l Fe^{2+})

Dosing	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
0	Replica	1	86.91	68.52	155.43	76.07	17.75	0.00	93.82	249.25
		2	133.24	94.07	227.32	104.08	38.04	0.00	142.12	369.44
	Average		110.08	81.30	191.37	90.08	27.89	0.00	117.97	309.34
	Stdev		32.77	18.07	50.83	19.80	14.35	0.00	34.15	84.99
1	Replica	1	91.93	72.89	164.82	81.05	18.39	0.00	99.45	264.26
		2	84.92	58.42	143.34	70.84	16.29	0.00	87.13	230.47
	Average		88.42	65.66	154.08	75.95	17.34	0.00	93.29	247.37
	Stdev		4.96	10.23	15.19	7.22	1.49	0.00	8.71	23.90
2	Replica	1	93.67	71.67	165.35	46.55	0.00	0.00	46.55	211.90
		2	90.07	72.21	162.27	67.29	0.00	0.00	67.29	229.57
	Average		91.87	71.94	163.81	56.92	0.00	0.00	56.92	220.73
	Stdev		2.55	0.38	2.17	14.67	0.00	0.00	14.67	12.49
3	Replica	1	106.46	79.13	185.59	72.65	0.00	0.00	72.65	258.24
		2	96.78	68.69	165.47	65.24	0.00	0.00	65.24	230.70
	Average		101.62	73.91	175.53	68.94	0.00	0.00	68.94	244.47
	Stdev		6.85	7.39	14.23	5.24	0.00	0.00	5.24	19.47
4	Replica	1	183.41	103.45	286.86	47.13	0.00	0.00	47.13	333.99
		2	186.21	63.40	249.61	78.52	0.00	0.00	78.52	328.13
	Average		184.81	83.43	268.24	62.82	0.00	0.00	62.82	331.06
	Stdev		1.98	28.32	26.34	22.19	0.00	0.00	22.19	4.14
5	Replica	1	186.21	32.24	218.45	32.44	0.00	0.00	32.44	250.90
		2	121.20	34.48	155.68	36.35	0.00	0.00	36.35	192.03
	Average		153.70	33.36	187.06	34.40	0.00	0.00	34.40	221.46
	Stdev		45.97	1.58	44.39	2.76	0.00	0.00	2.76	41.63
6	Replica	1	101.05	0.00	101.05	0.00	0.00	0.00	0.00	101.05
		2	173.24	61.89	235.13	41.01	0.00	0.00	41.01	276.14
	Average		137.14	30.94	168.09	20.50	0.00	0.00	20.50	188.59
	Stdev		51.05	43.76	94.81	29.00	0.00	0.00	29.00	123.81

Notes: - PAH represented as mg/kg
- Dosing step no 4-7: 100,000 mg/l H_2O_2 + 10,000 mg/l Fe^{2+}

Table B.12. (Continued)

Dosing	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
7	Replica	1	79.02	0.00	79.02	0.00	0.00	0.00	0.00	79.02
		2	83.14	0.00	83.14	0.00	0.00	0.00	0.00	83.14
	Average		81.08	0.00	81.08	0.00	0.00	0.00	0.00	81.08
	Stdev		2.91	0.00	2.91	0.00	0.00	0.00	0.00	2.91

Notes: - PAH represented as mg/kg
- Dosing step no 4-7: 100,000 mg/l H_2O_2 + 10,000 mg/l Fe^{2+}

Table B.13. PAH Results for Fenton's Reagent Treatment of the Lake Superior Sediment (100,000 mg/l H_2O_2 + 10,00 mg/l Fe^{2+})

Dosing	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
0	Replica	1	90.93	73.14	164.08	77.37	17.65	0.00	95.01	259.09
		2	112.65	74.65	187.30	64.91	0.00	0.00	64.91	252.21
	Average		101.79	73.90	175.69	71.14	8.82	0.00	79.96	255.65
	Stdev		15.36	1.07	16.42	8.81	12.48	0.00	21.28	4.86
1	Replica	1	155.65	121.39	277.04	0.00	0.00	0.00	0.00	277.04
		2	106.41	72.80	179.21	43.06	0.00	0.00	43.06	222.27
	Average		131.03	97.09	228.12	21.53	0.00	0.00	21.53	249.65
	Stdev		34.82	34.36	69.18	30.45	0.00	0.00	30.45	38.73
2	Replica	1	92.29	81.60	173.89	47.31	0.00	0.00	47.31	221.20
		2	122.93	52.21	175.14	0.00	0.00	0.00	0.00	175.14
	Average		107.61	66.91	174.52	23.65	0.00	0.00	23.65	198.17
	Stdev		21.66	20.78	0.88	33.45	0.00	0.00	33.45	32.57
3	Replica	1	100.90	54.26	155.16	30.93	0.00	0.00	30.93	186.09
		2	101.41	52.23	153.64	0.00	0.00	0.00	0.00	153.64
	Average		101.16	53.24	154.40	15.47	0.00	0.00	15.47	169.86
	Stdev		0.36	1.43	1.07	21.87	0.00	0.00	21.87	22.95

Note: - PAH represented as mg/kg

Table B.13. (Continued)

Dosing	PAH category	2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
4	Replica	1	211.12	146.42	357.54	54.18	0.00	0.00	54.18
		2	251.15	100.39	351.54	58.68	0.00	0.00	58.68
	Average		231.14	123.40	354.54	56.43	0.00	0.00	56.43
	Stdev		28.31	32.55	4.24	3.18	0.00	0.00	3.18
5	Replica	1	251.15	0.00	251.15	0.00	0.00	0.00	0.00
		2	90.34	0.00	90.34	0.00	0.00	0.00	0.00
	Average		170.74	0.00	170.74	0.00	0.00	0.00	0.00
	Stdev		113.71	0.00	113.71	0.00	0.00	0.00	0.00
6	Replica	1	198.02	0.00	198.02	0.00	0.00	0.00	0.00
		2	86.63	26.37	113.00	0.00	0.00	0.00	0.00
	Average		142.33	13.18	155.51	0.00	0.00	0.00	0.00
	Stdev		78.76	18.64	60.12	0.00	0.00	0.00	0.00
7	Replica	1	42.98	0.00	42.98	0.00	0.00	0.00	0.00
		2	54.21	0.00	54.21	0.00	0.00	0.00	0.00
	Average		48.59	0.00	48.59	0.00	0.00	0.00	0.00
	Stdev		7.94	0.00	7.94	0.00	0.00	0.00	0.00

Note: - PAH represented as mg/kg

APPENDIX C

SUMMARY OF EXPERIMENTAL DATA FOR PHASE I: INTEGRATED EXPERIMENTS

Notes:

2-ring PAH: Naphthalene
3-ring PAHs: Acenaphthylene, Acenaphthene, Fluorene, Anthracene, and Phenanthrene
4-ring PAHs: Fluoranthene, Pyrene, Benzo[a]anthracene, and Chrysene
5-ring PAHs: Benzo[k]fluoranthene, Benzo[b]fluoranthene, Benzo[a]pyrene, and Dibenz[a,h]anthracene
6-ring PAHs: Benzo[g,h,i] perylene and Indeno[1,2,3-cd]perylene
Ave: Average
Stdev: Standard deviation

Table C.1. PAH Results for Chemical Priming of the Scioto River Sediment

Condition	Dosing	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
Biotic Control	0	Replica	1	0.00	1.13	1.13	3.81	1.18	2.61	7.60	8.73
			2	0.00	2.33	2.33	10.63	6.65	6.01	23.29	25.62
		Average		0.00	1.73	1.73	7.22	3.91	4.31	15.44	17.17
		Stdev		0.00	0.85	0.85	4.82	3.87	2.41	11.10	11.94
	1	Replica	1	0.00	0.91	0.91	8.62	5.46	0.28	14.37	15.27
			2	0.00	0.00	0.00	9.67	0.00	0.00	9.67	9.67
		Average		0.00	0.45	0.45	9.15	2.73	0.14	12.02	12.47
		Stdev		0.00	0.64	0.64	0.75	3.86	0.20	3.32	3.96
	2	Replica	1	0.00	0.00	0.00	3.97	0.00	0.00	3.97	3.97
			2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Average		0.00	0.00	0.00	1.99	0.00	0.00	1.99	1.99
		Stdev		0.00	0.00	0.00	2.81	0.00	0.00	2.81	2.81
	3	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Average		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Stdev		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	4	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Average		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Stdev		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	5	Replica	1	0.00	0.00	0.00	7.01	0.00	0.00	7.01	7.01
			2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Average		0.00	0.00	0.00	3.51	0.00	0.00	3.51	3.51
		Stdev		0.00	0.00	0.00	4.96	0.00	0.00	4.96	4.96
	6	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Average		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Stdev		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Notes:
- PAH represented as mg/kg
- Dosing step no. 1: 20,000 mg/l H_2O_2 + 2,000 mg/l Fe^{2+}; steps no. 2-3: 50,000 mg/l H_2O_2 + 5,000 mg/l Fe^{2+}; steps no. 4-8: 100,000 mg/l H_2O_2 + 10,000 mg/l Fe^{2+}

Table C.1. (Continued)

Condition	Dosing	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
Biotic Control	7	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Average		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Stdev		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	8	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Average		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Stdev		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
100:20:5	0	Replica	1	0.00	1.96	1.96	8.79	8.44	7.44	24.68	26.64
			2	0.00	1.04	1.04	6.67	5.16	6.15	17.98	19.02
		Average		0.00	1.50	1.50	7.73	6.80	6.80	21.33	22.83
		Stdev		0.00	0.65	0.65	1.50	2.32	0.91	4.74	5.39
	1	Replica	1	0.00	0.00	0.00	0.63	0.00	0.00	0.63	0.63
			2	0.00	3.80	3.80	12.53	0.46	1.62	14.60	18.41
		Average		0.00	1.90	1.90	6.58	0.23	0.81	7.61	9.52
		Stdev		0.00	2.69	2.69	8.42	0.32	1.14	9.88	12.57
	2	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	0.00	0.00	0.00	2.09	0.00	0.00	2.09	2.09
		Average		0.00	0.00	0.00	1.05	0.00	0.00	1.05	1.05
		Stdev		0.00	0.00	0.00	1.48	0.00	0.00	1.48	1.48
	3	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Average		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Stdev		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	4	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	0.00	0.00	0.00	12.08	0.00	0.00	12.08	12.08
		Average		0.00	0.00	0.00	6.04	0.00	0.00	6.04	6.04
		Stdev		0.00	0.00	0.00	8.54	0.00	0.00	8.54	8.54

Notes:
- PAH represented as mg/kg
- Dosing step no. 1: 20,000 mg/l H_2O_2 + 2,000 mg/l Fe^{2+}; steps no. 2-3: 50,000 mg/l H_2O_2 + 5,000 mg/l Fe^{2+}; steps no. 4-8: 100,000 mg/l H_2O_2 + 10,000 mg/l Fe^{2+}
- 100:20:5 represent PAH:N:P ratio

Table C.1. (Continued)

Condition	Dosing	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
100:20:5	5	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	0.00	0.00	0.00	1.88	0.00	0.00	1.88	1.88
		Average		0.00	0.00	0.00	0.94	0.00	0.00	0.94	0.94
		Stdev		0.00	0.00	0.00	1.33	0.00	0.00	1.33	1.33
	6	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Average		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Stdev		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	7	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Average		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Stdev		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	8	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Average		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Stdev		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
AS.+ 100:20:5	0	Replica	1	0.00	0.01	0.01	1.54	0.00	1.96	3.50	3.51
			2	0.00	5.62	5.62	10.92	0.00	3.30	14.23	19.84
		Average		0.00	2.81	2.81	6.23	0.00	2.63	8.86	11.68
		Stdev		0.00	3.97	3.97	6.63	0.00	0.95	7.58	11.55
	1	Replica	1	0.00	3.47	3.47	16.44	8.61	7.20	32.26	35.74
			2	0.00	1.94	1.94	10.88	1.79	0.00	12.67	14.60
		Average		0.00	2.70	2.70	13.66	5.20	3.60	22.46	25.17
		Stdev		0.00	1.09	1.09	3.93	4.83	5.09	13.85	14.94

Notes:
- PAH represented as mg/kg
- Dosing step no. 1: 20,000 mg/l H_2O_2 + 2,000 mg/l Fe^{2+}; steps no. 2-3: 50,000 mg/l H_2O_2 + 5,000 mg/l Fe^{2+}; steps no. 4-8: 100,000 mg/l H_2O_2 + 10,000 mg/l Fe^{2+}
- AS.: Bioaugmentation with activated sludge from the return line of a local wastewater
- 100:20:5 represent PAH:N:P ratio

Table C.1. (Continued)

Condition	Dosing	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
AS.+100:20:5	2	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Average		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Stdev		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	3	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Average		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Stdev		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	4	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Average		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Stdev		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	5	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Average		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Stdev		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	6	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Average		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Stdev		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	7	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Average		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Stdev		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Notes:
- PAH represented as mg/kg
- Dosing step no. 1: 20,000 mg/l H_2O_2 + 2,000 mg/l Fe^{2+}; steps no. 2-3: 50,000 mg/l H_2O_2 + 5,000 mg/l Fe^{2+}; steps no. 4-8: 100,000 mg/l H_2O_2 + 10,000 mg/l Fe^{2+}
- AS: Bioaugmentation with activated sludge from the return line of a local wastewater
- 100:20:5 represent PAH:N:P ratio

Table C.1. (Continued)

Condition	Dosing	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
AS.+100:20:5	8	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Average		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Stdev		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
AS.+ 100:20:5 T80	0	Replica	1	0.25	23.19	23.45	38.00	17.40	4.60	60.00	83.45
			2	0.71	6.29	7.00	11.34	0.88	0.99	13.21	20.21
		Average		0.00	0.00	15.22	0.00	0.00	0.00	36.61	51.83
		Stdev		0.00	0.00	11.63	0.00	0.00	0.00	33.09	44.72
	1	Replica	1	7.63	4.65	12.29	25.94	0.00	0.00	25.94	38.23
			2	7.35	4.12	11.47	54.94	0.00	0.00	54.94	66.41
		Average		0.00	0.00	11.88	0.00	0.00	0.00	40.44	52.32
		Stdev		0.00	0.00	0.58	0.00	0.00	0.00	20.50	19.93
	2	Replica	1	1.32	6.68	8.00	20.72	0.00	0.00	20.72	28.72
			2	0.00	16.02	16.02	15.73	0.00	0.00	15.73	31.75
		Average		0.00	0.00	12.01	0.00	0.00	0.00	18.22	30.23
		Stdev		0.00	0.00	5.68	0.00	0.00	0.00	3.53	2.15
	3	Replica	1	0.00	26.71	26.71	17.53	0.00	0.00	17.53	44.24
			2	0.00	17.56	17.56	9.75	0.00	0.00	9.75	27.32
		Average		0.00	0.00	22.14	0.00	0.00	0.00	13.64	35.78
		Stdev		0.00	0.00	6.47	0.00	0.00	0.00	5.50	11.97
	4	Replica	1	0.00	11.44	11.44	6.80	0.00	0.00	6.80	18.25
			2	0.00	27.92	27.92	2.36	0.00	0.00	2.36	30.28
		Average		0.00	0.00	19.68	0.00	0.00	0.00	4.58	24.27
		Stdev		0.00	0.00	11.65	0.00	0.00	0.00	3.14	8.51

Notes:
- PAH represented as mg/kg
- Dosing step no. 1: 20,000 mg/l H_2O_2 + 2,000 mg/l Fe^{2+}; steps no. 2-3: 50,000 mg/l H_2O_2 + 5,000 mg/l Fe^{2+}; steps no. 4-8: 100,000 mg/l H_2O_2 + 10,000 mg/l Fe^{2+}
- AS.: Bioaugmentation with activated sludge from the return line of a local wastewater
- 100:20:5 represent PAH:N:P ratio
- T80: Tween 80 addition at 0.5% (w/w) the first week and 0.25% (w/w) the following weeks

Table C.1. (Continued)

Condition	Dosing	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
AS. + 100:20:5 T80	5	Replica	1	0.00	16.15	16.15	5.61	0.00	0.00	5.61	21.76
			2	0.00	12.67	12.67	1.46	0.00	0.00	1.46	14.13
		Average		0.00	0.00	14.41	0.00	0.00	0.00	3.53	17.94
		Stdev		0.00	0.00	2.46	0.00	0.00	0.00	2.94	5.39
	6	Replica	1	0.00	2.41	2.41	0.00	0.00	0.00	0.00	2.41
			2	0.00	3.91	3.91	0.00	0.00	0.00	0.00	3.91
		Average		0.00	0.00	3.16	0.00	0.00	0.00	0.00	3.16
		Stdev		0.00	0.00	1.06	0.00	0.00	0.00	0.00	1.06
	7	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	0.00	0.39	0.39	0.00	0.00	0.00	0.00	0.39
		Average		0.00	0.00	0.20	0.00	0.00	0.00	0.00	0.20
		Stdev		0.00	0.00	0.28	0.00	0.00	0.00	0.00	0.28
	8	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Average		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Stdev		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Notes:
- PAH represented as mg/kg
- Dosing step no. 1: 20,000 mg/l H_2O_2 + 2,000 mg/l Fe^{2+}; steps no. 2-3: 50,000 mg/l H_2O_2 + 5,000 mg/l Fe^{2+}; steps no. 4-8: 100,000 mg/l H_2O_2 + 10,000 mg/l Fe^{2+}
- AS: Bioaugmentation with activated sludge from the return line of a local wastewater
- 100:20:5 represent PAH:N:P ratio
- T80: Tween 80 addition at 0.5% (w/w) the first week and 0.25% (w/w) the following weeks

Table C.2. Selected PAH Results for Chemical Priming of the Scioto River Sediment

Dosing	Condition		Biotic Control			100:20:5			AS.+100:20:5			AS.+100:20:5+T80		
	PAH Compound		Phen	Fluo	BaA	Phen	Fluo	BaA	Phen	Fluo	BaA	Phen	Fluo	BaA
0	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.65	3.55
		2	0.00	0.00	0.00	0.00	4.41	0.00	0.00	1.67	1.97	0.00	2.74	3.40
	Average		0.00	0.00	0.00	0.00	2.20	0.00	0.00	0.84	0.99	0.00	2.19	3.47
	Stdev		0.00	0.00	0.00	0.00	3.12	0.00	0.00	1.18	1.40	0.00	0.78	0.10
1	Replica	1	0.00	0.48	6.48	0.00	0.63	0.00	0.00	1.11	12.05	1.73	6.93	9.60
		2	0.00	3.36	4.79	0.00	5.22	4.84	0.00	3.62	4.79	2.85	10.49	14.43
	Average		0.00	1.92	5.64	0.00	2.92	2.42	0.00	2.37	8.42	2.29	8.71	12.02
	Stdev		0.00	2.04	1.20	0.00	3.25	3.43	0.00	1.77	5.13	0.80	2.51	3.42
2	Replica	1	0.00	0.00	3.97	0.00	0.00	0.00	0.00	0.00	0.00	0.33	5.93	10.14
		2	0.00	0.00	0.00	0.00	2.09	0.00	0.00	0.00	0.00	5.05	3.52	8.58
	Average		0.00	0.00	1.99	0.00	1.05	0.00	0.00	0.00	0.00	2.69	4.73	9.36
	Stdev		0.00	0.00	2.81	0.00	1.48	0.00	0.00	0.00	0.00	3.34	1.71	1.10
3	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.61	7.67
		2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	10.56	2.72	0.77
	Average		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.28	3.67	4.22
	Stdev		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.47	1.34	4.88
4	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	11.44	3.54	0.00
		2	0.00	0.00	0.00	0.00	3.30	0.00	0.00	0.00	0.00	14.57	1.39	0.00
	Average		0.00	0.00	0.00	0.00	1.65	0.00	0.00	0.00	0.00	13.01	2.46	0.00
	Stdev		0.00	0.00	0.00	0.00	2.33	0.00	0.00	0.00	0.00	2.21	1.52	0.00
5	Replica	1	0.00	0.00	7.01	0.00	0.00	0.00	0.00	0.00	0.00	9.58	1.45	0.00
		2	0.00	0.00	0.00	0.00	1.88	0.00	0.00	0.00	0.00	12.67	0.00	0.00
	Average		0.00	0.00	3.51	0.00	0.94	0.00	0.00	0.00	0.00	11.13	0.72	0.00
	Stdev		0.00	0.00	4.96	0.00	1.33	0.00	0.00	0.00	0.00	2.18	1.02	0.00

Notes:
- PAH represented as mg/kg
- Dosing step no. 1: 20,000 mg/l H_2O_2 + 2,000 mg/l Fe^{2+}; steps no. 2-3: 50,000 mg/l H_2O_2 + 5,000 mg/l Fe^{2+}; steps no. 4-8: 100,000 mg/l H_2O_2 + 10,000 mg/l Fe^{2+}
- AS.: Bioaugmentation with activated sludge from the return line of a local wastewater
- 100:20:5 represent PAH:N:P ratio and T80: Tween 80 addition at 0.5% (w/w) the first week and 0.25% (w/w) the following weeks
- Phen, Fluo, and BaA indicate phenanthrene, Fluoranthene, and Benzo[a]anthracene

Table C.2. (Continued)

Dosing	Condition		Biotic Control			100:20:5			AS.+100:20:5			AS.+100:20:5+T80		
	PAH Compound		Phen	Fluo	BaA	Phen	Fluo	BaA	Phen	Fluo	BaA	Phen	Fluo	BaA
6	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.41	0.00	0.00
		2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.91	0.00	0.00
	Average		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.16	0.00	0.00
	Stdev		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.06	0.00	0.00
7	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.39	0.00	0.00
	Average		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.20	0.00	0.00
	Stdev		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.28	0.00	0.00
8	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Average		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Stdev		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Notes:
- PAH represented as mg/kg
- Dosing step no. 1: 20,000 mg/l H_2O_2 + 2,000 mg/l Fe^{2+}; steps no. 2-3: 50,000 mg/l H_2O_2 + 5,000 mg/l Fe^{2+}; steps no. 4-8: 100,000 mg/l H_2O_2 + 10,000 mg/l Fe^{2+}
- AS.: Bioaugmentation with activated sludge from the return line of a local wastewater
- 100:20:5 represent PAH:N:P ratio
- T80: Tween 80 addition at 0.5% (w/w) the first week and 0.25% (w/w) the following weeks
- Phen, Fluo, and BaA indicate phenanthrene, Fluoranthene, and Benzo[a]anthracene

APPENDIX D

SUMMARY OF EXPERIMENTAL DATA FOR PHASE II: BIOSLURRY AND INTEGRATED EXPERIMENTS

Notes:

2-ring PAH: Naphthalene
3-ring PAHs: Acenaphthylene, Acenaphthene, Fluorene, Anthracene, and Phenanthrene
4-ring PAHs: Fluoranthene, Pyrene, Benzo[a]anthracene, and Chrysene
5-ring PAHs: Benzo[k]fluoranthene, Benzo[b]fluoranthene, Benzo[a]pyrene, and Dibenz[a,h]anthracene
6-ring PAHs: Benzo[g,h,i] perylene and Indeno[1,2,3-cd]perylene
Ave: Average
Stdev: Standard deviation

Table D.1. Total Heterotrophic Counts for the Bioslurry Experiments

Condition	Biotic Control				Nutrients			
Day	1	2	Ave	Stdev	1	2	Ave	stdev
0	1.4e7	2.5e6	8.3e6	8.1e6	7.5e6	1.1e7	9.3e6	2.1e6
14	1.20e7	1.05e7	1.13e7	1.06e6	1.3e7	5.5e6	9.25e6	5.3e6
21	3.55e7	8.00e6	2.18e7	1.94e7	1.7e7	3.35e7	2.53e7	1.17e7
28	2.50e4	2.60e6	1.31e6	1.82e6	5.50e6	2.00e6	3.75e6	2.47e6
79	N/A	N/A	-	-	0	0	0	0
165	TLTC	2.2e6	1.1e6	-	1.9e7	2.6e6	1.1e7	1.1e7
Bio.+Nutrients					Bio.+Nutrients+Ext.C.			
Day	1	2	Ave	Stdev	1	2	Ave	stdev
0	3.5e6	9.50e6	6.50e6	4.2e6	8e6	3.4e6	5.7e6	3.3e6
14	2.00e6	4.50e6	3.25e6	1.77e6	1.25e7	1.09e8	6.05e7	6.79e7
21	1.08e8	1.50e7	6.15e7	6.57e7	2.76e8	2.80e7	1.52e8	1.75e7
28	6.55e7	6.90e7	6.73e7	2.47e6	1.10e7	1.50e8	8.05e7	9.83e7
79	N/A	N/A	-	-	N/A	N/A	-	-
165	65	56	61	6.4	1.67e7	1.02e7	1.4e7	4.6e6

Notes:
- Bio.: Bioaugmentation with naphthalene degraders
- Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions
- Heterotrophic counts represented as CFUs/ml
- Dosing steps no. 1 and 2: 25,000 H_2O_2 + 2,500 Fe^{2+}; dosing steps no. 3 and 4: 50,000 H_2O_2 + 5,000 Fe^{2+}; dosing steps no. 5 and 6: 100,000 H_2O_2 + 10,000 Fe^{2+}
- TLTC: Indicates too little to count

Table D.2. pH Results for Phase II: Bioslurry Experiments

Day	Condition															
	Biotic control				Nutrients				Bio.+ Nutrients				Bio.+Nutrients+Ext.C.			
	1	2	Ave	Stdev	1	2	Ave	Stdev	1	2	Ave	Stdev	1	2	Ave	Stdev
0	7.2	7.2	7.2	0.0	7.2	7.2	7.2	0.0	7.2	7.2	7.2	0.0	7.2	7.2	7.2	0.0
2	7.1	7.0	7.1	0.1	6.8	6.9	6.9	0.1	6.9	6.8	6.9	0.1	6.7	6.6	6.7	0.1
4	6.8	6.7	6.8	0.1	6.8	6.8	6.8	0.0	6.7	6.8	6.8	0.1	6.8	6.8	6.8	0.0
7	6.4	6.4	6.4	0.0	6.3	6.3	6.3	0.0	6.3	6.3	6.3	0.0	6.5	6.4	6.5	0.1
9	6.5	6.4	6.5	0.1	6.5	6.5	6.5	0.0	6.3	6.3	6.3	0.0	6.5	6.5	6.5	0.0
11	7.0	7.0	7.0	0.0	6.9	6.9	6.9	0.0	6.9	6.9	6.9	0.0	6.9	6.8	6.9	0.1
14	7.2	7.1	7.2	0.1	6.7	6.6	6.7	0.1	6.6	6.6	6.6	0.0	6.5	6.4	6.5	0.1
adj	N/A	N/A	-	-	6.9	6.9	6.9	0.0	6.8	7.2	7.0	0.3	7.1	6.9	7.0	0.1
16	7.1	7.1	7.1	0.0	6.6	6.6	6.6	0.0	6.6	6.5	6.6	0.1	6.4	6.6	6.5	0.1
adj	N/A	N/A	-	-	7.0	7.0	7.0	0.0	6.8	7.0	6.9	0.1	7.2	7.0	7.1	0.1
18	7.1	7.0	7.1	0.1	6.4	6.4	6.4	0.0	6.3	6.3	6.3	0.0	6.2	6.2	6.2	0.0
adj	N/A	N/A	-	-	7.2	7.0	7.1	0.1	6.9	7.1	7.0	0.1	7.2	6.9	7.1	0.2
21	7.2	7.2	7.2	0.0	6.6	6.6	6.6	0.0	6.5	6.5	6.5	0.0	6.4	6.2	6.3	0.1
adj	N/A	N/A	-	-	6.8	7.0	6.9	0.1	7.0	7.2	7.1	0.1	7.1	7.0	7.1	0.1
23	7.2	7.2	7.2	0.0	6.6	6.8	6.7	0.1	6.4	6.8	6.6	0.3	6.5	6.5	6.5	0.0
adj	N/A	N/A	-	-	7.0	6.8	6.9	0.1	7.1	6.8	7.0	0.2	7.0	7.0	7.0	0.0
25	7.1	7.2	7.2	0.1	6.6	6.7	6.7	0.1	6.6	6.6	6.6	0.0	6.4	6.5	6.5	0.1
adj	N/A	N/A	-	-	6.9	6.8	6.9	0.1	6.9	6.8	6.9	0.1	6.9	6.9	6.9	0.0
28	7.1	7.2	7.2	0.1	6.5	6.6	6.6	0.1	6.3	6.3	6.3	0.0	6.3	6.0	6.2	0.2
adj	N/A	N/A	-	-	7.0	6.9	7.0	0.1	7.0	7.0	7.0	0.0	7.1	6.8	7.0	0.2
32	7.2	7.1	7.2	0.1	6.3	6.4	6.4	0.1	6.3	6.3	6.3	0.0	6.7	6.6	6.7	0.1
adj	N/A	N/A	-	-	7.1	6.9	7.0	0.1	6.8	6.9	6.9	0.1	6.9	6.9	6.9	0.0
35	7.5	7.5	7.5	0.0	6.1	5.9	6.0	0.1	6.4	6.8	6.6	0.3	7.0	6.8	6.9	0.1
adj	7.1	7.1	7.1	0.0	6.9	6.9	6.9	0.0	7.0	6.8	6.9	0.1	7.0	6.8	6.9	0.1
37	7.4	7.4	7.4	0.0	6.7	6.2	6.5	0.4	6.7	6.5	6.6	0.1	6.7	6.7	6.7	0.0
adj	7.2	7.2	7.2	0.0	6.9	6.8	6.9	0.1	7.0	7.2	7.1	0.1	7.2	7.1	7.2	0.1
39	7.3	7.2	7.3	0.1	6.7	6.4	6.6	0.2	6.7	6.7	6.7	0.0	6.6	6.8	6.7	0.1
adj	7.2	N/A	-	-	7.0	6.9	7.0	0.1	6.9	7.0	7.0	0.1	7.2	N/A	-	-

Notes: N/A: Not available; adj: pH adjustment; Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions; Bio.: Bioaugmentation with naphthalene degraders; Ext.C.: 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% (w/w) Tween 80 additions

Table D.2. (Continued)

Day	Condition															
	Biotic control				Nutrients				Bio.+ Nutrients				Bio.+Nutrients+Ext.C.			
	1	2	Ave	Stdev	1	2	Ave	Stdev	1	2	Ave	Stdev	1	2	Ave	Stdev
42	7.0	6.8	6.9	0.1	6.6	6.5	6.6	0.1	6.7	6.9	6.8	0.1	7.0	6.9	7.0	0.1
44	7.1	7.0	7.1	0.1	6.7	6.7	6.7	0.0	6.6	6.7	6.7	0.1	6.9	6.8	6.9	0.1
46	7.2	7.1	7.2	0.1	6.8	6.7	6.8	0.1	6.8	6.8	6.8	0.0	6.9	6.8	6.9	0.1
49	7.0	7.0	7.0	0.0	6.7	6.7	6.7	0.0	6.7	6.8	6.8	0.1	7.0	6.7	6.9	0.2
51	7.1	7.0	7.1	0.1	6.7	6.6	6.7	0.1	6.7	6.8	6.8	0.1	6.9	6.7	6.8	0.1
53	7.2	7.1	7.2	0.1	N/A	N/A	-	-	6.4	6.5	6.5	0.1	7.0	6.8	6.9	0.1
adj	N/A	N/A	-	-	N/A	N/A	-	-	6.7	N/A	-	-	N/A	N/A	-	-
56	7.2	7.2	7.2	0.0	N/A	N/A	-	-	6.7	6.6	6.7	0.1	7.0	6.8	6.9	0.1
58	7.1	7.1	7.1	0.0	N/A	N/A	-	-	6.6	6.6	6.6	0.0	6.9	6.8	6.9	0.1
60	7.1	7.1	7.1	0.0	N/A	N/A	-	-	6.7	6.7	6.7	0.0	6.7	6.7	6.7	0.0
63	7.0	7.0	7.0	0.0	N/A	N/A	-	-	6.6	6.5	6.6	0.1	6.8	6.7	6.8	0.1
65	7.2	7.2	7.2	0.0	N/A	N/A	-	-	6.4	6.5	6.5	0.1	6.8	6.7	6.8	0.1
adj	N/A	N/A	-	-	N/A	N/A	-	-	6.7	N/A	-	-	N/A	N/A	-	-
67	7.1	7.0	7.1	0.1	N/A	N/A	-	-	6.6	6.5	6.6	0.1	6.8	6.7	6.8	0.1
70	7.2	7.1	7.2	0.1	N/A	N/A	-	-	6.6	6.5	6.6	0.1	6.8	6.7	6.8	0.1
72	7.1	7.2	7.2	0.1	N/A	N/A	-	-	6.7	6.6	6.7	0.1	6.9	6.8	6.9	0.1
74	7.0	7.0	7.0	0.0	N/A	N/A	-	-	6.6	6.5	6.6	0.1	6.8	6.7	6.8	0.1
77	7.3	7.3	7.3	0.0	N/A	N/A	-	-	6.8	6.7	6.8	0.1	7.8	7.8	7.8	0.0
79	7.1	7.1	7.1	0.0	4.8	4.7	4.8	0.1	6.6	6.7	6.7	0.1	8.0	7.4	7.7	0.4
adj	N/A	N/A	-	-	6.5	6.6	6.6	0.1	N/A	N/A	-	-	7.3	7.1	7.2	0.2
81	7.1	7.0	7.1	0.1	6.2	6.2	6.2	0.0	6.5	6.7	6.6	0.1	8.1	7.2	7.7	0.6
adj	N/A	N/A	-	-	6.6	6.6	6.6	0.0	N/A	N/A	-	-	7.2	N/A	-	-
84	7.0	7.3	7.2	0.2	8.3	8.2	8.3	0.1	6.3	6.4	6.4	0.1	7.5	7.2	7.4	0.2
adj	N/A	N/A	-	-	7.2	6.7	7.0	0.4	N/A	N/A	-	-	N/A	N/A	-	-
86	7.1	7.3	7.2	0.1	8.2	8.1	8.2	0.1	6.5	6.6	6.6	0.1	6.7	7.5	7.1	0.6
adj	N/A	N/A	-	-	7.4	7.3	7.4	0.1	N/A	N/A	-	-	N/A	N/A	-	-
88	7.1	7.1	7.1	0.0	8.0	7.9	8.0	0.1	6.4	6.5	6.5	0.1	6.6	7.4	7.0	0.6
91	7.2	7.2	7.2	0.0	8.0	8.0	8.0	0.0	6.4	6.6	6.5	0.1	5.8	7.3	6.6	1.1

Notes: N/A: Not available; adj: pH adjustment; Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions; Bio.: Bioaugmentation with naphthalene degraders; Ext.C.: 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% (w/w) Tween 80 additions

Table D.2. (Continued)

Day	Condition															
	Biotic control				Nutrients				Bio.+ Nutrients				Bio.+Nutrients+Ext.C.			
	1	2	Ave	Stdev	1	2	Ave	Stdev	1	2	Ave	Stdev	1	2	Ave	Stdev
93	7.1	7.2	7.2	0.1	7.9	7.9	7.9	0.0	6.5	6.6	6.6	0.1	5.7	7.3	6.5	1.1
95	7.1	7.1	7.1	0.0	7.8	7.5	7.7	0.2	6.4	6.5	6.5	0.1	5.5	7.2	6.4	1.2
adj	N/A	N/A	-	-	N/A	N/A	-	-	N/A	N/A	-	-	7.3	N/A	-	-
98	7.2	7.1	7.2	0.1	6.9	7.0	7.0	0.1	6.5	6.7	6.6	0.1	6.3	7.2	6.8	0.6
100	7.1	7.2	7.2	0.1	6.9	7.0	7.0	0.1	6.5	6.6	6.6	0.1	6.2	7.3	6.8	0.8
104	7.1	7.2	7.2	0.1	7.1	7.0	7.1	0.1	6.6	6.7	6.7	0.1	6.0	7.3	6.7	0.9
109	7.1	7.2	7.2	0.1	7.0	7.1	7.1	0.1	6.6	6.7	6.7	0.1	5.4	7.3	6.4	1.3
111	7.2	7.1	7.2	0.1	7.1	6.9	7.0	0.1	6.6	6.6	6.6	0.0	6.9	7.3	7.1	0.3
114	7.2	7.1	7.2	0.1	7.1	7.0	7.1	0.1	6.5	6.7	6.6	0.1	7.0	7.3	7.2	0.2
117	7.2	7.3	7.3	0.1	7.1	7.1	7.1	0.0	6.6	6.7	6.7	0.1	7.0	7.3	7.2	0.2
119	7.1	7.2	7.2	0.1	7.0	7.1	7.1	0.1	6.6	6.6	6.6	0.0	6.8	7.3	7.1	0.4
126	7.0	7.0	7.0	0.0	6.8	6.8	6.8	0.0	N/A	N/A	-	-	6.6	7.0	6.8	0.3
129	7.1	7.1	7.1	0.0	6.9	6.9	6.9	0.0	N/A	N/A	-	-	6.8	7.2	7.0	0.3
131	7.0	7.2	7.1	0.1	6.3	6.2	6.3	0.1	5.7	5.7	5.7	0.0	7.7	7.2	7.5	0.4
adj	N/A	N/A	-	-	6.9	7.0	7.0	0.0	7.1	7.2	7.2	0.1	7.6	7.2	7.4	0.3
133	7.2	7.2	7.2	0.0	6.5	6.4	6.5	0.1	6.8	6.5	6.7	0.2	7.6	7.1	7.4	0.4
136	7.3	7.5	7.4	0.1	6.3	6.5	6.4	0.1	6.6	6.3	6.5	0.2	5.9	7.0	6.5	0.8
138	7.2	7.5	7.4	0.2	7.0	6.5	6.8	0.4	6.6	6.7	6.7	0.1	7.0	7.2	7.1	0.1
140	7.3	7.3	7.3	0.0	7.0	6.6	6.8	0.3	6.5	6.4	6.5	0.1	6.7	7.2	7.0	0.4
143	7.2	7.3	7.3	0.1	6.9	6.6	6.8	0.2	6.4	6.2	6.3	0.1	6.4	7.0	6.7	0.4
145	7.2	7.3	7.3	0.1	6.8	6.5	6.7	0.2	6.4	6.1	6.3	0.2	6.4	7.0	6.7	0.4
150	7.2	7.3	7.3	0.1	6.9	6.4	6.7	0.4	6.4	6.1	6.3	0.2	6.4	7.0	6.7	0.4
152	7.5	7.4	7.5	0.1	6.8	6.5	6.7	0.2	6.3	6.4	6.4	0.1	6.2	6.9	6.6	0.5
154	7.3	7.4	7.4	0.1	7.0	6.6	6.8	0.3	6.5	6.5	6.5	0.0	6.3	7.1	6.7	0.6
157	7.3	7.4	7.4	0.1	7.0	6.6	6.8	0.3	6.5	6.5	6.5	0.0	6.3	7.1	6.7	0.6
164	7.1	7.3	7.2	0.1	6.2	6.0	6.1	0.1	6.0	6.0	6.0	0.0	5.9	7.2	6.6	0.9
adj	N/A	N/A	-	-	7.3	6.7	7.0	0.4	7.1	7.1	7.1	0.0	6.5	N/A	-	-
168	7.1	7.2	7.2	0.1	6.5	6.0	6.3	0.4	6.5	6.4	6.5	0.1	5.9	7.2	6.6	0.9

Notes: N/A: Not available; adj: pH adjustment; Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions; Bio.: Bioaugmentation with naphthalene degraders; Ext.C.: 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% (w/w) Tween 80 additions

Table D.3. Dissolved Oxygen Readings for Phase II: Bioslurry Experiments

Day	Condition															
	Biotic control				Nutrients				Bio.+ Nutrients				Bio.+Nutrients+Ext.C.			
	1	2	Ave	Stdev	1	2	Ave	Stdev	1	2	Ave	Stdev	1	2	Ave	Stdev
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	3.0	2.6	2.8	0.3	2.3	1.7	2.0	0.4	0.2	0.2	0.2	0.0	0.2	0.3	0.3	0.0
4	2.7	3.3	3.0	0.4	2.4	3.3	2.9	0.6	0.9	1.2	1.0	0.2	0.1	0.1	0.1	0.0
7	1.6	1.6	1.6	0.0	3.1	1.5	2.3	1.2	0.8	1.9	1.3	0.8	1.6	1.3	1.4	0.2
9	5.5	5.7	5.6	0.1	5.3	5.4	5.4	0.1	5.6	5.5	5.5	0.1	5.2	5.3	5.3	0.1
11	4.8	5.0	4.9	0.2	5.3	5.2	5.2	0.1	4.0	4.9	4.5	0.7	5.0	5.0	5.0	0.0
14	4.4	4.5	4.5	0.1	5.2	5.1	5.2	0.1	5.2	5.2	5.2	0.0	5.1	5.1	5.1	0.0
16	5.1	5.3	5.2	0.2	5.3	5.3	5.3	0.0	5.0	5.3	5.1	0.2	4.8	4.8	4.8	0.0
18	6.2	5.1	5.6	0.8	5.4	5.9	5.6	0.4	5.6	5.8	5.7	0.2	5.6	5.5	5.5	0.1
21	5.5	5.2	5.3	0.2	4.4	5.0	4.7	0.5	4.6	4.7	4.7	0.0	5.2	5.0	5.1	0.2
23	5.8	6.3	6.1	0.3	6.0	6.0	6.0	0.0	5.8	5.8	5.8	0.0	5.4	5.8	5.6	0.3
25	6.2	6.3	6.2	0.1	6.2	6.1	6.1	0.1	5.9	5.8	5.8	0.0	5.4	5.8	5.6	0.3
30	5.6	5.7	5.7	0.1	5.5	5.6	5.6	0.1	5.3	5.4	5.4	0.0	5.7	5.7	5.7	0.0
32	5.7	5.7	5.7	0.0	5.3	5.3	5.3	0.0	4.8	5.3	5.1	0.4	5.3	5.4	5.4	0.1
35	5.7	5.7	5.7	0.0	5.4	5.0	5.2	0.3	5.9	5.6	5.8	0.2	5.7	5.7	5.7	0.0
37	5.4	5.4	5.4	0.0	5.4	4.9	5.1	0.4	5.6	5.7	5.7	0.0	5.4	5.7	5.6	0.2
39	5.6	5.7	5.7	0.1	5.5	5.6	5.6	0.1	5.3	5.4	5.4	0.0	5.7	5.7	5.7	0.0
42	5.2	5.2	5.2	0.0	5.5	5.6	5.6	0.1	5.5	5.6	5.5	0.0	5.5	5.5	5.5	0.0
44	5.5	5.4	5.4	0.0	5.4	4.4	4.9	0.7	5.5	5.5	5.5	0.0	5.2	5.4	5.3	0.2
46	5.1	4.9	5.0	0.1	5.2	4.2	4.7	0.7	5.1	4.4	4.7	0.5	4.9	4.9	4.9	0.0
49	5.5	5.3	5.4	0.1	5.6	5.5	5.5	0.1	5.2	5.9	5.5	0.5	5.4	5.4	5.4	0.0
51	5.1	5.1	5.1	0.0	5.1	5.2	5.2	0.1	5.2	4.9	5.1	0.2	5.2	5.2	5.2	0.0
53	7.8	7.0	7.4	0.6	N/A	N/A	-	-	6.9	6.3	6.6	0.4	7.0	7.0	7.0	0.0
56	7.0	6.8	6.9	0.1	N/A	N/A	-	-	7.0	6.9	6.9	0.1	6.7	6.9	6.8	0.1
58	6.4	5.7	6.0	0.5	N/A	N/A	-	-	6.1	6.0	6.1	0.1	6.9	7.0	7.0	0.1

Notes: Dissolved oxygen represented as ppm; N/A: Not available; Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions; Bio.: Bioaugmentation with naphthalene degraders; Ext.C.: 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% (w/w) Tween 80 additions

Table D.3. (Continued)

Day	Condition															
	Biotic control				Nutrients				Bio.+ Nutrients				Bio.+Nutrients+Ext.C.			
	1	2	Ave	Stdev	1	2	Ave	Stdev	1	2	Ave	Stdev	1	2	Ave	Stdev
60	7.1	6.8	6.9	0.2	N/A	N/A	-	-	6.9	6.8	6.9	0.1	6.8	6.8	6.8	0.0
63	6.9	6.8	6.8	0.0	N/A	N/A	-	-	6.9	6.8	6.9	0.1	6.6	6.7	6.7	0.1
65	6.8	6.8	6.8	0.0	N/A	N/A	-	-	6.8	6.9	6.8	0.1	6.6	6.8	6.7	0.1
67	6.8	6.7	6.8	0.1	N/A	N/A	-	-	6.6	6.8	6.7	0.1	6.7	6.7	6.7	0.0
70	7.0	7.0	7.0	0.0	N/A	N/A	-	-	7.0	6.9	7.0	0.1	6.8	6.9	6.9	0.1
72	6.8	6.8	6.8	0.0	N/A	N/A	-	-	6.8	6.9	6.9	0.0	6.8	6.9	6.8	0.1
74	6.6	6.4	6.5	0.1	N/A	N/A	-	-	6.5	6.5	6.5	0.0	6.4	6.6	6.5	0.1
77	6.7	6.6	6.7	0.1	N/A	N/A	-	-	6.7	6.6	6.7	0.1	0.1	0.0	0.1	0.0
79	6.3	6.5	6.4	0.1	6.6	6.5	6.6	0.1	6.7	6.3	6.5	0.3	3.9	0.0	2.0	2.8
81	6.4	6.4	6.4	0.0	6.0	5.7	5.9	0.2	6.4	6.1	6.3	0.2	4.9	0.0	2.4	3.4
84	6.4	6.5	6.5	0.1	6.2	5.8	6.0	0.3	6.5	6.3	6.4	0.1	4.6	0.0	2.3	3.2
86	6.8	6.5	6.7	0.2	6.5	6.3	6.4	0.1	6.5	6.3	6.4	0.1	5.0	0.6	2.8	3.1
88	6.5	6.7	6.6	0.2	6.5	6.2	6.4	0.2	6.5	6.4	6.4	0.1	0.3	0.1	0.2	0.1
91	6.4	6.4	6.4	0.0	6.3	6.2	6.3	0.1	6.4	6.3	6.4	0.1	4.7	0.1	2.4	3.3
93	6.2	6.2	6.2	0.0	6.3	6.1	6.2	0.2	6.4	6.2	6.3	0.1	5.1	0.1	2.6	3.6
95	6.1	6.0	6.1	0.1	6.0	5.4	5.7	0.4	6.3	6.2	6.2	0.1	5.5	0.0	2.8	3.9
100	6.1	6.1	6.1	0.0	6.1	5.7	5.9	0.3	6.2	6.1	6.1	0.1	4.8	0.1	2.4	3.3
102	6.2	6.2	6.2	0.0	6.2	6.1	6.1	0.1	6.1	6.1	6.1	0.0	4.2	0.1	2.1	2.9
107	6.1	6.1	6.1	0.0	6.2	6.0	6.1	0.1	6.1	6.1	6.1	0.0	5.7	0.1	2.9	3.9
109	6.1	6.0	6.0	0.1	6.1	5.9	6.0	0.2	6.1	6.1	6.1	0.0	3.0	0.1	1.5	2.1
112	6.0	5.9	6.0	0.1	6.1	6.0	6.0	0.0	6.0	6.0	6.0	0.0	3.8	0.1	1.9	2.7
114	5.9	5.9	5.9	0.0	6.0	5.9	6.0	0.1	5.9	6.0	5.9	0.0	5.3	0.1	2.7	3.7
116	6.1	5.9	6.0	0.1	6.0	5.9	6.0	0.1	6.0	5.9	6.0	0.1	5.2	0.1	2.6	3.7

Notes: Dissolved oxygen represented as mg/l; N/A: Not available; Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions; Bio.: Bioaugmentation with naphthalene degraders; Ext.C.: 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% (w/w) Tween 80 additions

Table D.3. (Continued)

Day	Condition															
	Biotic control				Nutrients				Bio.+ Nutrients				Bio.+Nutrients+Ext.C.			
	1	2	Ave	Stdev	1	2	Ave	Stdev	1	2	Ave	Stdev	1	2	Ave	Stdev
128	6.4	6.5	6.4	0.1	6.3	5.4	5.8	0.7	6.5	6.5	6.5	0.0	0.0	0.1	0.1	0.0
130	6.1	6.3	6.2	0.1	6.0	6.2	6.1	0.1	6.1	6.0	6.1	0.0	0.1	0.1	0.1	0.1
133	6.1	6.1	6.1	0.0	6.3	6.2	6.2	0.1	6.2	6.2	6.2	0.0	5.1	0.1	2.6	3.5
135	6.0	6.2	6.1	0.1	6.3	4.9	5.6	0.9	6.3	6.0	6.1	0.2	4.9	0.0	2.5	3.4
137	6.1	5.9	6.0	0.1	6.1	4.3	5.2	1.3	5.9	5.8	5.9	0.1	4.9	0.0	2.5	3.5
140	5.9	5.9	5.9	0.0	5.9	4.8	5.4	0.8	5.9	6.0	5.9	0.0	5.4	0.0	2.7	3.8
142	5.4	5.7	5.5	0.2	5.7	4.5	5.1	0.8	5.7	5.6	5.6	0.1	4.6	0.0	2.3	3.2
147	5.8	5.8	5.8	0.1	5.8	4.6	5.2	0.8	5.8	5.9	5.8	0.0	5.1	0.0	2.6	3.6
149	5.4	5.3	5.3	0.0	5.2	4.3	4.7	0.7	5.2	5.3	5.2	0.1	4.9	0.0	2.5	3.5
151	4.7	5.2	5.0	0.3	5.3	3.9	4.6	1.0	5.2	5.2	5.2	0.0	4.7	0.0	2.3	3.3
154	4.7	5.1	4.9	0.3	5.2	3.9	4.6	0.9	5.1	5.1	5.1	0.0	4.6	0.0	2.3	3.2
161	4.6	4.6	4.6	0.0	4.6	0.6	2.6	2.8	4.7	4.7	4.7	0.0	4.1	0.0	2.0	2.9
165	6.2	6.2	6.2	0.0	5.5	0.8	3.2	3.4	5.8	5.8	5.8	0.0	5.3	0.0	2.7	3.7

Notes: Dissolved oxygen represented as mg/l; N/A: Not available; Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions; Bio.: Bioaugmentation with naphthalene degraders; Ext.C.: 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% (w/w) Tween 80 additions

Table D.4. Oxygen Uptake Rate Results for Phase II: Bioslurry Experiments

Day	Condition															
	Biotic control				Nutrients				Bio. + Nutrients				Bio.+Nutrients+Ext.C.			
	1	2	Ave	Stdev	1	2	Ave	Stdev	1	2	Ave	Stdev	1	2	Ave	Stdev
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4	4.9	4.6	4.7	0.2	6.1	5.6	5.9	0.4	4.2	4.1	4.2	0.0	0.5	0.5	0.5	0.0
7	3.7	7.6	5.6	2.8	1.5	0.1	0.8	1.0	3.9	5.0	4.5	0.8	2.2	3.1	2.6	0.7
9	1.3	1.4	1.4	0.0	2.3	1.1	1.7	0.8	2.5	2.3	2.4	0.1	3.0	2.9	3.0	0.0
14	1.8	3.5	2.7	1.2	2.0	1.0	1.5	0.7	1.0	1.3	1.1	0.3	0.8	1.3	1.1	0.3
18	1.4	3.6	2.5	1.6	1.3	1.2	1.3	0.1	0.5	1.6	1.0	0.7	2.3	2.6	2.4	0.2
21	0.0	1.1	0.5	0.8	1.2	1.0	1.1	0.1	2.1	1.8	2.0	0.2	3.1	3.8	3.5	0.6
25	0.0	0.1	0.1	0.1	0.8	0.3	0.6	0.4	0.4	0.4	0.4	0.0	2.0	2.2	2.1	0.2
30	0.0	0.3	0.1	0.2	1.5	1.4	1.5	0.1	1.5	2.1	1.8	0.4	2.7	0.5	1.6	1.6
32	0.0	0.0	0.0	0.0	4.0	3.1	3.5	0.6	1.0	0.1	0.5	0.6	0.3	0.5	0.4	0.1
39	0.5	1.2	0.9	0.5	0.4	1.0	0.7	0.4	1.1	0.5	0.8	0.4	1.0	1.1	1.1	0.1
42	0.0	0.7	0.3	0.5	0.3	0.8	0.5	0.3	0.5	1.0	0.8	0.3	1.2	0.2	0.7	0.7
46	0.1	0.2	0.1	0.1	0.7	0.0	0.4	0.5	0.4	0.2	0.3	0.2	0.2	0.6	0.4	0.3
49	0.8	0.4	0.6	0.3	0.6	0.3	0.5	0.2	0.1	0.0	0.0	0.0	0.7	1.1	0.9	0.3
53	0.7	1.9	1.3	0.8	N/A	N/A	-	-	2.6	2.2	2.4	0.3	1.7	2.2	2.0	0.3
56	0.1	0.7	0.4	0.4	N/A	N/A	-	-	1.1	1.0	1.1	0.1	0.7	0.4	0.5	0.3
60	1.2	1.4	1.3	0.2	N/A	N/A	-	-	1.0	0.8	0.9	0.1	1.2	0.2	0.7	0.7
63	0.8	0.9	0.8	0.1	N/A	N/A	-	-	0.6	1.3	1.0	0.5	0.8	1.4	1.1	0.4
67	1.9	0.0	0.9	1.3	N/A	N/A	-	-	0.2	0.3	0.3	0.0	1.8	1.0	1.4	0.6
70	0.7	2.6	1.7	1.4	N/A	N/A	-	-	0.9	0.8	0.8	0.1	1.0	1.1	1.1	0.1
74	0.9	0.54	0.7	0.3	N/A	N/A	-	-	1.14	0.6	0.9	0.4	1.02	0.78	0.9	0.2
77	1.26	0.48	0.9	0.6	N/A	N/A	-	-	0.84	0.9	0.9	0.0	0.3	0	0.2	0.2
81	1.14	0.78	1.0	0.3	2.76	2.52	2.6	0.2	1.2	0.96	1.1	0.2	3.6	0.3	2.0	2.3
84	0.36	1.14	0.7	0.6	2.46	2.58	2.5	0.1	0.84	0.96	0.9	0.1	6.24	0.24	3.0	4.6
86	0.06	1.56	0.8	1.1	1.44	1.14	1.3	0.2	0.66	1.2	0.9	0.4	0.84	0.12	0.5	0.5

Notes: Oxygen uptake rate represented as mg/l-hr; N/A: Not available; Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions; Bio.: Bioaugmentation with naphthalene degraders; Ext.C.: 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% (w/w) Tween 80 additions

Table D.4. (Continued)

Day	Condition															
	Biotic control				Nutrients				Bio.+ Nutrients				Bio.+Nutrients+Ext. C.			
	1	2	Ave	Stdev	1	2	Ave	Stdev	1	2	Ave	Stdev	1	2	Ave	Stdev
89	0.66	1.02	0.8	0.3	1.02	1.38	1.2	0.3	0.48	0.9	0.7	0.3	6.42	0	3.2	4.5
93	0.6	0.96	0.8	0.3	1.86	2.76	2.3	0.6	0.42	1.2	0.8	0.6	3.96	0	2.0	2.8
96	1.02	1.02	1.0	0.0	2.16	1.84	2.0	0.2	0.72	0.96	0.8	0.2	5.7	0	2.9	4.0
100	1.14	1.26	1.2	0.1	0.54	1.2	0.9	0.5	0.42	0.66	0.5	0.2	7.44	0	3.7	5.3
107	0.06	0.6	0.3	0.4	0.48	0.66	0.6	0.1	0	0.96	0.5	0.7	4.14	0	2.1	2.9
110	0.24	0.12	0.2	0.1	0.36	0.66	0.5	0.2	0.48	0.3	0.4	0.1	8.46	0	4.2	6.0
114	1.2	0.54	0.9	0.5	0	0	0.0	0.0	1.26	0.6	0.9	0.5	3	0	1.5	2.1
121	0.84	0.72	0.8	0.1	0	0	0.0	0.0	0.42	1.2	0.8	0.6	2.7	0.42	1.6	1.6
124	0.84	0.78	0.8	0.0	0	0	0.0	0.0	0.72	0.96	0.8	0.2	3.18	0.36	1.8	2.0
128	0	0.42	0.2	0.3	1.26	1.14	1.2	0.1	0.6	0.96	0.8	0.3	0.36	0.06	0.2	0.2
131	0.66	0.3	0.5	0.3	1.14	0.72	0.9	0.3	0.18	0.54	0.4	0.3	3.6	0	1.8	2.5
135	0.6	0	0.3	0.4	0.72	0	0.4	0.5	0.3	0	0.1	0.2	2.82	0	1.4	2.0
145	0.12	0.9	0.5	0.6	0.84	0	0.4	0.6	0.48	0.9	0.7	0.3	2.82	0	1.4	2.0
149	0.12	0.54	0.3	0.3	0.6	0	0.3	0.4	1.14	1.2	1.2	0.0	3	0	1.5	2.1
159	0	0	0.0	0.0	0	0	0.0	0.0	0	0.18	0.1	0.1	2.28	0	1.1	1.6
163	1.44	0.78	1.1	0.5	1.08	0	0.5	0.8	0	0.72	0.4	0.5	2.28	0.12	1.2	1.5

Notes: Oxygen uptake rate represented as mg/l-hr; N/A: Not available; Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions; Bio.: Bioaugmentation with naphthalene degraders; Ext.C.: 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% (w/w) Tween 80 additions

Table D.5. Total Organic Carbon Results for Phase II: Bioslurry Experiments

Condition	Biotic control				Nutrients			
Day	1	2	Average	Stdev	1	2	Average	Stdev
0	103349	89905	96627	9506	103349	89905	96627	9506
7	31833	33577	32705	1233	23102	34579	28840	8116
14	33208	34642	33925	1014	-1991	31123	14565	23416
21	27272	31071	29172	2689	31268	31317	31292	35
35	33421	30419	31920	2123	27076	31757	29414	3313
49	31471	34002	32737	1790	33306	34923	34114	1143
63	29055	29845	29450	559	N/A	N/A	-	-
Bio.+Nutrients					Bio.+Nutrients+Ext.C.			
Day	1	2	Average	Stdev	1	2	Average	Stdev
0	103349	89905	96627	9506	103349	89905	96627	9506
7	24976	33190	29083	5808	26004	31087	28545	3594
14	21559	34454	28006	9118	29673	35009	32341	3773
21	20875	30982	25928	7146	31430	-1775	14828	23480
35	32574	31656	32115	650	26111	27844	26978	1225
49	34385	34639	34512	180	28972	29216	29094	173
63	30154	29346	29750	571	25804	27566	26685	1246
69	32657	36551	34604	2754	33830	35835	34833	1418
69	32152	30286	31219	1319	N/A	N/A	-	-

Notes: Total organic carbon represented as mg/kg; N/A: Not available; Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions; Bio.: Bioaugmentation with naphthalene degraders; Ext.C.: 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% (w/w) Tween 80 additions

Table D.6. Bioreactor Headspace Oxygen Results for Phase II: Bioslurry Experiments

Day	Biotic control				Nutrients			
	1	2	Ave	Stdev	1	2	Ave	Stdev
0	20.9	20.9	20.9	0.0	20.9	20.9	20.9	0.0
14	20.9	20.9	20.9	0.0	20.9	20.9	20.9	0.0
21	20.7	20.7	20.7	0.0	20.7	20.7	20.7	0.0
28	20.9	20.9	20.9	0.0	20.9	20.9	20.9	0.0
35	20.9	20.9	20.9	0.0	20.9	20.9	20.9	0.0
42	20.8	20.7	20.8	0.1	20.8	20.9	20.9	0.1
49	20.4	20.6	20.5	0.1	20.7	20.7	20.7	0.0
59	20.9	20.9	20.9	0.0	N/A	N/A	-	-
77	20.8	20.7	20.8	0.1	N/A	N/A	-	-
84	20.9	20.9	20.9	0.0	20.9	20.9	20.9	0.0
Day	Bio.+Nutrients				Bio.+Nutrients+Ext.C.			
	1	2	Ave	Stdev	1	2	Ave	Stdev
0	20.9	20.9	20.9	0.0	20.9	20.9	20.9	0.0
14	20.9	20.9	20.9	0.0	20.8	20.9	20.9	0.1
21	20.7	20.6	20.7	0.1	20.7	20.8	20.8	0.1
28	20.8	20.9	20.9	0.1	20.9	20.9	20.9	0.0
35	20.9	20.9	20.9	0.0	20.9	20.9	20.9	0.0
42	20.9	20.9	20.9	0.0	20.9	20.9	20.9	0.0
49	20.8	20.7	20.8	0.1	20.5	20.5	20.5	0.0
59	20.9	20.9	20.9	0.0	20.9	20.9	20.9	0.0
77	20.9	20.9	20.9	0.0	15.9	15.0	15.5	0.6
84	20.9	20.9	20.9	0.0	20.6	19.3	20.0	0.9

Notes: Oxygen content represented as %; N/A: Not available; Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions; Bio.: Bioaugmentation with naphthalene degraders; Ext.C.: 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% (w/w) Tween 80 additions

Table D.7. Bioreactor Headspace Carbon Dioxide Results for Phase II: Bioslurry Experiments

Day	Biotic control				Nutrients				Bio.+Nutrients				Bio.+Nutrients+Ext.C.			
	1	2	Ave	Stdev	1	2	Ave	Stdev	1	2	Ave	Stdev	1	2	Ave	Stdev
0	0.2	0.3	0.3	0.1	0.1	0.1	0.1	0	0.2	0.2	0.2	0	0	0	0.0	0.0
7	0.2	0.2	0.2	0.0	0.2	0.2	0.2	0	0.2	0.2	0.2	0	0.2	0.2	0.2	0.0
14	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0	0.0
21	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0	0.0
28	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0	0.0
35	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0	0.0
42	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0	0.0
49	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0	0.0
59	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0	0.0
77	0	0	0	0	N/A	N/A	-	-	0	0	0	0	3.5	4.1	3.8	0.4
84	0	0	0	0	0	0	0	0	0	0	0	0	0	0.6	0.3	0.4

Notes: Carbon dioxide content represented as %; N/A: Not available; Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions; Bio.: Bioaugmentation with naphthalene degraders; Ext.C.: 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% (w/w) Tween 80 additions

Table D.8. Bioreactor Headspace Volatile Organic Carbons Results for Phase II: Bioslurry Experiments

Day	Biotic control				Nutrients			
	1	2	Ave	Stdev	1	2	Ave	Stdev
0	300	400	350.0	70.7	300	360	330.0	42.4
7	480	740	610.0	183.8	1020	1000	1010.0	14.1
14	1540	1620	1580.0	56.6	1560	1600	1580.0	28.3
21	2460	2640	2550.0	127.3	2660	2660	2660.0	0.0
28	480	200	340.0	198.0	0	260	130.0	183.8
35	860	540	700.0	226.3	460	400	430.0	42.4
42	1500	1420	1460.0	56.6	1120	1140	1130.0	14.1
49	1720	1320	1520.0	282.8	1300	1520	1410.0	155.6
59	0	60	30.0	42.4	N/A	N/A	-	-
77	760	900	830.0	99.0	N/A	N/A	-	-
84	840	200	520.0	452.5	0	0	0	0
Day	Bio.+Nutrients				Bio.+Nutrients+Ext.C.			
0	1	2	Ave	Stdev	1	2	Ave	Stdev
7	320	400	360.0	56.6	360	300	330.0	42.4
14	980	1100	1040.0	84.9	820	1720	1270.0	636.4
21	1540	1520	1530.0	14.1	1520	1460	1490.0	42.4
28	2880	2820	2850.0	42.4	3200	3260	3230.0	42.4
35	840	640	740.0	141.4	540	460	500.0	56.6
42	100	160	130.0	42.4	180	160	170.0	14.1
49	1040	1080	1060.0	28.3	960	1140	1050.0	127.3
59	1740	1720	1730.0	14.1	1440	1400	1420.0	28.3
77	20	0	10.0	14.1	40	680	360.0	452.5
84	1020	1000	1010.0	14.1	1060	1300	1180.0	169.7

Notes: Volatile organic carbon content represented as %; N/A: Not available; Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions; Bio.: Bioaugmentation with naphthalene degraders; Ext.C.: 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% (w/w) Tween 80 additions

Table D.9. Total Solid Results for Phase II: Bioslurry Experiments

Condition	Biotic control				Nutrients				Bio.+Nutrients				Bio.+Nutrients+Ext.C.			
Day	1	2	Average	Stdev	1	2	Average	Stdev	1	2	Average	Stdev	1	2	Average	Stdev
0	30.2%	29.3%	29.8%	0.7%	30.1%	29.3%	29.7%	0.5%	29.2%	26.1%	27.6%	2.2%	29.5%	26.3%	27.9%	2.3%
4	35.8%	35.6%	35.7%	0.1%	36.4%	35.2%	35.8%	0.9%	32.8%	33.1%	33.0%	0.2%	37.2%	30.5%	33.8%	4.7%
7	35.8%	35.6%	35.7%	0.1%	36.4%	35.2%	35.8%	0.9%	32.8%	33.1%	33.0%	0.2%	37.2%	30.5%	33.8%	4.7%
11	29.0%	32.4%	30.7%	2.4%	28.8%	29.9%	29.3%	0.7%	24.9%	27.3%	26.1%	1.7%	28.0%	22.3%	25.2%	4.1%
14	30.6%	33.2%	31.9%	1.8%	31.4%	32.9%	32.1%	1.1%	34.5%	33.4%	33.9%	0.7%	33.8%	33.8%	33.8%	0.0%
18	37.2%	37.2%	37.2%	0.0%	34.3%	37.5%	35.9%	2.3%	39.4%	36.7%	38.0%	1.9%	36.8%	38.3%	37.5%	1.0%
21	42.3%	42.5%	42.4%	0.1%	39.8%	42.6%	41.2%	1.9%	43.9%	42.1%	43.0%	1.3%	41.2%	42.6%	41.9%	1.0%
25	28.1%	28.6%	28.4%	0.4%	29.8%	30.4%	30.1%	0.4%	28.6%	28.0%	28.3%	0.5%	30.1%	28.7%	29.4%	1.0%
28	32.2%	31.6%	31.9%	0.4%	30.7%	29.6%	30.2%	0.8%	31.8%	32.3%	32.0%	0.3%	28.3%	30.9%	29.6%	1.8%
30	32.2%	31.6%	31.9%	0.4%	30.7%	29.6%	30.2%	0.8%	31.8%	32.3%	32.0%	0.3%	28.3%	30.9%	29.6%	1.8%
32	38.1%	36.8%	37.5%	0.9%	32.3%	35.5%	33.9%	2.3%	38.8%	37.7%	38.3%	0.8%	33.4%	34.5%	34.0%	0.7%
35	30.1%	33.2%	31.7%	2.1%	28.5%	32.3%	30.4%	2.7%	30.4%	31.3%	30.9%	0.6%	32.2%	30.7%	31.4%	1.1%
39	34.6%	34.0%	34.3%	0.4%	30.6%	32.9%	31.8%	1.6%	33.7%	34.2%	34.0%	0.4%	29.8%	32.0%	30.9%	1.6%
42	45.6%	43.4%	44.5%	1.6%	39.0%	38.6%	38.8%	0.3%	44.0%	42.1%	43.0%	1.3%	38.6%	42.2%	40.4%	2.5%
46	35.6%	35.7%	35.7%	0.1%	31.8%	32.5%	32.2%	0.5%	34.7%	32.2%	33.4%	1.7%	31.7%	32.4%	32.1%	0.5%
49	35.0%	36.0%	35.5%	0.8%	31.8%	30.7%	31.3%	0.7%	44.2%	33.8%	39.0%	7.3%	27.5%	32.3%	29.9%	3.4%
53	36.5%	38.0%	37.2%	1.0%	N/A	N/A	-	-	30.6%	30.6%	30.6%	0.0%	25.6%	27.7%	26.6%	1.4%
56	38.4%	38.6%	38.5%	0.2%	N/A	N/A	-	-	34.0%	33.0%	33.5%	0.7%	26.9%	31.0%	29.0%	2.9%
60	27.1%	21.7%	24.4%	3.8%	N/A	N/A	-	-	26.8%	25.7%	26.2%	0.8%	27.4%	30.5%	28.9%	2.2%

Notes: Total solid content as % (w/w); N/A: Not available; Nutrients: 1,000 mg/l nitrate and 400 mg/lphosphate additions; Bio.: Bioaugmentation with naphthalene degraders; Ext.C.: 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% (w/w) Tween 80 additions

Table D.9. (Continued)

Condition	Biotic Control				Nutrients				Bio.+Nutrients				Bio.+Nutrients+Ext.C.			
Day	1	2	Average	Stdev	1	2	Average	Stdev	1	2	Average	Stdev	1	2	Average	Stdev
63	23.2%	26.7%	24.9%	2.4%	N/A	N/A	-	-	32.2%	28.0%	30.1%	3.0%	29.5%	28.8%	29.1%	0.5%
67	28.1%	28.1%	28.1%	0.0%	N/A	N/A	-	-	31.8%	26.9%	29.3%	3.5%	30.7%	26.8%	28.7%	2.8%
70	27.8%	28.4%	28.1%	0.4%	N/A	N/A	-	-	29.4%	27.5%	28.4%	1.4%	25.8%	25.0%	25.4%	0.6%
74	30.1%	27.7%	28.9%	1.7%	N/A	N/A	-	-	32.6%	26.8%	29.7%	4.1%	27.2%	25.3%	26.3%	1.3%
77	31.8%	28.5%	30.2%	2.3%	N/A	N/A	-	-	31.5%	31.1%	31.3%	0.3%	29.6%	25.7%	27.7%	2.8%
81	34.1%	35.5%	34.8%	1.0%	29.0%	39.3%	34.1%	7.3%	36.9%	36.9%	36.9%	0.0%	38.2%	45.6%	41.9%	5.2%
84	28.7%	25.8%	27.2%	2.0%	23.6%	17.0%	20.3%	4.6%	30.6%	25.3%	27.9%	3.7%	23.6%	20.5%	22.1%	2.2%
88	36.5%	34.7%	35.6%	1.3%	43.5%	35.9%	39.7%	5.4%	47.2%	35.3%	41.3%	8.4%	35.1%	38.3%	36.7%	2.3%
91	31.5%	26.3%	28.9%	3.7%	20.4%	18.1%	19.3%	1.7%	28.9%	25.0%	26.9%	2.7%	27.2%	21.6%	24.4%	3.9%
95	31.5%	39.5%	35.5%	5.7%	32.5%	37.1%	34.8%	3.3%	30.5%	37.9%	34.2%	5.2%	45.7%	47.7%	46.7%	1.5%
102	19.1%	20.9%	20.0%	1.3%	22.9%	29.5%	26.2%	4.7%	34.0%	24.9%	29.4%	6.4%	38.7%	32.6%	35.7%	4.3%
109	29.4%	24.8%	27.1%	3.3%	17.4%	16.9%	17.1%	0.3%	26.9%	23.7%	25.3%	2.3%	24.9%	16.5%	20.7%	5.9%
123	31.2%	27.1%	29.2%	2.9%	19.5%	19.5%	19.5%	0.0%	N/A	N/A	-	-	25.4%	20.6%	23.0%	3.4%
130	28.9%	25.5%	27.2%	2.4%	17.5%	15.6%	16.6%	1.3%	22.4%	26.9%	24.6%	3.2%	19.8%	19.3%	19.6%	0.4%
137	28.2%	26.3%	27.2%	1.4%	18.3%	15.7%	17.0%	1.8%	24.0%	28.0%	26.0%	2.9%	20.6%	19.2%	19.9%	1.0%
151	24.9%	25.4%	25.2%	0.4%	15.8%	14.8%	15.3%	0.7%	24.0%	26.8%	25.4%	2.0%	19.6%	17.2%	18.4%	1.7%
161	24.9%	25.4%	25.2%	0.4%	15.8%	14.8%	15.3%	0.7%	24.0%	26.8%	25.4%	2.0%	19.6%	17.2%	18.4%	1.7%
165	12.5%	28.6%	20.6%	11.4%	10.2%	13.3%	11.8%	2.2%	26.9%	28.9%	27.9%	1.4%	18.9%	17.4%	18.2%	1.0%

Notes: Total solid content represented as % (w/w); N/A: Not available; Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions; Bio.: Bioaugmentation with naphthalene degraders; Ext.C.: 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% (w/w) Tween 80 additions

Table D.10. Nitrate Results for Phase II: Bioslurry Experiments

Condition	Biotic Control				Nutrients				Bio.+Nutrients				Bio.+Nutrients+Ext.C.			
Day	1	2	Ave	Stdev	1	2	Ave	Stdev	1	2	Ave	Stdev	1	2	Ave	Stdev
0	8.68	8.68	8.68	0	8.68	8.68	8.68	0	8.68	8.68	8.68	0	8.68	8.68	8.68	0
7	316.2	396.8	356.5	56.993	322.4	297.6	310	17.54	607.6	613.8	610.7	4.384	582.8	322.4	452.6	184.131
14	198.4	210.8	204.6	8.7681	1798	2046	1922	175.4	1984	1674	1829	219.2	1364	1550	1457	131.522
21	365.8	372	368.9	4.3841	2852	3348	3100	350.7	3224	2914	3069	219.2	2480	2480	2480	0
35	204.6	192.2	198.4	8.7681	2294	2418	2356	87.68	2480	2232	2356	175.4	1798	1922	1860	87.6812
42	421.6	465	443.3	30.688	3100	3596	3348	350.7	3410	3162	3286	175.4	2108	2542	2325	306.884
49	186	297.6	241.8	78.913	2418	2666	2542	175.4	2666	2294	2480	263	1860	2232	2046	263.044
56	272.8	310	291.4	26.304	N/A	N/A	-	-	2790	2480	2635	219.2	1612	1798	1705	131.522
63	291.4	248	269.7	30.688	N/A	N/A	-	-	2294	1984	2139	219.2	1736	1922	1829	131.522
91	365.8	322.4	344.1	30.688	N/A	N/A	-	-	3162	2604	2883	394.6	26.04	21.7	23.87	3.06884
98	303	241.8	272.4	43.275	1674	1612	1643	43.84	2418	2108	2263	219.2	1860	21.08	940.54	1300.31
109	384.4	328.6	356.5	39.457	2356	2542	2449	131.5	2976	2976	2976	0	2356	3410	2883	745.291
116	744	682	713	43.841	5270	5270	5270	0	5828	4836	5332	701.4	6200	86.8	3143.4	4322.69
123	868	992	930	87.681	6820	6820	6820	0	7440	6820	7130	438.4	9300	117.8	4708.9	6492.8
130	613.8	682	647.9	48.225	7440	5890	6665	1096	N/A	N/A	-	-	8060	53.94	4056.97	5661.14
137	806	806	806	0	8060	7440	7750	438.4	7440	7440	7440	0	1550	60.76	805.38	1053.05
151	744	4464	2604	2630.4	12400	9300	10850	2192	8060	8060	8060	0	4092	130.2	2111.1	2801.42

Notes: Nitrate represented as mg/l; N/A: Not available; Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions; Bio.: Bioaugmentation with naphthalene degraders; Ext.C.: 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% (w/w) Tween 80 additions

Table D.11. Ortho-Phosphate Results for Phase II: Bioslurry Experiments

Condition	Biotic Control				Nutrients				Bio.+Nutrients				Bio.+Nutrients+Ext.C.			
Day	1	2	Ave	Stdev	1	2	Ave	Stdev	1	2	Ave	Stdev	1	2	Ave	Stdev
0	0.22	0.19	0.205	0.0212	0.46	0.46	0.46	0	0.47	0.41	0.44	0.042	0.33	0.39	0.36	0.042
7	0.1	0.08	0.09	0.0141	0.19	0.21	0.2	0.014	0.19	0.16	0.175	0.021	0.15	0.17	0.16	0.014
14	0.11	0.11	0.11	0	0.45	0.57	0.51	0.085	0.64	0.6	0.62	0.028	0.33	0.37	0.35	0.028
21	0.22	0.19	0.205	0.0212	0.46	0.46	0.46	0	0.47	0.41	0.44	0.042	0.33	0.39	0.36	0.042
35	0.1	0.08	0.09	0.0141	0.19	0.21	0.2	0.014	0.19	0.16	0.175	0.021	0.15	0.17	0.16	0.014
42	0.08	0.1	0.09	0.0141	0.22	0.19	0.205	0.021	0.17	0.24	0.205	0.049	0.23	0.22	0.225	0.007
49	0.09	0.07	0.08	0.0141	0.18	0.11	0.145	0.049	0.11	0.12	0.115	0.007	0.14	0.18	0.16	0.028
56	0.07	0.08	0.075	0.0071	N/A	N/A	-	-	12.95	12.35	12.65	0.424	7.45	6.5	6.975	0.672
63	0.08	0.11	0.095	0.0212	N/A	N/A	-	-	5.35	5.4	5.375	0.035	4.45	4.3	4.375	0.106
77	0.05	0.06	0.055	0.0071	N/A	N/A	-	-	12.15	12.65	12.4	0.354	4.35	4.3	4.325	0.035
91	0.1	0.12	0.11	0.0141	1.05	0.87	0.96	0.127	37.5	44	40.75	4.596	13.65	10.35	12	2.333
98	0.23	0.1	0.165	0.0919	0.55	0.35	0.45	0.141	20	24.75	22.38	3.359	2.91	2.05	2.48	0.608
109	0.17	0.13	0.15	0.0283	0.53	0.49	0.51	0.028	16.5	21	18.75	3.182	3.49	2.89	3.19	0.424
116	0.23	0.13	0.18	0.0707	0.56	0.51	0.535	0.035	12	17.25	14.63	3.712	4.69	2.99	3.84	1.202
123	0.17	0.2	0.185	0.0212	0.59	0.39	0.49	0.141	0	0	0	0	4.1	2.92	3.51	0.834
130	0.19	0.13	0.16	0.0424	5.39	16	10.7	7.502	8.5	6.5	7.5	1.414	3.78	2.58	3.18	0.849
137	0.12	0.16	0.14	0.0283	11.25	6	8.625	3.712	6	3.75	4.875	1.591	4.44	3.11	3.775	0.940
151	0.25	0.09	0.17	0.1131	6.5	4	5.25	1.768	5.5	3	4.25	1.768	4.62	2.43	3.525	1.549

Notes: Ortho-phosphate represented as mg/l; N/A: Not available; Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions; Bio.: Bioaugmentation with naphthalene degraders; Ext.C.: 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% (w/w) Tween 80 additions

Table D.12. Ammonia Results for Phase II: Bioslurry Experiments

Condition	Biotic Control				Nutrients				Bio.+Nutrients				Bio.+Nutrients+Ext.C.			
Day	1	2	Ave	Stdev	1	2	Ave	Stdev	1	2	Ave	Stdev	1	2	Ave	Stdev
0	0.36	0.36	0.357	0	0.36	0.36	0.357	0	0.36	0.36	0.357	0	0.36	0.36	0.357	0
7	0.27	0.09	0.1819	0.1274	0.07	0.15	0.11	0.059	0.17	0.14	0.155	0.022	0.06	0.05	0.05	0.00
14	0.46	0.41	0.4335	0.0361	0.41	0.43	0.417	0.012	0.44	0.46	0.451	0.012	0.41	0.39	0.40	0.01
21	0.17	0.12	0.1454	0.0349	0.48	0.51	0.493	0.024	0.58	0.53	0.553	0.036	0.41	0.32	0.37	0.06
35	0.22	0.19	0.204	0.024	0.14	0.13	0.133	0.011	0.12	0.10	0.111	0.013	0.09	0.08	0.09	0.01
42	0.06	0.05	0.0553	0.0012	0.07	0.07	0.071	0.006	0.06	0.06	0.06	0.004	0.06	0.05	0.05	0.00
49	0.06	0.06	0.0561	0	0.05	0.05	0.053	0.002	0.05	0.05	0.048	0.001	0.05	0.04	0.05	0.00
56	0.06	0.06	0.0561	0	N/A	N/A	-	-	0.05	0.05	0.048	0.001	0.05	0.04	0.05	0.00
63	0.06	0.05	0.057	0.006	N/A	N/A	-	-	0.05	0.05	0.048	0.001	0.05	0.04	0.05	0.00
77	0.06	0.05	0.0561	0.0072	N/A	N/A	-	-	0.05	0.04	0.046	0.007	0.05	0.03	0.04	0.02
91	0.07	0.26	0.1641	0.1286	4.76	5.61	5.185	0.601	0.05	0.08	0.065	0.017	0.56	30.60	15.58	21.24
98	0.27	0.05	0.1624	0.1551	0.07	0.06	0.066	0.005	0.04	0.07	0.056	0.022	0.04	7.14	3.59	5.02
109	0.06	0.05	0.0587	0.006	0.06	0.05	0.056	0.002	0.05	0.05	0.049	0.005	0.07	3.91	1.99	2.71
116	0.49	0.29	0.391	0.1442	0.06	0.05	0.056	0.005	0.04	0.04	0.037	0.002	0.05	4.25	2.15	2.97
123	0.08	0.10	0.0884	0.0144	0.03	0.03	0.031	0.001	0.00	0.00	0	0	0.20	6.80	3.50	4.66
130	0.12	0.07	0.0927	0.0373	0.05	0.05	0.048	0.001	0.22	0.10	0.162	0.083	0.78	1.28	1.03	0.35
151	0.06	0.02	0.0417	0.0252	0.01	0.01	0.013	7E-04	0.01	0.01	0.01	0.001	0.00	0.19	0.10	0.13

Notes: Ammonia represented as mg/l; N/A: Not available; Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions; Bio.: Bioaugmentation with naphthalene degraders; Ext.C..: 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% (w/w) Tween 80 additions

Table D.13. PAH Results for Phase II: Bioslurry Experiments

Condition	Day	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
Biotic control	0	Replica	1	158.47	137.81	296.28	132.86	64.72	28.15	225.72	522.01
			2	189.00	167.38	356.38	157.70	75.48	30.18	263.36	619.74
		Average		173.74	152.60	326.33	145.28	70.10	29.17	244.54	570.87
		Stdev		21.59	20.90	42.50	17.57	7.61	1.44	26.61	69.11
	7	Replica	1	136.33	92.02	228.35	109.80	67.08	27.93	204.81	433.15
			2	168.62	94.56	263.18	114.00	79.42	30.57	223.99	487.17
		Average		152.48	93.29	245.76	111.90	73.25	29.25	214.40	460.16
		Stdev		22.84	1.80	24.63	2.97	8.73	1.87	13.56	38.19
	14	Replica	1	110.93	70.26	181.18	78.17	50.14	21.54	149.85	331.04
			2	146.14	96.69	242.83	114.41	72.96	29.88	217.25	460.08
		Average		128.53	83.47	212.01	96.29	61.55	25.71	183.55	395.56
		Stdev		24.90	18.69	43.59	25.62	16.14	5.90	47.66	91.25
	21	Replica	1	123.18	82.19	205.37	95.17	60.18	23.60	178.95	384.32
			2	122.48	84.68	207.16	101.99	66.90	23.98	192.87	400.03
		Average		122.83	83.44	206.27	98.58	63.54	23.79	185.91	392.18
		Stdev		0.50	1.76	1.26	4.83	4.75	0.26	9.84	11.10
	28	Replica	1	132.70	143.71	276.41	175.64	99.94	36.26	311.84	588.24
			2	126.68	86.18	212.86	115.99	88.90	32.39	237.27	450.13
		Average		129.69	114.94	244.63	145.81	94.42	34.32	274.55	519.19
		Stdev		4.25	40.68	44.93	42.18	7.81	2.73	52.72	97.66
	35	Replica	1	82.56	51.12	133.68	57.07	22.27	18.22	97.57	231.25
			2	94.81	60.55	155.36	71.79	38.74	21.05	131.57	286.93
		Average		88.69	55.83	144.52	64.43	30.51	19.63	114.57	259.09
		Stdev		8.66	6.67	15.33	10.40	11.64	2.00	24.04	39.37
	42	Replica	1	110.53	73.13	183.66	88.34	47.59	25.86	161.79	345.46
			2	91.39	63.57	154.96	77.59	41.20	23.25	142.04	297.01
		Average		100.96	68.35	169.31	82.97	44.40	24.56	151.92	321.23
		Stdev		13.54	6.76	20.29	7.60	4.52	1.85	13.97	34.26

Notes:
- PAH represented as mg/kg
- N/A: Not available
- Naphthalene is a 2-ring PAH

Table D.13. (Continued)

Condition	Day	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
Biotic Control	49	Replica	1	121.27	82.20	203.47	103.75	59.74	28.05	191.54	395.00
			2	114.64	76.73	191.37	97.47	62.89	25.83	186.19	377.56
		Average		117.95	79.46	197.42	100.61	61.32	26.94	188.87	386.28
		Stdev		4.69	3.86	8.55	4.44	2.23	1.57	3.78	12.33
	56	Replica	1	90.99	58.53	149.52	77.37	51.73	20.12	149.22	298.73
			2	86.10	56.15	142.25	69.04	42.54	20.22	131.80	274.06
		Average		88.55	57.34	145.89	73.21	47.13	20.17	140.51	286.40
		Stdev		3.46	1.68	5.14	5.89	6.50	0.07	12.31	17.45
	63	Replica	1	118.68	76.73	195.41	92.67	46.59	28.68	167.95	363.36
			2	114.71	74.06	188.77	89.98	49.56	27.16	166.70	355.47
		Average		116.70	75.39	192.09	91.33	48.08	27.92	167.33	359.42
		Stdev		2.81	1.89	4.69	1.90	2.10	1.08	0.88	5.57
	70	Replica	1	80.37	51.75	132.12	65.20	30.93	13.33	109.45	241.57
			2	91.70	63.76	155.46	81.69	38.31	23.12	143.13	298.59
		Average		86.03	57.75	143.79	73.44	34.62	18.22	126.29	270.08
		Stdev		8.01	8.49	16.51	11.67	5.23	6.92	23.81	40.32
	77	Replica	1	97.28	66.14	163.43	83.12	51.25	24.55	158.92	322.34
			2	79.65	53.30	132.96	66.36	27.01	20.50	113.87	246.82
		Average		88.47	59.72	148.19	74.74	39.13	22.53	136.39	284.58
		Stdev		12.47	9.08	21.54	11.85	17.14	2.87	31.86	53.40
	84	Replica	1	52.35	40.54	92.89	51.57	27.40	15.75	94.71	187.60
			2	127.01	81.43	208.44	106.74	73.17	31.64	211.54	419.98
		Average		89.68	60.98	150.66	79.15	50.28	23.69	153.13	303.79
		Stdev		52.79	28.91	81.70	39.01	32.36	11.24	82.61	164.32
	91	Replica	1	75.86	51.91	127.77	67.33	44.10	19.50	130.92	258.69
			2	123.07	76.55	199.62	97.80	65.23	28.49	191.52	391.13
		Average		99.46	64.23	163.69	82.57	54.66	23.99	161.22	324.91
		Stdev		33.38	17.43	50.80	21.55	14.94	6.36	42.85	93.65

Notes:
- PAH represented as mg/kg
- N/A: Not available
- Naphthalene is a 2-ring PAH

Table D.13. (Continued)

Condition	Day	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
Biotic Control	98	Replica	1	115.53	46.42	161.95	74.02	13.16	0.00	87.18	249.13
			2	81.03	38.17	119.20	52.12	0.00	0.00	52.12	171.32
		Average		98.28	42.30	140.57	63.07	6.58	0.00	69.65	210.23
		Stdev		24.40	5.83	30.23	15.48	9.31	0.00	24.79	55.02
	105	Replica	1	145.21	89.36	234.58	114.77	76.26	33.51	224.54	459.12
			2	91.83	71.17	163.00	90.68	40.50	24.62	155.79	318.80
		Average		118.52	80.27	198.79	102.72	58.38	29.06	190.16	388.96
		Stdev		37.75	12.86	50.61	17.04	25.29	6.29	48.61	99.22
	127	Replica	1	54.86	59.28	114.14	80.25	37.88	13.41	131.54	245.68
			2	143.75	88.74	232.48	126.93	66.66	32.22	225.81	458.30
		Average		99.30	74.01	173.31	103.59	52.27	22.82	178.67	351.99
		Stdev		62.85	20.83	83.68	33.01	20.35	13.30	66.67	150.34
	144	Replica	1	132.17	78.44	210.61	97.38	64.60	31.38	193.36	403.96
			2	109.29	69.67	178.97	92.52	45.75	28.85	167.12	346.09
		Average		120.73	74.06	194.79	94.95	55.18	30.12	180.24	375.03
		Stdev		16.18	6.20	22.37	3.44	13.33	1.78	18.55	40.92
Nutrients	0	Replica	1	184.00	149.61	333.60	138.77	71.11	30.22	240.11	573.71
			2	134.44	111.42	245.86	107.68	51.97	22.47	182.11	427.97
		Average		159.22	130.51	289.73	123.23	61.54	26.34	211.11	500.84
		Stdev		35.04	27.01	62.04	21.99	13.54	5.48	41.01	103.05
	7	Replica	1	136.27	93.39	229.66	112.12	67.65	27.23	207.00	436.66
			2	144.24	95.71	239.95	119.11	78.51	26.75	224.37	464.32
		Average		140.26	94.55	234.80	115.61	73.08	26.99	215.69	450.49
		Stdev		5.64	1.64	7.28	4.94	7.68	0.34	12.28	19.56
	14	Replica	1	122.84	79.38	202.22	91.46	49.07	24.00	164.53	366.75
			2	134.04	85.69	219.73	95.58	62.76	25.22	183.56	403.28
		Average		128.44	82.54	210.97	93.52	55.91	24.61	174.04	385.02
		Stdev		7.92	4.46	12.38	2.91	9.68	0.86	13.45	25.83

Notes:
- PAH represented as mg/kg
- N/A: Not available
- Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions
- Naphthalene is a 2-ring PAH

Table D.13. (Continued)

Condition	Day	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
Nutrients	21	Replica	1	123.96	68.63	192.59	81.03	53.48	22.07	156.58	349.17
			2	109.68	68.77	178.45	80.56	54.06	19.99	154.61	333.06
		Average		116.82	68.70	185.52	80.80	53.77	21.03	155.60	341.12
		Stdev		10.10	0.10	10.00	0.33	0.41	1.47	1.39	11.39
	28	Replica	1	118.29	75.57	193.85	86.35	57.10	25.48	168.93	362.79
			2	122.31	81.03	203.34	97.69	64.59	27.85	190.14	393.48
		Average		120.30	78.30	198.60	92.02	60.85	26.67	179.53	378.13
		Stdev		2.85	3.86	6.71	8.02	5.29	1.68	14.99	21.70
	35	Replica	1	131.81	82.43	214.24	96.06	62.75	27.55	186.36	400.59
			2	95.86	63.37	159.23	76.83	40.80	21.38	139.01	298.24
		Average		113.83	72.90	186.73	86.45	51.77	24.46	162.68	349.42
		Stdev		25.42	13.48	38.89	13.60	15.52	4.36	33.48	72.37
	42	Replica	1	110.96	72.02	182.97	92.49	64.03	24.69	181.21	364.19
			2	84.67	63.59	148.26	77.46	34.70	22.11	134.27	282.53
		Average		97.81	67.80	165.62	84.98	49.37	23.40	157.74	323.36
		Stdev		18.59	5.96	24.55	10.63	20.74	1.83	33.19	57.74
	49	Replica	1	102.29	69.80	172.09	83.81	44.10	24.48	152.39	324.48
			2	144.19	98.46	242.65	122.49	82.57	30.06	235.11	477.77
		Average		123.24	84.13	207.37	103.15	63.33	27.27	193.75	401.12
		Stdev		29.63	20.27	49.90	27.35	27.20	3.94	58.49	108.39
	56	Replica	1	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
			2	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
		Average		-	-	-	-	-	-	-	-
		Stdev		-	-	-	-	-	-	-	-
	63	Replica	1	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
			2	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
		Average		-	-	-	-	-	-	-	-
		Stdev		-	-	-	-	-	-	-	-

Notes:
- PAH represented as mg/kg
- N/A: Not available
- Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions
- Naphthalene is a 2-ring PAH

Table D.13. (Continued)

Condition	Day	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
Nutrients	70	Replica	1	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
			2	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
		Average		-	-	-	-	-	-	-	-
		Stdev		-	-	-	-	-	-	-	-
	77	Replica	1	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
			2	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
		Average		-	-	-	-	-	-	-	-
		Stdev		-	-	-	-	-	-	-	-
	84	Replica	1	47.80	34.70	82.50	41.03	12.89	0.00	53.92	136.42
			2	125.35	76.76	202.11	93.18	48.33	28.88	170.40	372.51
		Average		86.58	55.73	142.31	67.10	30.61	14.44	112.16	254.47
		Stdev		54.84	29.74	84.58	36.88	25.06	20.42	82.37	166.94
	91	Replica	1	54.19	33.86	88.05	39.21	15.86	3.36	58.43	146.48
			2	141.83	80.61	222.44	97.07	50.64	29.36	177.07	399.51
		Average		98.01	57.24	155.24	68.14	33.25	16.36	117.75	272.99
		Stdev		61.97	33.05	95.02	40.92	24.59	18.38	83.89	178.92
	98	Replica	1	80.27	46.26	126.54	43.32	27.59	7.98	78.88	205.42
			2	85.83	48.25	134.08	58.40	35.23	7.79	101.43	235.50
		Average		83.05	47.26	130.31	50.86	31.41	7.89	90.15	220.46
		Stdev		3.93	1.41	5.33	10.67	5.40	0.13	15.94	21.27
	105	Replica	1	71.30	42.38	113.68	49.97	17.32	0.00	67.29	180.97
			2	86.95	66.97	153.92	79.69	19.92	0.00	99.61	253.53
		Average		79.12	54.68	133.80	64.83	18.62	0.00	83.45	217.25
		Stdev		11.07	17.39	28.45	21.02	1.84	0.00	22.85	51.31
	127	Replica	1	47.68	59.86	107.54	76.39	18.56	7.16	102.10	209.64
			2	150.49	84.57	235.06	97.75	29.91	0.00	127.65	362.71
		Average		99.09	72.21	171.30	87.07	24.23	3.58	114.88	286.18
		Stdev		72.70	17.47	90.17	15.10	8.03	5.06	18.07	108.24

Notes:
- PAH represented as mg/kg
- N/A: Not available
- Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions
- Naphthalene is a 2-ring PAH

Table D.13. (Continued)

Condition	Day	PAH Category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
Nutrients	144	Replica	1	114.62	74.69	189.31	91.93	46.77	15.36	154.06	343.36
			2	150.79	92.14	242.93	115.85	51.76	19.97	187.59	430.52
		Average		132.70	83.41	216.12	103.89	49.27	17.67	170.82	386.94
		Stdev		25.58	12.34	37.92	16.92	3.53	3.26	23.71	61.63
Bio.+ Nutrients	0	Replica	1	154.61	136.69	291.30	136.56	70.18	28.27	235.00	526.31
			2	232.47	161.13	393.60	144.81	70.91	30.28	246.00	639.60
		Average		193.54	148.91	342.45	140.69	70.54	29.28	240.50	582.95
		Stdev		55.06	17.28	72.33	5.84	0.52	1.42	7.77	80.11
	7	Replica	1	127.46	93.11	220.56	112.49	66.59	27.26	206.34	426.91
			2	185.74	150.36	336.10	183.41	113.15	38.35	334.90	671.00
		Average		156.60	121.74	278.33	147.95	89.87	32.80	270.62	548.95
		Stdev		41.21	40.49	81.70	50.15	32.92	7.84	90.91	172.60
	14	Replica	1	108.76	79.98	188.75	88.21	47.42	23.77	159.41	348.15
			2	130.69	85.46	216.15	100.81	63.30	25.35	189.46	405.61
		Average		119.73	82.72	202.45	94.51	55.36	24.56	174.43	376.88
		Stdev		15.50	3.87	19.38	8.91	11.23	1.12	21.25	40.63
	21	Replica	1	70.20	137.97	208.17	137.04	69.04	22.76	228.84	437.02
			2	154.48	102.39	256.87	125.76	80.33	26.68	232.77	489.64
		Average		112.34	120.18	232.52	131.40	74.69	24.72	230.81	463.33
		Stdev		59.60	25.16	34.43	7.98	7.98	2.77	2.78	37.21
	28	Replica	1	132.82	82.33	215.16	98.15	63.19	25.83	187.17	402.33
			2	104.05	67.55	171.60	79.22	60.46	22.31	161.99	333.59
		Average		118.44	74.94	193.38	88.69	61.82	24.07	174.58	367.96
		Stdev		20.35	10.45	30.80	13.39	1.93	2.49	17.81	48.61

Notes:
- Bio.: Bioaugmentation with naphthalene degraders
- PAH represented as mg/kg
- N/A: Not available
- Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions
- Naphthalene is a 2-ring PAH

Table D.13. (Continued)

Condition	Day	PAH category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
Bio.+ Nutrients	35	Replica	1	105.43	120.94	226.37	140.71	75.99	31.01	247.70	474.07
			2	119.94	78.17	198.11	95.55	52.30	25.87	173.72	371.83
		Average		112.68	99.56	212.24	118.13	64.15	28.44	210.71	422.95
		Stdev		10.26	30.24	19.98	31.93	16.75	3.63	52.31	72.29
	49	Replica	1	125.09	79.74	204.82	101.81	68.08	28.69	198.58	403.41
			2	104.73	68.11	172.85	86.40	62.09	21.92	170.41	343.25
		Average		114.91	73.93	188.83	94.11	65.09	25.30	184.50	373.33
		Stdev		14.39	8.22	22.61	10.90	4.24	4.79	19.92	42.54
	56	Replica	1	113.49	70.72	184.20	89.09	65.55	25.20	179.85	364.05
			2	62.91	65.48	128.40	82.87	44.20	20.99	148.05	276.45
		Average		88.20	68.10	156.30	85.98	54.87	23.09	163.95	320.25
		Stdev		35.76	3.70	39.46	4.40	15.10	2.98	22.48	61.94
	63	Replica	1	69.61	55.57	125.18	65.89	25.88	11.05	102.81	227.99
			2	88.38	64.84	153.22	84.79	53.18	22.70	160.66	313.88
		Average		79.00	60.20	139.20	75.34	39.53	16.87	131.74	270.94
		Stdev		13.27	6.56	19.83	13.36	19.31	8.23	40.90	60.73
	70	Replica	1	98.10	88.19	186.29	84.90	50.80	24.01	159.72	346.01
			2	82.96	61.00	143.96	76.02	40.58	22.59	139.19	283.15
		Average		90.53	74.59	165.12	80.46	45.69	23.30	149.46	314.58
		Stdev		10.70	19.22	29.93	6.28	7.23	1.00	14.51	44.44
	77	Replica	1	78.28	54.53	132.81	67.79	29.24	21.29	118.32	251.12
			2	77.66	51.17	128.83	63.07	26.16	19.49	108.71	237.55
		Average		77.97	52.85	130.82	65.43	27.70	20.39	113.52	244.34
		Stdev		0.44	2.37	2.81	3.34	2.18	1.28	6.79	9.60
	84	Replica	1	62.33	42.74	105.07	54.75	30.71	16.76	102.22	207.30
			2	105.60	71.42	177.02	89.70	60.72	26.83	177.25	354.27
		Average		83.97	57.08	141.05	72.23	45.72	21.79	139.73	280.78
		Stdev		30.59	20.28	50.88	24.71	21.22	7.12	53.05	103.93

Notes: PAH represented as mg/kg; N/A: Not available; Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions; Bio.: Bioaugmentation with naphthalene degraders; Naphthalene is a 2-ring PAH

Table D.13. (Continued)

Condition	Day	PAH Category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
Bio+ Nutrients	91	Replica	1	72.23	46.20	118.42	56.40	38.50	17.24	112.14	230.56
			2	124.59	76.07	200.66	96.94	54.71	28.70	180.35	381.01
		Average		98.41	61.13	159.54	76.67	46.61	22.97	146.24	305.79
		Stdev		37.03	21.12	58.15	28.67	11.46	8.11	48.23	106.38
	98	Replica	1	104.79	66.88	171.67	87.05	36.07	22.75	145.87	317.54
			2	80.29	49.60	129.89	63.57	42.01	18.27	123.85	253.74
		Average		92.54	58.24	150.78	75.31	39.04	20.51	134.86	285.64
		Stdev		17.33	12.21	29.54	16.60	4.20	3.17	15.57	45.11
	105	Replica	1	95.66	59.76	155.42	75.30	30.76	22.13	128.19	283.61
			2	96.90	161.30	258.19	178.40	69.30	33.88	281.58	539.77
		Average		96.28	110.53	206.81	126.85	50.03	28.01	204.89	411.69
		Stdev		0.88	71.79	72.67	72.90	27.25	8.31	108.46	181.13
	127	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Average		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Stdev		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	144	Replica	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Average		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Stdev		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0
Bio.+ Nutrients + Ext. C.	0	Replica	1	177.57	148.50	326.07	139.42	68.67	30.79	238.88	564.95
			2	224.75	184.72	409.47	173.82	85.98	35.87	295.67	705.14
		Average		201.16	166.61	367.77	156.62	77.33	33.33	267.28	635.05
		Stdev		33.36	25.61	58.97	24.33	12.24	3.59	40.15	99.13
	7	Replica	1	141.62	91.21	232.82	109.04	66.62	26.90	202.55	435.37
			2	180.90	138.68	319.58	163.64	100.11	34.21	297.97	617.56
		Average		161.26	114.95	276.20	136.34	83.36	30.56	250.26	526.46
		Stdev		27.78	33.57	61.35	38.61	23.69	5.17	67.47	128.82

Notes: PAH represented as mg/kg; N/A: Not available; Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions; Bio.: Bioaugmentation with naphthalene degraders; Ext.C.: 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% (w/w) Tween 80 additions; Naphthalene is a 2-ring PAH

Table D.13. (Continued)

Condition	Day	PAH Category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
Bio.+ Nutrients + Ext.C.	14	Replica	1	108.79	71.80	180.59	78.13	30.09	23.68	131.89	312.48
			2	138.54	90.95	229.49	102.41	64.48	26.07	192.96	422.45
		Average		123.66	81.38	205.04	90.27	47.28	24.87	162.43	367.46
		Stdev		21.04	13.54	34.58	17.16	24.32	1.69	43.18	77.76
	21	Replica	1	70.01	93.77	163.78	116.55	71.26	25.25	213.05	376.83
			2	139.82	101.30	241.13	124.59	78.69	25.76	229.04	470.17
		Average		104.92	97.54	202.45	120.57	74.97	25.50	221.05	423.50
		Stdev		49.37	5.33	54.69	5.69	5.25	0.36	11.31	66.00
	28	Replica	1	107.55	69.97	177.52	88.38	56.23	22.45	167.06	344.58
			2	130.56	90.09	220.65	105.17	71.16	30.10	206.42	427.06
		Average		119.05	80.03	199.08	96.77	63.69	26.27	186.74	385.82
		Stdev		16.27	14.23	30.49	11.87	10.56	5.41	27.83	58.32
	35	Replica	1	99.00	67.33	166.33	82.81	57.15	24.14	164.09	330.42
			2	87.58	55.31	142.88	66.00	26.06	20.06	112.13	255.01
		Average		93.29	61.32	154.61	74.41	41.60	22.10	138.11	292.71
		Stdev		8.08	8.50	16.58	11.88	21.98	2.88	36.74	53.32
	42	Replica	1	115.26	74.93	190.19	86.34	54.46	24.99	165.79	355.97
			2	85.88	58.44	144.32	68.45	28.98	16.51	113.95	258.27
		Average		100.57	66.68	167.25	77.40	41.72	20.75	139.87	307.12
		Stdev		20.77	11.66	32.43	12.65	18.02	5.99	36.65	69.08
	49	Replica	1	125.08	78.23	203.32	94.44	59.32	27.49	181.25	384.56
			2	130.43	111.54	241.97	131.93	82.69	29.56	244.18	486.15
		Average		127.76	94.88	222.64	113.19	71.00	28.53	212.71	435.36
		Stdev		3.78	23.55	27.33	26.50	16.53	1.47	44.50	71.83
	56	Replica	1	87.76	69.33	157.09	80.16	41.71	21.68	143.55	300.63
			2	71.22	67.08	138.30	84.63	51.16	23.41	159.20	297.50
		Average		79.49	68.20	147.69	82.39	46.44	22.54	151.37	299.07
		Stdev		11.69	1.59	13.28	3.17	6.68	1.22	11.06	2.22

Notes: - PAH represented as mg/kg; N/A: Not available; Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions; Bio.: Bioaugmentation with naphthalene degraders; Ext.C.: 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% (w/w) Tween 80 additions; Naphthalene is a 2-ring PAH

Table D.13. (Continued)

Condition	Day	PAH Category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
Bio+ Nutrients+ Ext.C.	63	Replica	1	77.18	52.92	130.10	64.00	26.54	11.44	101.98	232.08
			2	93.72	59.92	153.63	72.93	41.44	22.61	136.97	290.61
		Average		85.45	56.42	141.87	68.47	33.99	17.02	119.48	261.34
		Stdev		11.70	4.94	16.64	6.31	10.53	7.90	24.74	41.38
	70	Replica	1	61.32	39.83	101.15	45.61	18.97	10.90	75.48	176.63
			2	105.55	70.37	175.92	86.89	41.08	26.60	154.57	330.49
		Average		83.43	55.10	138.53	66.25	30.03	18.75	115.03	253.56
		Stdev		31.28	21.59	52.87	29.19	15.64	11.10	55.93	108.80
	77	Replica	1	109.17	72.10	181.27	88.80	44.89	26.78	160.47	341.74
			2	97.87	64.42	162.29	80.33	38.83	24.36	143.52	305.80
		Average		103.52	68.26	171.78	84.57	41.86	25.57	152.00	323.77
		Stdev		7.99	5.43	13.42	5.99	4.29	1.71	11.99	25.41
	84	Replica	1	40.58	27.74	68.32	34.47	12.21	6.30	52.98	121.30
			2	102.59	68.40	170.99	86.84	39.20	28.26	154.30	325.28
		Average		71.58	48.07	119.65	60.65	25.71	17.28	103.64	223.29
		Stdev		43.85	28.75	72.60	37.03	19.08	15.53	71.64	144.24
	91	Replica	1	45.11	32.33	77.44	37.87	14.46	7.30	59.63	137.07
			2	89.34	59.33	148.67	74.52	32.55	24.73	131.81	280.48
		Average		67.22	45.83	113.05	56.20	23.50	16.02	95.72	208.77
		Stdev		31.28	19.09	50.37	25.92	12.79	12.32	51.03	101.40
	98	Replica	1	49.36	53.11	102.47	62.58	36.61	15.08	114.27	216.74
			2	45.36	29.52	74.88	38.22	16.01	12.17	66.40	141.28
		Average		47.36	41.31	88.68	50.40	26.31	13.62	90.33	179.01
		Stdev		2.83	16.68	19.51	17.23	14.57	2.06	33.85	53.36
	105	Replica	1	53.43	35.05	88.48	43.78	24.08	8.75	76.61	165.09
			2	87.65	59.66	147.31	75.13	39.62	7.39	122.15	269.46
		Average		70.54	47.35	117.90	59.46	31.85	8.07	99.38	217.28
		Stdev		24.20	17.40	41.60	22.17	10.99	0.96	32.20	73.80

Notes: PAH represented as mg/kg; N/A: Not available; Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions; Bio.: Bioaugmentation with naphthalene degraders; Ext.C.: 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% (w/w) Tween 80 additions; Naphthalene is a 2-ring PAH

Table D.13. (Continued)

Condition	Day	PAH Category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
Bio+ Nutrients+ Ext.C.	127	Replica	1	82.22	51.09	133.31	64.92	23.58	12.88	101.38	234.68
			2	115.15	72.06	187.21	93.80	47.25	31.94	172.99	360.21
		Average		98.69	61.58	160.26	79.36	35.41	22.41	137.18	297.45
		Stdev		23.29	14.83	38.12	20.42	16.74	13.48	50.64	88.76
	144	Replica	1	139.55	97.32	236.87	131.07	69.91	37.95	238.92	475.79
			2	149.03	95.02	244.06	126.25	77.91	43.44	247.60	491.65
		Average		144.29	96.17	240.46	128.66	73.91	40.69	243.26	483.72
		Stdev		6.70	1.62	5.08	3.41	5.66	3.89	6.14	11.22

Notes: PAH represented as mg/kg; N/A: Not available; Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions; Bio.: Bioaugmentation with naphthalene degraders; Ext.C.: 1,000 mg/l glucose, 100 mg/l sodium acetate, 25 mg/l naphthalene solution, and 5% and 2.5% (w/w) Tween 80 additions; Naphthalene is a 2-ring PAH

Table D.14. Summary of Selected Results for Phase II: Chemical Oxidation of the Nutrients Set (Reactors 3 and 4)

Chemical Oxidation / Parameters		pH	DO, mg/l	Ammonia, mg/l	Nitrate, mg/l	O-P, mg/l	TOC, mg/kg
Fenton's Reagent[1]	Replica	2.5	5.4	0.026	1054.0	0.350	34368.4
		2.5	5.6	0.029	930.0	0.280	27347.7
	Average	2.5	5.5	0.027	992	0.315	30858.1
	stdev	0.0	0.1	0.002	87.681	0.049	4964.4
Ozone[1]	Replica	5.3	4.2	0.022	2356.0	0.090	31306.0
		5.4	5.7	0.022	2666.0	0.100	33149.0
	Average	5.4	4.9	0.022	2511	0.095	32227.5
	stdev	0.1	1.1	0.000	219.2	0.007	1303.2
Peroxone[1]	Replica	5.2	1.9	0.020	2356.0	0.330	27635.0
		5.4	5.1	0.020	2418.0	0.430	33024.0
	Average	5.3	3.5	0.020	2387	0.380	30329.5
	stdev	0.1	2.3	0.000	43.841	0.071	3810.6

Notes:
[1]No CFU's were observed after oxidation
- Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions
- DO: Indicates dissolved oxygen
- O-P: Indicates Ortho-phosphate
- TOC: Indicates Total Organic Carbon

Table D.15. PAH Results for Phase II: Ozonation of the Nutrients Set (Reactors 3 and 4)

Hour	PAH Category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
0	Replica	1	102.29	69.80	172.09	83.81	44.10	24.48	152.39	324.48
		2	144.19	98.46	242.65	122.49	82.57	30.06	235.11	477.77
	Average		123.24	84.13	207.37	103.15	63.33	27.27	193.75	401.12
	Stdev		29.63	20.27	49.90	27.35	27.20	3.94	58.49	108.39
4	Replica	1	46.45	36.39	82.85	43.28	16.24	11.95	71.46	154.31
		2	27.68	25.26	52.94	28.84	6.81	0.00	235.11	288.05
	Average		37.06	30.83	67.89	36.06	11.52	5.97	153.29	221.18
	Stdev		13.28	7.87	21.15	10.21	6.67	8.45	115.72	94.57
8	Replica	1	91.03	61.22	152.25	74.44	29.54	24.01	127.99	280.24
		2	99.73	66.50	166.23	82.97	53.33	23.70	235.11	401.34
	Average		95.38	63.86	159.24	78.71	41.44	23.85	181.55	340.79
	Stdev		6.15	3.73	9.88	6.03	16.82	0.21	75.75	85.63

Notes:
- Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions
- PAH represented as mg/kg
- 3% (w/w) ozone at 2.5 scfh

Table D.16. PAH Results for Phase II: Peroxone Treatment of the Nutrients Set (Reactors 3 and 4)

Hour	PAH Category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
0	Replica	1	102.29	69.80	172.09	83.81	44.10	24.48	152.39	324.48
		2	144.19	98.46	242.65	122.49	82.57	30.06	235.11	477.77
	Average		123.24	84.13	207.37	103.15	63.33	27.27	193.75	401.12
	Stdev		29.63	20.27	49.90	27.35	27.20	3.94	58.49	108.39
4	Replica	1	62.54	41.74	104.27	51.17	33.48	15.32	99.97	204.24
		2	79.75	53.60	133.35	66.51	44.63	19.21	235.11	368.47
	Average		71.15	47.67	118.81	58.84	39.06	17.26	167.54	286.36
	Stdev		12.17	8.39	20.56	10.85	7.88	2.75	95.56	116.12
8	Replica	1	141.62	98.33	239.96	122.53	79.95	34.84	237.32	477.28
		2	93.66	60.70	154.36	74.51	48.95	21.63	235.11	389.48
	Average		117.64	79.52	197.16	98.52	64.45	28.23	236.22	433.38
	Stdev		33.91	26.61	60.53	33.96	21.92	9.35	1.56	62.09

Notes:
- Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions
- PAH represented as mg/kg
- 3% (w/w) ozone at 2.5 scfh
- Hydrogen peroxide addition at 100 mg/l every hour for the first four hours and 500 mg/l every hour for the next four hours

Table D.17. PAH Results for Phase II: Fenton's Reagent Treatment of the Nutrients Set (Reactors 3 and 4)

Dosing	PAH Category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
0	Replica	1	102.29	69.80	172.09	83.81	44.10	24.48	152.39	324.48
		2	144.19	98.46	242.65	122.49	82.57	30.06	235.11	477.77
	Average		123.24	84.13	207.37	103.15	63.33	27.27	193.75	401.12
	Stdev		29.63	20.27	49.90	27.35	27.20	3.94	58.49	108.39
1	Replica	1	92.47	64.45	156.91	77.74	40.34	21.34	139.43	296.34
		2	116.27	68.30	184.57	83.28	55.37	23.97	235.11	419.69
	Average		104.37	66.37	170.74	80.51	47.85	22.65	187.27	358.01
	Stdev		16.83	2.72	19.56	3.91	10.62	1.86	67.66	87.22
2	Replica	1	115.40	68.89	184.29	83.85	45.43	24.93	154.21	338.50
		2	78.45	56.68	135.13	70.06	27.64	20.75	235.11	370.24
	Average		96.93	62.78	159.71	76.96	36.53	22.84	194.66	354.37
	Stdev		26.12	8.64	34.76	9.75	12.58	2.96	57.21	22.45
3	Replica	1	100.10	64.57	164.67	80.19	31.55	25.60	137.34	302.01
		2	71.65	53.94	125.60	69.32	45.65	19.90	235.11	360.71
	Average		85.88	59.25	145.13	74.75	38.60	22.75	186.23	331.36
	Stdev		20.12	7.51	27.63	7.69	9.97	4.03	69.13	41.50
4	Replica	1	116.22	70.67	186.89	90.41	36.67	28.63	155.71	342.60
		2	88.62	56.94	145.56	69.14	28.81	22.83	235.11	380.68
	Average		102.42	63.81	166.23	79.77	32.74	25.73	195.41	361.64
	Stdev		19.51	9.71	29.22	15.05	5.56	4.10	56.15	26.93
5	Replica	1	105.92	41.56	147.49	35.14	0.00	0.00	35.14	182.62
		2	58.94	25.01	83.95	31.15	0.00	0.00	235.11	319.07
	Average		82.43	33.29	115.72	33.14	0.00	0.00	135.13	250.85
	Stdev		33.22	11.70	44.93	2.82	0.00	0.00	141.41	96.48

Notes:
- Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions
- PAH represented as mg/kg
- Dosing steps no. 1 and 2: 25,000 H_2O_2 + 2,500 Fe^{2+}; dosing steps no. 3 and 4: 50,000 H_2O_2 + 5,000 Fe^{2+}; dosing steps no. 5 and 6: 100,000 H_2O_2 + 10,000 Fe^{2+}

Table D.17 (Continued)

Dosing	PAH Category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
6	Replica	1	47.59	0.00	47.59	0.00	0.00	0.00	0.00	47.59
		2	102.38	54.03	156.41	43.95	0.00	0.00	235.11	391.52
	Average		74.98	27.02	102.00	21.97	0.00	0.00	117.56	219.56
	Stdev		38.74	38.21	76.95	31.08	0.00	0.00	166.25	243.20

Notes:
- Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions
- PAH represented as mg/kg
- Dosing steps no. 1 and 2: 25,000 H_2O_2 + 2,500 Fe^{2+}; dosing steps no. 3 and 4: 50,000 H_2O_2 + 5,000 Fe^{2+}; dosing steps no. 5 and 6: 100,000 H_2O_2 + 10,000 Fe^{2+}

Table D.18. Summary of Selected Results for Phase II: Chemical Oxidation of the Bio.+ Nutrients Set (Reactors 5 and 6)

Chemical Oxidation / Parameters		pH	DO, mg/l	Ammonia, mg/l	Nitrate, mg/l	O-P, mg/l	THC, CFUs/ml
Fenton's Reagent	Replica	4.8	5.7	342	1348	0.26	71
		3.9	5.7	169	3240	0.24	50
	Average	4.4	5.7	255	2294	0.25	61
	stdev	0.6	0.0	122	1338	0.01	15

Notes:
- Bio.: Bioaugmentation with naphthalene degraders
- Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions
- DO: Indicates dissolved oxygen
- O-P: Indicates Ortho-phosphate
- THC: Indicates Total heterotrophic counts

Table D.19. PAH Results for Phase II: Fenton's Reagent Treatment of the Bio.+ Nutrients Set (Reactors 5 and 6)

Dosing	PAH Category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
0	Replica	1	95.66	59.76	155.42	75.30	30.76	22.13	128.19	283.61
		2	96.90	161.30	258.19	178.40	69.30	33.88	235.11	493.31
	Average		96.28	110.53	206.81	126.85	50.03	28.01	181.65	388.46
	Stdev		0.88	71.79	72.67	72.90	27.25	8.31	75.60	148.28
1	Replica	1	102.21	60.57	162.78	82.29	35.04	26.14	143.48	306.27
		2	57.80	129.69	187.49	196.01	109.21	56.11	235.11	422.60
	Average		80.01	95.13	175.14	139.15	72.13	41.13	189.30	364.43
	Stdev		31.41	48.88	17.47	80.41	52.44	21.19	64.79	82.26
2	Replica	1	16.05	60.71	76.75	86.19	34.97	13.83	134.99	211.74
		2	54.80	63.43	118.23	64.81	16.05	0.00	235.11	353.34
	Average		35.42	62.07	97.49	75.50	25.51	6.91	185.05	282.54
	Stdev		27.40	1.92	29.33	15.12	13.37	9.78	70.80	100.13
3	Replica	1	72.59	45.97	118.56	68.54	41.40	10.00	119.94	238.49
		2	121.90	59.03	180.93	93.05	52.67	26.85	235.11	416.04
	Average		97.25	52.50	149.74	80.79	47.04	18.42	177.52	327.27
	Stdev		34.87	9.23	44.10	17.33	7.97	11.91	81.44	125.54
4	Replica	1	150.96	76.16	227.13	110.66	59.51	36.63	206.80	433.93
		2	20.02	39.72	59.74	59.83	26.69	10.11	235.11	294.85
	Average		85.49	57.94	143.43	85.25	43.10	23.37	220.96	364.39
	Stdev		92.59	25.77	118.36	35.94	23.21	18.76	20.02	98.34
5	Replica	1	83.16	45.65	128.81	63.73	44.48	11.77	119.99	248.80
		2	84.95	59.29	144.24	92.60	38.77	28.95	235.11	379.35
	Average		84.06	52.47	136.52	78.17	41.63	20.36	177.55	314.08
	Stdev		1.26	9.65	10.91	20.41	4.04	12.14	81.40	92.31

Notes:
- Bio.: Bioaugmentation with naphthalene degraders
- Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions
- PAH represented as mg/kg
- Dosing steps no. 1 and 2: 25,000 H_2O_2 + 2,500 Fe^{2+}; dosing steps no. 3 and 4: 50,000 H_2O_2 + 5,000 Fe^{2+}; dosing steps no. 5 and 6: 100,000 H_2O_2 + 10,000 Fe^{2+}

Table A.19. (Continued)

Dosing	PAH Category		2-ring PAH	3-ring PAH	Light PAHs	4-ring PAH	5-ring PAH	6-ring PAH	Heavy PAHs	Total PAHs
6	Replica	1	50.53	35.39	85.92	51.54	21.82	0.00	73.37	159.29
		2	91.98	42.84	134.82	64.68	30.77	20.37	235.11	369.93
	Average		71.26	39.12	110.37	58.11	26.30	10.18	154.24	264.61
	Stdev		29.31	5.27	34.58	9.29	6.33	14.40	114.37	148.95

Notes:
- Bio.: Bioaugmentation with naphthalene degraders
- Nutrients: 1,000 mg/l nitrate and 400 mg/l phosphate additions
- PAH represented as mg/kg
- Dosing steps no. 1 and 2: 25,000 H_2O_2 + 2,500 Fe^{2+}; dosing steps no. 3 and 4: 50,000 H_2O_2 + 5,000 Fe^{2+}; dosing steps no. 5 and 6: 100,000 H_2O_2 + 10,000 Fe^{2+}

Table D.20. pH Levels of Ferrous Sulfate and Hydrogen Peroxide

		Before Addition		After Addition
		Ferrous Sulfate[1]	Hydrogen Peroxide[2]	Ferrous Sulfate + Hydrogen Peroxide
Replica	1	3.18	3.37	1.65
	2	3.14	3.7	1.71
Average		3.16	3.54	1.68
Stdev		0.03	0.23	0.04

Notes:
[1]25,000 mg/l ferrous sulfate solution
[2]150,000 mg/l hydrogen peroxide solution