Project Report No. ---

Use of Compost to Biodegrade Sediments Contaminated with Polycyclic Aromatic Hydrocarbons

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Executive Summary

Recently, concentrations of polycyclic aromatic hydrocarbons (PAHs) that are above the Minnesota Pollution Control Agency's recommended limits for unrestricted use have been detected in stormwater pond sediments. Effective treatment methods are needed to remediate these PAH contaminated sediments to allow for unrestricted use and cost-effective disposal options. Based on the idea that PAHs in contaminated soil can be biodegraded when mixed with compost, this research sought to evaluate the effectiveness of using compost to biodegrade PAHs in contaminated sediment. Two bench top experiments were performed that allowed for the simulation of the conditions in a compost pile that would favor biodegradation of PAHs bound to sediment. These experiments were able to effectively simulate the conditions of a compost pile and demonstrated that composting occurred as measured by carbon dioxide respiration, volatile solids content changes and temperature changes. Despite significant microbiological activity, only the three ring PAH phenanthrene, was found to be significantly degraded in all experiments. No PAH with four or more rings was found to be significantly degraded during the extent of composting. An assay that estimated bioavailability by measuring the desorption of PAHs from the contaminated sediment into the aqueous phase indicated that all but one PAH had a potentially bioavailable fraction. Since each PAH had a potentially bioavailable fraction, PAH biodegradation was likely limited both by a microbial community with only a small potential to degrade four to six ring PAHs and low aqueous PAH partitioning from the sediment.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. Simcik for letting me use his facilities to perform analytical analyses and for providing help in interpreting the results. Two undergraduate researchers, Sam Bircher and Mike Maki helped perform this research. We would like to thank Jeff Lanners, Joan Manzara, Patrick McNamara, Greg LeFevre, Zheng Teng, and Bethany Brinkman for their support in the lab. We would also like to thank the Project Manager, Bruce C. Wilson, of the Minnesota Pollution Control Agency for supporting this project.

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I. Introduction

Wet detention ponds are used to treat stormwater by settling and collecting suspended sediment. The amount of sediment a wet detention pond can accumulate in the Twin Cities metro area can range from 200 to 1450 kg/ha/year, dependent on pond trap efficiency and watershed sediment yield (Polta et al. 2006). The City of Plymouth, MN, for example, could accumulate 101,000 cubic feet of sediment per year in its over 700 wet detention ponds assuming a conservative load of 500 kg/ha/year and a trap efficiency of 80%. Since the City of Plymouth, MN represents only 0.4% of Minnesota's area, and roughly 1% of Minnesta's urban area, the total volume of sediments accumulated in Minnesota wet detention ponds would be substantially larger. Wet detention ponds in Minnesota are typically designed with a 25 year design life, and many of the wet detention ponds in Minnesota are reaching the end of their design life and have a sediment load that requires dredging to maintain performance.

The management of dredged material in Minnesota is subject to regulatory control. In order to determine appropriate reuse or disposal stormwater pond sediment must be tested for pollutants prior to the initiation of any dredging activity. Municipal pond sediments are typically tested for common parameters such as heavy metals copper and arsenic, sieve size analysis and PAHs; other parameters such as nitrogen, phosphorus, organic content as needed or, based on the reasonable likelihood of their occurrence, the sediments could be tested for other contaminants. The Minnesota Pollution Control Agency has developed dredged material soil reference toxicity values that categorize sediment contaminants into different management tiers depending on their potential for toxicity. The three management tiers categorize sediments as either 1) safe for residential reuse 2) safe for industrial reuse 3) as having contamination that might remediation.

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compound regulated under the MPCAs dredged material guidelines. They are products of incomplete combustion and have suspected or confirmed carcinogenicity (Larsen et. al., 2003, Hoffman et. al., 2009, Bouchard et al., 2009). While naturally occurring PAHs can accumulate in sediments (Achten C., 2009), the majority of PAH contaminated sediments worldwide can be traced to anthropogenic sources (Arp et. al, 2009). Anthropogenic sources of PAHs in sediments are typically associated with fossil fuel combustion and other industrial sources (Jiao et al., 2009). Recently, there has been an emerging trend relating

urbanization to PAH concentration in sediments (Mahler et. al. 2005 & 2010, Cavalcante et. al, 2009).

Concern about PAH concentration in Minnesota wet detention pond sediments prompted the City of White Bear Lake to commission a study by Braun Intertec that showed that certain ponds in the White Bear Lake area had elevated levels of PAHs. A few ponds sediments exceeded the third tier of the states soil reference value toxicity guidelines for PAHs and could potentially require disposal in a confined disposal facility. The study also documented that PAH concentrations showed strong spatial variability both in terms of depth and location within a wet detention pond. While some these PAH concentrations are above the Minnesota third tier regulatory limit, the sediment concentrations are approximately 4 to 225 times lower than PAH concentrations found in typical industrially contaminated sites such as creosote factories or a manufacturing gas plant (Antizar-Ladislao et. al. 2004).

Given the substantial volumes of wet detention pond sediments in Minnesota and the potential for a portion of these sediment to be contaminated with PAHs, various methods of PAH remediation have been considered. Bioremediation using compost was identified as a possible method to remediate PAH contaminated sediments. Various authors have found that by mixing compost with PAH contaminated soil or waste, naturally occurring organisms will degrade PAHs both at the bench scale (Hafidi et al. 2008, Carlstrom et al. 2003, Potter et al., 1999) and at the field scale (Cai. et al. 2007, Amir et al 2005). PAH concentrations typically exhibit a first order decay in a compost pile with smaller ringed PAHs being degraded faster than larger ringed PAHs. A small fraction (typically 4-21% of total PAH) cannot be degraded with this fraction being dominated by 4-6 ring PAHs (Antizar-Ladislao, 2005). Several key factors have been identified in using compost to bioremediate contaminated wastes such as maintaining aerobic conditions, ensuring adequate moisture, providing nutrients in the correct ratios and ensuring that the compost pile doesn't exceed temperatures that might inhibit microbial growth and diversity (Semple et al. 2001, Loick et al., 2009). Bioremediation with composting provides a number of benefits over other remediation methods because it can be accomplished at a large scale, uses local waste material and has the potential to be less expensive than other remediation methods.

While the bioremediation of PAH contaminated soils has been extensively documented, the composting of PAH contaminated sediment has not, to the authors knowledge, been documented. The goal of this study is to evaluate the feasibility of using compost to biodegrade PAHs in the

contaminated wet detention pond sediment from one pond in the City of White Bear Lake. There is not only significant variability between the sampling sites within this pond but the types of PAH compounds can vary significantly between ponds.

II. Methods

Two laboratory-scale composting systems were used in this research to simulate the conditions in a compost pile that might favor PAH biodegradation: (1) a glass bottle reactor system adapted from the experiments of Antizar-Ladislao et al. (2006) and (2) a larger-scale adiabatic reactor system borrowed and adapted from that used by Cook et al. (1994). The glass bottle reactor experiments were chosen because they could be maintained at a constant mesophilic temperatures. The adiabatic reactors were chosen because they had the ability to generate the changes in microbial community structure that accompany natural temperature changes in a large scale compost pile (Hermann and Shann, 1997). Both reactor systems were designed to simultaneously test the efficacy of using compost to degrade PAH contaminated sediments and the effects of varying the ratio of sediment to compost on PAH biodegradation. A PAH bioavailability assay on the contaminated sediment was also completed as a way to explain the extent of PAH biodegradation.

Sediment sampling

Stormwater pond sediments were sampled from the north end of Pepper Tree pond in White Bear Lake, MN. This location was selected because it had the highest PAH levels of any stormwater pond sediment in a report by Braun Intertec to the city of White Bear Lake (Gionfriddo and Bergstrom, 2008). Samples were collected from a sediment depth of 0 to 12 inches using a sediment corer or a shovel from within a 5 meter radius of the north stormwater inlet of the pond. Samples were immediately placed in hexane washed glass or PTFE containers. In total, approximately 20 liters of sediment were collected. Upon arrival at the laboratory, all of the samples were combined and homogenized to create one composite sample which was then stored in the dark in a freezer at -20°C until further use.

Sediment Characterization

Moisture content was determined by measuring the mass lost upon drying 10 to 15 grams of sediment at 105°C for 24 hours (Table 2.1). Ash content was determined using a loss upon ignition method, where dried sediment was heated to 550°C for 4 hours and the final mass was then normalized by the original mass of dried sediment. The sediment pH was determined by adding 10 grams of sediment to 30 mL of deionized water and measuring the pH of the water using a calibrated pH probe after 30 minutes of equilibration at room temperature. Carbon, nitrogen and sulfate content were analyzed at the University of Minnesota Soil Testing Center in duplicate. All other analyses were performed in triplicate.

Table 2.1 Characteristics of Pepper Tree Pond Sediment.

Parameter	Value
pH	6.41±0.03
Moisture Content	21.04%±0.721
Ash Content	98.03%±1.13
Carbon Content	0.97%
Nitrogen Content	0.038%
Sulfate Content	30 ppm

The ash, carbon, nitrogen and sulfate content are all expressed relative to dry weight. The uncertainty is expressed as standard deviation among three replicate samples when three replicate samples were available.

Preparation of Compost

The compost was composed of lawn clippings, wood chips, dried leaves and urea (Table 2.2). This compost mix was inoculated with two separate inoculums: one from the city of Roseville, MN leaf composting facility and one from the city of Roseville, MN municipal mulch pile. These inoculums were chosen because they likely contained microbes capable of degrading lignin (Hofrichter, 2002) and lignin degrading microbes have been demonstrated to have enzymes associated with PAH degradation (Lau et al., 2002). The yard waste compost mixture was adjusted with urea dissolved in water to have an overall carbon to nitrogen (C:N) ratio of 30 to 1.

The sediment was combined with the yard waste compost in a clean glass container by using previously determined moisture contents to mix the sediment and compost at dry mass ratios of 60%/40%, 75%/25% and 85%/15% sediment to compost. These ratios were chosen because they represent approximate volumetric ratios of sediment to compost of 14:1, 8:1 and 3:1, respectively. All compost mixes were adjusted to have moisture contents of 50 percent with DI water before composting.

Table 2.2 Composition of yard waste compost mixture

	% by Wet Mass	% Water	C:N	% N by Dry Mass
Leaf Innoculum	6.8	57	54[2]	0.75
Wood Chip Innoculum	6.9	39	92[2]	0.535
Lawn Clippings	47.9	76	15[1]	2.4
Dried Leaves	24.4	14	54[2]	0.75
Wood Chips	13.7	8	92[2]	0.535
Urea	0.3	0	0.43	46.6

[1] C:N ratio obtained from Haug (1993)
[2] C:N ratio determined at the University of Minnesota Soil Testing laboratory.

Constant Temperature Composting Experiments

A total of thirty-six 0.5 liter glass bottle reactors were prepared by adding 70-120 g of one of the three sediment/compost mixes on top of ~100 mL of pea gravel. Twelve reactors were prepared for each of the sediment/compost mixtures. The gravel served to distribute the air that was supplied to each reactor via a tube (Figure 2.1). The reactors were connected to an air distribution manifold that supplied humidified air using positive pressure at a rate of 1.3 m^3 day^{-1} kg^{-1} during for the first ten days and then was decreased to a rate of 0.7 m^3 $day^{-1}kg^{-1}$ until the end of the experiment as in Cook et al. (1994) The glass bottle reactors were incubated in a walk-in constant temperature room at 38ºC to maintain mesophilic composting conditions. Twelve reactors were used for each of the three amendments of 60%, 75% and 85% of sediment to compost by dry mass. After 0, 10, 25, and 60 days of incubation, three reactors were sacrificed from each amendment and the sediment/compost mix was removed and stored at -20°C until analysis. We had planned to collect a sample after 90 days, but the experiment was terminated on day 64 because the heating system for the temperature controlled room failed.

Figure 2.1 Photos of the temperature controlled reactor. The left photo shows a close up of the 0.5L reactors. The photo shows the entire apparatus including the air humidifying operation, the air distribution manifolds and the 36 reactors.

Adiabatic Composting Experiments

Three 4.8 L reactors were considered adiabatic because they were equipped with an external heating jacket and temperature control system that adjusted the temperature on the outside edge of the reactor to correspond with the temperature in the center of the compost. Thus, there was minimal heat loss to the surroundings that mimicked the insulating properties of a large compost pile and allowed for a natural 'self-heating'. Each reactor was loaded with 1000-2000 g wet sediment-compost at either 60%, 75% or 85% sediment by dry weight. The reactors were operated for 90 days. Air was supplied continuously via a vacuum pump at a rate of 1.3 m^3 day^{-1} kg^{-1} during for the first ten days and then was decreased to a rate of 0.7 m^3 $day^{-1}kg^{-1}$ until the end of the experiment as in Cook et. al., 1994. Compost samples of 80-100 ml were taken from each reactor at 0, 10, 25, 60, and 90 days and stored in a freezer at -20°C until analysis. Moisture content was monitored at each sampling period and maintained at 50 percent by humidifying the air prior to entering reactor and by direct addition of deionized water to the compost pile when necessary.

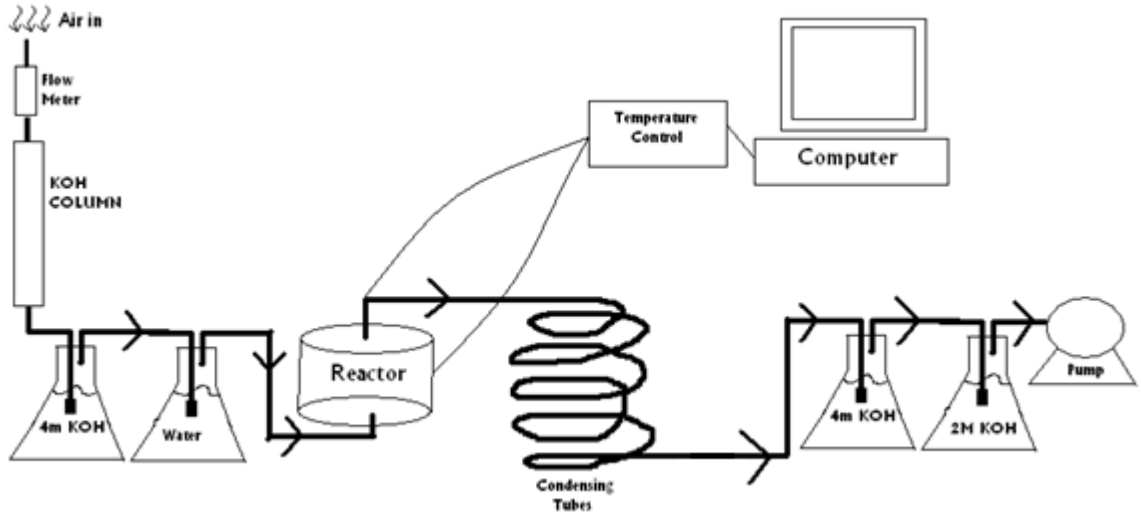

Figure 2.2. Diagram of the adiabatic compost reactor system showing only one of the three compost reactors.

Carbon dioxide was removed from the influent air using solid KOH and 4 M KOH in series. The solid KOH was changed at 30 and 60 days. The influent carbon dioxide scrubbing train was occasionally monitored for carbon dioxide breakthrough in the KOH column by measuring cardon dioxide content in the 4M KOH and none was observed. Carbon dioxide generated in the compost piles was trapped in 1.6 L of 4 M KOH and 0.8 L of 2 M KOH in series (Figure 2.2). The KOH for each reactor was changed and analyzed for carbon dioxide content at 0, 2, 4, 6, 8, 11, 24, 29, 42, 57 and 90 days. Carbon dioxide content in solution was measured by precipitating trapped carbon dioxide using excess barium chloride and then titrating with 1M HCl using phenolphthalein red as an indicator (Weaver, 1994). The first KOH trap effectively captured >99% of all respired carbon dioxide.

Quantification of PAHs in Sediment or Compost

Approximately 3 to 5 grams of homogenized sediment or compost were ground with excess pre-ashed sodium sulfate in a mortar and pestle to extract moisture from the sample. This mixture was then Soxhlet extracted with ~125 mL of dichloromethane for 24 hours. D10-Acenapthene, D10-Phenanthrene, D10-Pyrene, D12-Chrysene, D12-Benzo[a]pyrene (Cambridge Isotope Laboratories, Inc., Andover, MA) were added as surrogate standards and the extract was reduced on a rotary evaporator to a sample volume of ~3mL. The concentrated extracts were then transferred to activated alumina/silica cleanup columns and eluted with washes of 30 ml hexane, 30 ml hexane/dichloromethane (60%/40%), and then 100 ml hexane. The eluent was then rotary evaporated

to ~1 ml and transferred to a nitrogen blow down unit to further reduce the volume to 1 mL. D8-acenaphthylene, D10-Anthracene, D10-Fluoranthene, D12-Benz[a]anthracene, D14-dibenzo[ah]anthracene (Cambridge Isotope Laboratories, Inc., Andover, MA) were used as internal standards. Surrogate recovery rates of D10-Acenapthene, D10-Phenanthrene, D10-Pyrene, D12-Chrysene, D12-Benzo[a]pyrene were (± standard deviation, n=43) 88.2 ± 11.6%, 95.2 ± 12.7%, 86 ± 9.8%, 84.3 ± 8.3%, and 82.4 ± 6.9%, respectively. Surrogate recoveries between 70% and 120% were deemed acceptable. Results for samples with recoveries that were outside of the acceptable range were discarded. Process blanks (i.e., no sediment or compost) were analyzed routinely (1/6 of all analyses) and were consistently free of PAH contamination. The surrogate recoveries of the blanks were not significantly different from the samples (t-test, p=0.04).

The PAHs in the sample extracts were quantified via gas chromatography-mass spectrometry (GC-MS; Hewlett-Packard 5890 series GC with a 5973 series MS). The injection port on the 5890 GC was operated in split mode with a 1:1 split ratio and a temperature of 290°C. Helium served as the carrier gas with a constant flow of 1 ml min^{-1}. The injection volume was 2 µL. Compounds were separated on a Restek RTX®-XLB column (#800129, 30 m × 0.25 mm × 0.25 µm). The initial column temperature was 85°C and was increased to 125°C at 25°C min^{-1} and held for five minutes, temperature was then increased to 290°C at 8°C min^{-1} and then to 310°C at 8°C min^{-1} until 39 minutes. A set of six calibration standards containing the 16 USEPA priority PAHs (at concentrations ranging from 0.02 to 200 mg L^{-1}) together with surrogate and internal standards were injected during each sample run. One of the calibration standards and a hexane blank were injected after every six samples to account for signal drift and sample carryover. The instrument detection limit for each PAH determined using the method of Hubaux and Vos (1970) (Table 2.3). The method detection limit for each PAH was conservatively calculated using the method detection limits, the lowest measured surrogate recovery among all samples and a sediment dry mass of 1 gram.

Table 2.3 Instrument and method detection limits.

	Instrument Detection Limit (mg/L)	Method Detection Limit (µg/g)
acenaphthylene	0.123	0.054
acenaphthene	0.218	0.095
fluorene	0.175	0.076
phenanthrene	0.143	0.058
anthracene	0.142	0.057
fluoranthene	0.142	0.062
pyrene	0.136	0.059
benz[a]anthracene	0.100	0.044
chrysene	0.087	0.038
benzo[bjk]fluoranthene	0.296	0.130
benzo[a]pyrene	0.103	0.045
dibenzo[ah]anthracene	0.069	0.031
indeno[cd123]pyrene	0.054	0.024
benzo[ghi]perylene	0.064	0.028

PAH Bioavailability Assay

PAH bioavailability was determined using a resin-assisted PAH desorption method similar to that of Hawthorne et al., 2002. In this method, an excess of resin beads (Amberlite XAD-2, Supelco, Bellefonte, PA) are incubated with a sediment slurry and the PAHs taken up by the resin serves as a direct measure of the PAHs desorbed from the sediment into the aqueous phase.

First, the resin beads were pre-cleaned by soaking in methanol for 24 hours and the volume of methanol was exchanged four times over this period. The methanol was then changed with a solution of 0.01 M $CaCl_2$ and 0.01 M NaN_3 ten times to remove the methanol. 1.0-1.1 grams of sediment was added to a clean 100 ml glass centrifuge tube with a PTFE cap and then 30 ml of a solution of 0.01 M $CaCl_2$ and 0.01 M NaN_3 was added. Then, 100 µL of a surrogate standard mixture (D10-Acenapthene, D10-Phenanthrene, D10-Pyrene, D12-Chrysene, D12-Benzo[a]pyrene, each compound at ~10 µg/mL in methanol) was added. Next, 1.5-1.7 g of clean resin was added to each tube and the tubes were incubated on a rotary shaker for up to 14 days at room temperature (21-23°C). At the desired sampling times (i.e., 1, 2 and 14 days), 3 sediment-containing tubes and 1 sediment-free blanks were sacrificed to determine the masses of PAHs taken up by the resin. Then, 2.7 g of K_2CO_3 was added

to each sacrificed tube to increase the density of the solution so that the beads would float on top of the water column. The samples were then centrifuged at 28000g for 10 minutes. The beads were harvested from each tube by vacuuming with an inverted Pasteur pipette plugged with glass wool.

The beads in the Pasteur pipette were washed with 20 ml of 0.01 M $CaCl_2$ to remove the K_2CO_3. The beads were dried under a gentle stream of N_2 for approximately five minutes. Then, the PAHs were eluted from the resin by passing 15 ml of 1:1 hexane/acetone followed by 5 ml of dichloromethane through the Pasteur pipette. A rotary evaporator was used to remove the acetone and DCM and to reduce the total sample volume to ~3 ml. Sodium sulfate was added to each vial to remove water from the solvent phase and further N_2 evaporation was used to reduce the volume to ~1 ml before transfer to GC autosampler vials. D8-acenaphthylene, D10-Anthracene, D10-Fluoranthene, D12-Benz[a]anthracene, D14-dibenzo[ah]anthracene (Cambridge Isotope Laboratories, Inc., Andover, MA) in hexane were then added to serve as internal standards. The surrogate recoveries determined using the process blanks were used to correct the PAH masses on the beads from the tubes with sediment. The surrogate recoveries from the blanks were as follows: D10-Acenapthene (64-73%), D10-Phenanthrene (59-78%), D10-Pyrene (63-88%), D12-Chrysene (99-111%), and D12-Benzo[a]pyrene (87-102%).

III. Results and Discussion

Characterization of PAH-contaminated Sediment

The total PAH concentration in the sediment from the pond selected for investigation was 42.6 mg/kg-dry weight (Figure 3.1). This PAH concentration is above the 85th percentile for 40 sampled rural and urban lake sediments across the U.S. (Van Metre and Mahler, 2010) but is significantly lower than in sediments contaminated directly as a result of industrial activities (total PAH levels 352-23,600 mg/kg-dry weight, Antizar-ladislao et al. 2004). Of the total PAH mass, 87% was comprised of PAHs with four or more rings, which is relevant because PAHs with four or more rings have degradation rates that are slower and often more limited by mass transfer from the solid phase than two or three ring PAHs (Haritash and Kaushik, 2009; Harms and Bosma, 1996).

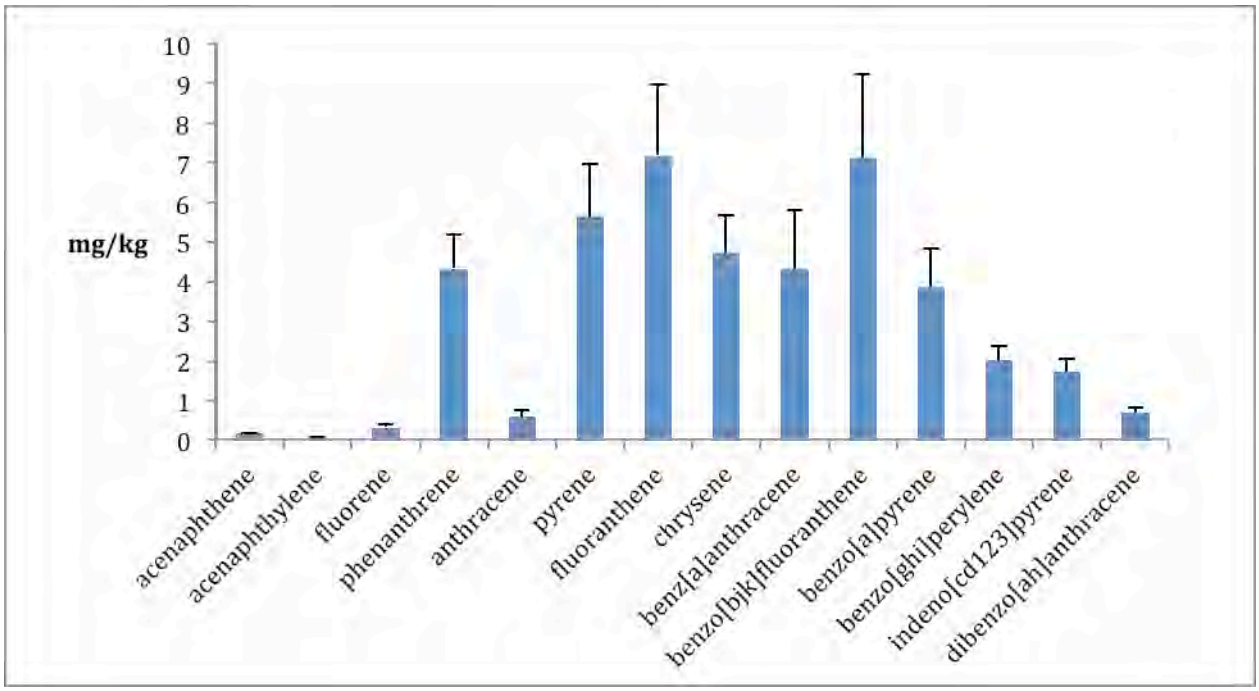

Figure 3.1. Mean concentration of PAHs present in the Pepper Tree Pond sediment sample. The error bars represent the standard deviation of the three replicate PAH extractions. PAHs are plotted in order of increasing octanol to water partitioning coefficient.

Constant Temperature Composting Experiments

All reactors had a significant increase in ash content over the course of composting (t-test, $p>0.05$, Figure 3.2). Aerobic composting decreases the volatile solids content of the compost primarily by converting organic matter into water vapor and carbon dioxide while leaving the inorganic solids behind (Finstein, 1986). Thus, over the course of a composting trial, the ash content

should increase. The significant increases in volatile solids for all three sediment to compost ratios is a strong indicator of significant biological activity in the reactors. Six of the thirtysix reactors had moisture contents below 45 percent, likely because of preferential flow paths causing excess drying. These low moisture content reactors were discarded.

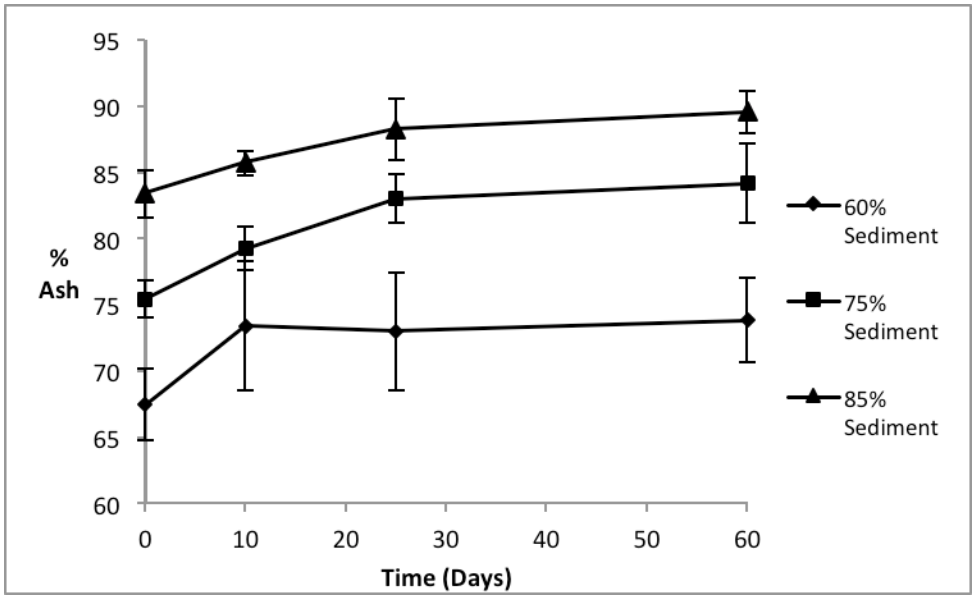

Figure 3.2 Ash content normalized to dry mass content of the reactors over sixty days of composting. The error bars represent the standard deviation of triplicate analyses.

The changes in PAH concentrations during composting in the glass bottle reactors are summarized in Figures 3.3 and 3.4 and Table 3.1. The 75% sediment reactors exhibited significant degradation of only phenanthrene (t-test, $p>0.05$, Figure 3.3, Table 3.1). The 85% sediment reactors exhibited significant degradation of only fluorene and phenanthrene (t-test, $p>0.05$, Figure 3.4, Table 3.1). No PAHs with four or more rings were significantly degraded in either the 75% or 85% sediment reactors. The increases in PAH concentrations for PAHs having more than four rings can be explained by error attributable to sample heterogeneity. The 60% sediment reactors were not analyzed due to poor surrogate recoveries during PAH analysis. The samples collected at ten and twenty five days were not analyzed because little biodegradation was noted upon analysis of the samples collected at sixty days of composting.

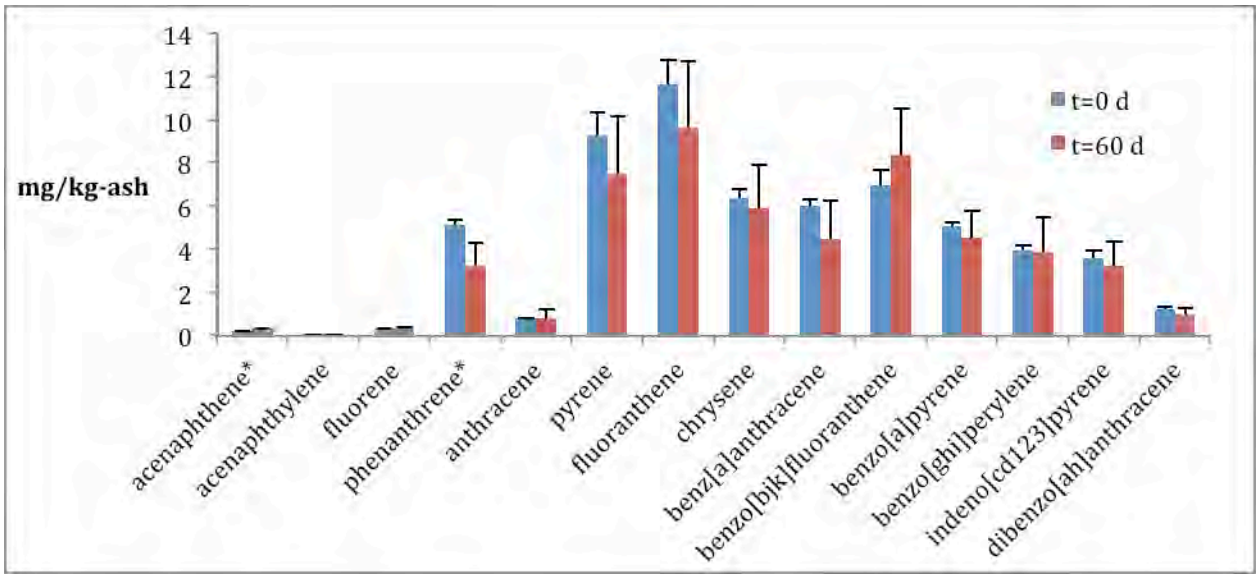

Figure 3.3. Concentration of PAHs normalized to ash content at zero and sixty days of composting for the 75% sediment mix. The error bars represent standard deviation of three replicate extractions of the same sample.

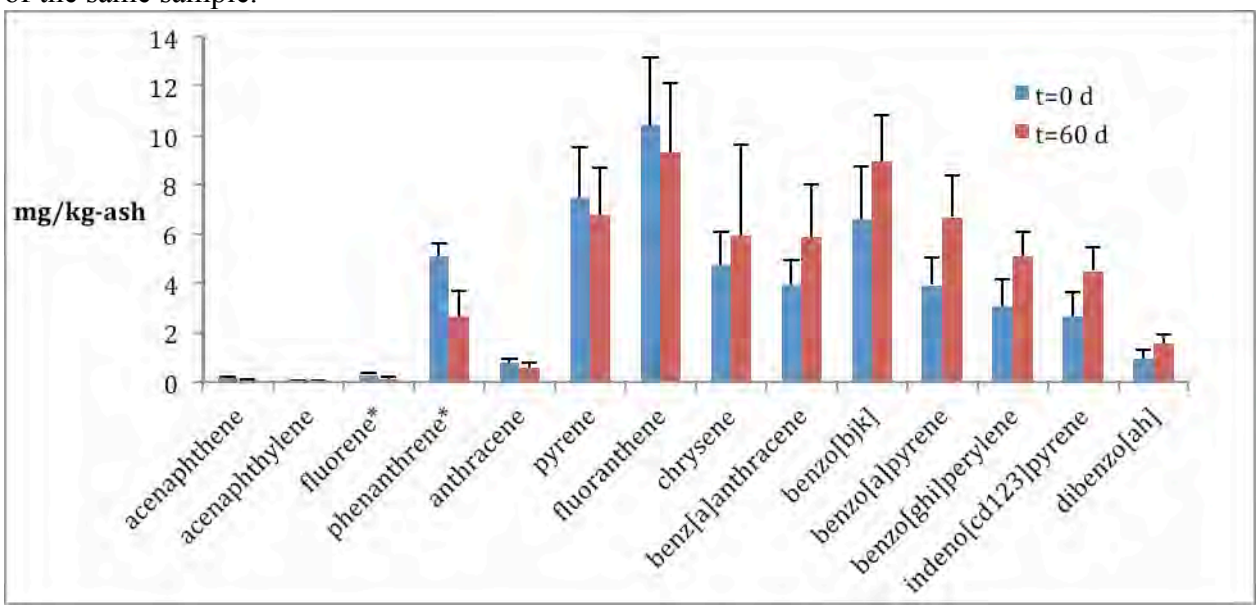

Figure 3.4. Concentration of PAHs normalized to ash content at zero and sixty days of composting for the 85% sediment mix. The error bars represent standard deviation of replicate extractions of the same sample.

Table 3.1. Change in PAH concentrations after 60 days of composting in the glass bottle reactors. The asterisks indicate a statistically significant decrease. The numbers in parenthesis is the p-value of the t-test comparing PAH concentrations of three replicate extractions at time zero and final.

PAH	75% Sediment	85% Sediment
acenaphthene	74.8 (.28)	-51.7 (0.019)
acenaphthylene	37.6 (1E-5)	-2.6 (0.095)
fluorene	13.3 (.40)	-67.4* (0.035)
phenanthrene	-37.0* (0.031)	-48.1* (0.022)
anthracene	1.8 (0.95)	-27.2 (0.31)
pyrene	-18.8 (0.35)	-9.9 (0.83)
fluoranthene	-17.3 (0.346)	-10.7 (0.85)
chrysene	-7.8 (0.21)	24.9 (0.16)
benz[a]anthracene	-25.9 (0.71)	48.7 (0.55)
benzo[bjk]fluoranthene	20.8 (0.33)	35.7 (.12)
benzo[a]pyrene	-10.3 (0.54)	70.8 (0.044)
benzo[ghi]perylene	-0.9 (0.26)	65.5 (0.053)
indeno[cd123]pyrene	-9.7 (0.64)	68.1 (0.039)
dibenzo[ah]anthracene	-20.2 (0.97)	68 (0.036)

Adiabatic Composting Experiments

Temperature

All of the reactors exhibited an increase in temperature above baseline (25°C) for a period of ten days. The 60%, 75% and 85% sediment reactors self-heated to maximum temperatures of 39.1°C, 32.9°C and 29.2°C, respectively (Figure 3.5). The 60% sediment reactor reached significantly higher temperatures than both the 75% and 85% reactors (paired t-test, $p>0.01$) and the 75% sediment reactor had higher temperatures than the 85% sediment reactor (paired t-test, $p>0.01$. All reactors

approached a baseline temperature of 26-28°C after eight days of composting, indicating most of the readily available organic matter had been utilized by that time. After opening the reactors at ten days for sample collection, all reactors maintained a temperature within 0.25°C of the baseline temperature of 25°C for the remainder of the experiment (Figure 3.5).

Only the 60% sediment adiabatic reactor entered the mesophilic temperature region. All of the reactors did self-heat to temperatures above baseline, however, indicating biological activity within all the reactors during the first ten days of composting.

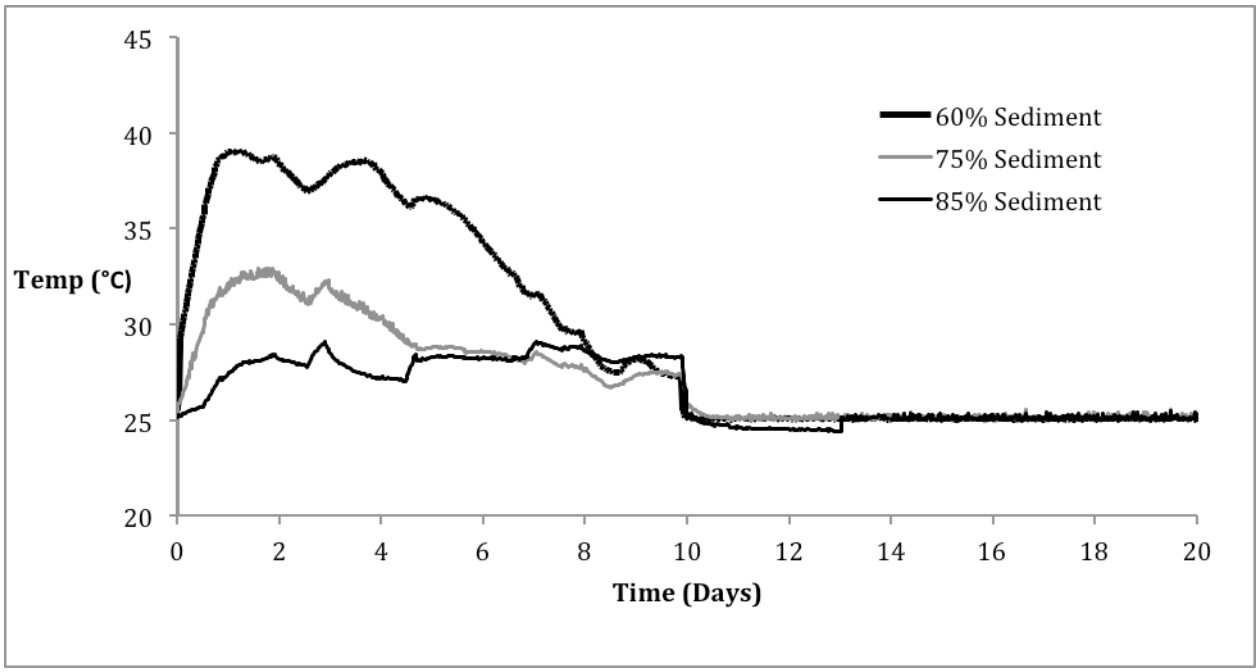

Figure 3.5. Temperature of the adiabatic reactors from zero to twenty days of composting.

Carbon Dioxide Evolution

The 60%, 75% and 85% sediment reactors evolved 50%, 43% and 42%, respectively of total initial carbon mass in the reactors as carbon dioxide (Figure 3.6). All three reactors released greater than 50% of their total evolved carbon dioxide during the first ten days of composting. The maximum rates of carbon dioxide evolution was 8.6-10.0% of total C per day from two to four days of composting and the minimum rate of carbon dioxide evolution was 0.21-0.61% of total C per day from days 57 to 90, indicating a decrease in biological activity as composting time progressed.

The carbon evolved from a compost pile is proportional to total microbial activity, i.e. when there are high rates of carbon dioxide evolution there are also high rates of substrate transformation (Hellman et al., 1997, Cook et al. 1997). All three reactors showed measurable and significant carbon

dioxide evolution throughout the course of composting, indicating that there was microbial activity and substrate transformation throughout the course of the trial, with higher activity during the initial phase of composting.

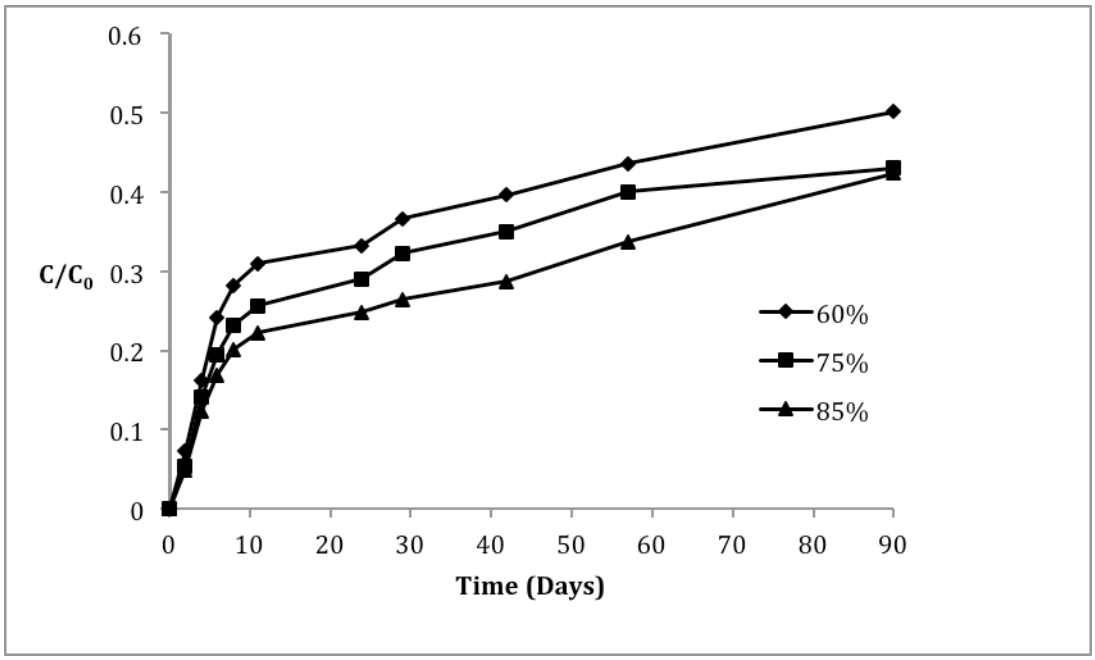

Figure 3.6. Carbon dioxide evolved from each adiabatic reactor over ninety days of composting. The evolved carbon dioxide is normalized as cumulative carbon evolved to the total initial mass of carbon present in the reactor.

Volatile Solids Losses

The 75% and 85% sediment to compost reactors both had significant increases in percent ash content (7.58% and 6.12% respectively) after ninety days of composting (t-test, $p<0.05$, Figure 3.7) indicating losses of volatile solids during composting caused by microbial utilization of organic matter. The 60% sediment to compost reactor did not have a significant increase in percent ash content (t-test, $p=0.77$) but the lack of significant difference can be attributed to large standard deviations owing to high sample heterogeneity. The significant increases in percent ash content in two of the three reactors is a strong indicator of significant biological activity within the compost piles.

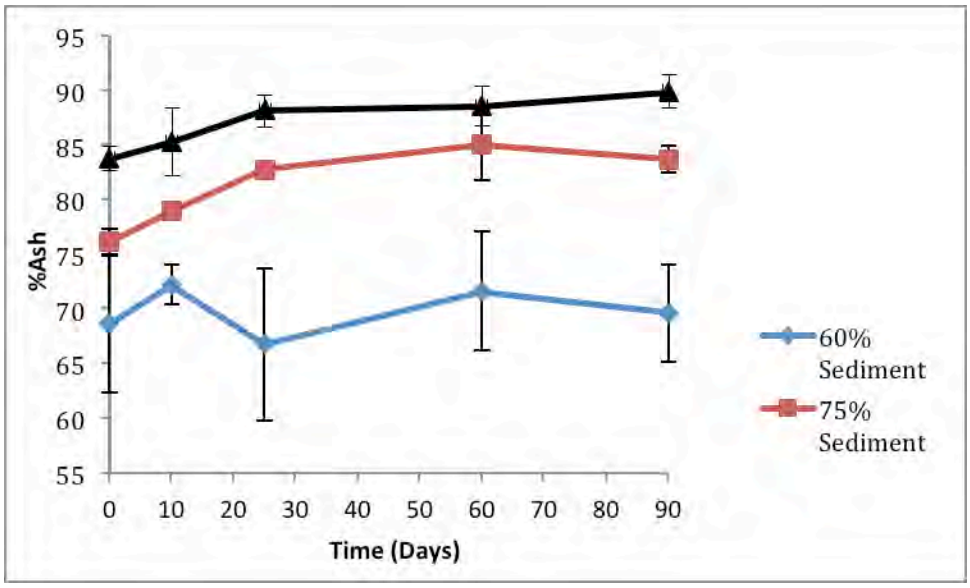

Figure 3.7. Ash content of the variable temperature reactors over ninety days of composting. The error bars express standard deviation among three replicate samples.

PAH Levels During Composting

Phenanthrene was the only three ring PAH significantly degraded at the 95% confidence level in all three adiabatic reactors (t-test,$p>0.05$, Figures 3.8-3.10,Table 3.2). Acenapthene was the only other PAH significantly degraded in the 85% reactor (t-test, $p=0.03$). There were no significant decreases of any four, five or six ring PAH concentrations at the 95% confidence level in any of the reactors after ninety days of composting ($p<0.05$).

Table 3.2. Percent differences of the individual PAHs concentrations after 90 days of composting. The numbers in parenthesis is the p-value of the t-test comparing PAH concentrations of three replicate extractions at time zero and final.

PAH	60% Sediment	75% Sediment	85% Sediment
acenaphthene	17 (0.48)	-19 (0.44)	-23* (0.03)
acenaphthylene	-51 (0.24)	14 (0.53)	7.4 (0.64)
fluorene	-18 (0.35)	-23 (0.42)	-27 (0.16)
phenanthrene	-41* (0.033)	-20* (0.046)	-21* (0.049)
anthracene	-26 (0.43)	-9.8 (0.97)	4.4 (0.67)
pyrene	16 (0.53)	-12 (0.86)	16 (0.19)
fluoranthene	28 (0.056)	-9.1 (0.99)	11 (0.13)
chrysene	-5.0 (0.82)	-8.1 (0.94)	5.5 (0.52)
benz[a]anthracene	-17 (0.36)	-7.2 (.96)	14 (0.51)
benzo[bjk]fluoranthene	-15 (0.72)	-17 (0.78)	7.2 (0.58)
benzo[a]pyrene	-6.3 (0.84)	3.2 (0.61)	7.6 (0.56)
benzo[ghi]perylene	11 (0.63)	-9.2 (0.99)	1.5 (0.64)
indeno[cd123]pyrene	23 (0.23)	-15 (0.71)	5.7 (0.52)
dibenzo[ah]anthracene	3.2 (0.67)	-16 (0.47)	4.5 (0.46)

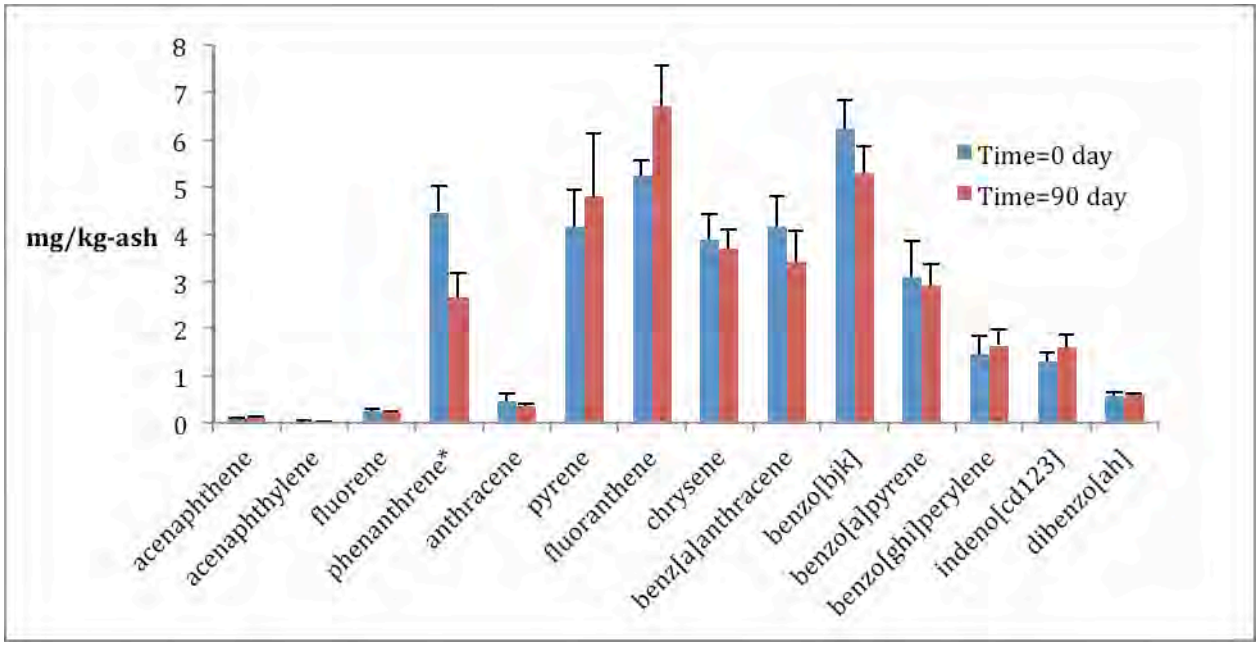

Figure 3.8. Concentrations of PAH 60% mix in the adiabatic reactors at time zero and ninety days of composting.

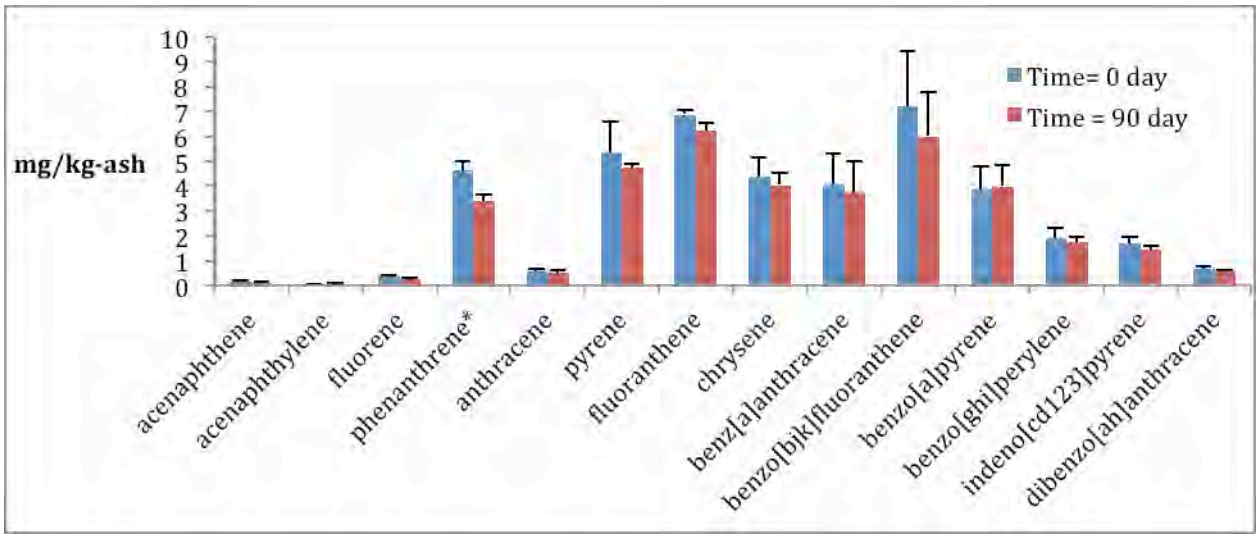

Figure 3.9. Concentrations of PAH 75% mix in the adiabatic reactors at time zero and ninety days of composting.

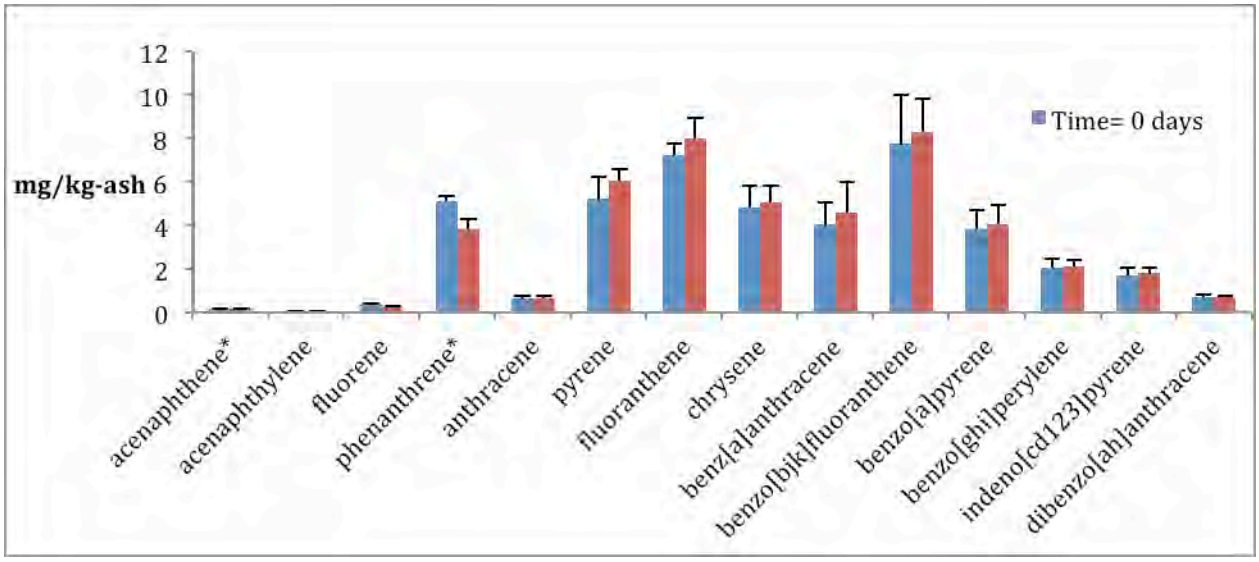

Figure 3.10. Concentrations of PAH 85% mix in the adiabatic reactors at time zero and ninety days of composting.

PAH Bioavailability and Degradation

All PAHs except acenapthylene partitioned from sediment to water over fourteen days of XAD-2 assisted desorption (Figure 3.11). No acenapthylene desorption was observed likely because of its relatively low concentration in the original sediment. The extent of PAH desorption increased with time during the experiment (paired t-test, $p<0.01$). The fraction of PAHs remaining on the

sediment at the end of the 14-day incubation period (8% to 85%) generally increased as the octanol-water partitioning coefficient increased. Typically, the results of such desorption or bioavailability studies are analyzed by considering two fractions: 'slow' and 'fast' desorbing. The 'fast' desorbing fractions are defined as those desorbing within 0 to 15 days of XAD-2 assisted desorption and 'slow' desorbing fractions are defined as those desorbing from 15 to 120 days of XAD-2 assisted desorption (Hawthorne et al., 2001, Ghosh et al. 2001).

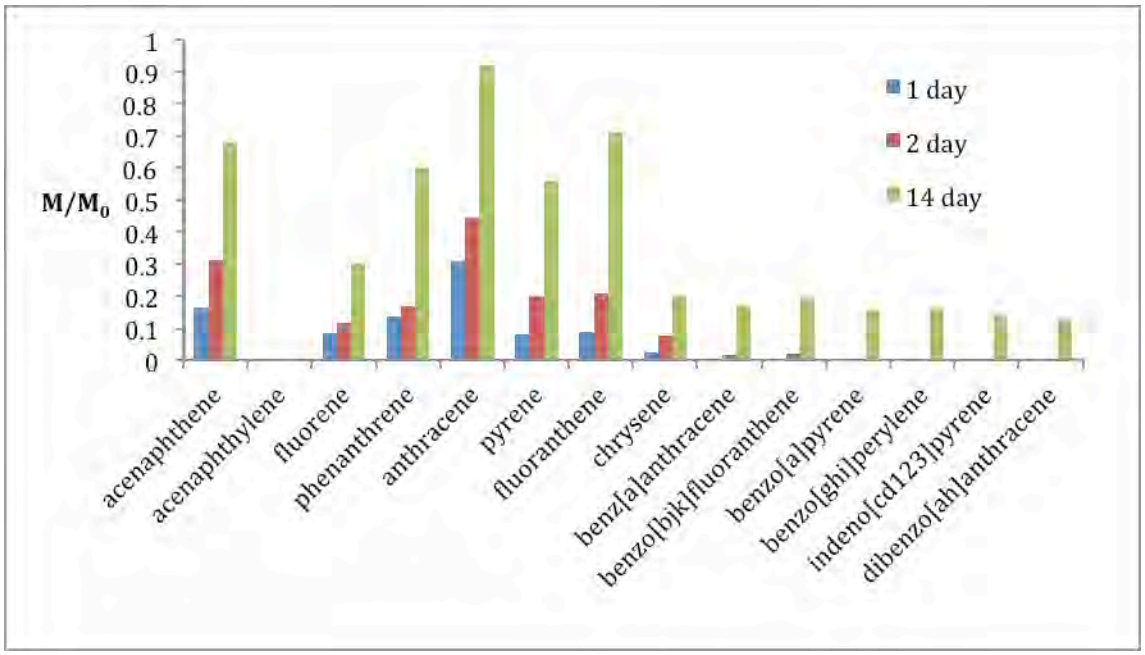

Figure 3.11. Fraction of PAH mass desorbed into the aqueous phase from the sediment after 1, 2 and 14 days normalized to the original PAH mass in the sediment.

The limiting process during bioremediation of PAH-contaminated soil or sediment is considered to be the partitioning of the 'fast-fraction' to the aqueous phase where the PAHs become available for microbial degradation (Hawthorne et al. 2001, Cornelissen et al. 2005, Lei et al. 2004). The 'fast' desorbing fraction has been shown to be a good predictor of the extent of biodegradation during soil or sediment PAH remediation (Talley et al. 2002, Ghosh et. al 2003, Gomez-Lahoz and Ortega-Calvo, 2005). In composting of highly PAH-contaminated soil, it is common for four, five and six ring PAHs to be degraded to a lower extent than two or three ring PAHs. It is also common to observe a recalcitrant fraction for all PAHs (Juhasz et al. 2010, Cajthaml et al. 2002).

However, in our experiments no significant relationship was found between the bioavailability assay of PAHs over any time period and the recalcitrant fraction of PAHs in both the glass bottle

reactors and the adiabatic reactors. The lack of PAH biodegradation during our experiments is not likely limited by microbial activity because all reactors had significant biological activity as evidenced by carbon dioxide respiration levels, adiabatic increases in reactor temperature and volatile solid losses. The significant degradation of phenanthrene in all reactors suggests that PAH-degrading microorganisms capable of degrading three-ring PAHs were present. The degradation rate of phenanthrene is similar to the degradation rates of other three ring PAHs (Wammers and Peter, 2005) and partitions similarly to various solid phases as other three ring PAHs (Ghosh et al., 2010). It is likely that phenanthrene was the only 3-ring PAH that was significantly degraded because it was the three-ring PAH present in the sediment at the highest initial concentration and thus potentially had the largest fraction easily available for desorption and subsequent degradation. The four ring PAHs, Pyrene and Fluoranthene, were found to desorb from the sediment at relatively high fractions (56% and 71%) over 14 days indicating a relatively large bioavailable fraction, however no biodegradation of these compounds was noted. The biodegradation of PAHs with greater than four rings can be limited by slower microbial biodegradation kinetics (Wammer and Peters, 2005) and PAH desorption limitations (Ghosh et al., 2010). The lack of biodegradation of four to six ring compounds in this study is likely limited by the absence of bacterial-eukaryotic consortium capable of degrading PAHs with four or more rings.

IV. Conclusions

Two sets of reactors were developed to simulate the conditions in a composting pile that would favor the biodegradation of PAHs in contaminated stormwater pond sediment. The adiabatic reactors demonstrated effective composting as evidenced by cumulative respired carbon dioxide, natural temperature progression and volatile solid losses. The glass bottle reactors demonstrated effective composting as evidenced by volatile solids losses. All analyzed reactors had small but significant decreases in phenanthrene concentrations over the extent of composting, which indicates PAH biodegradation was not limited by the complete absence of PAH degrading microbes. The PAH bioavailability assay did not effectively predict the extent of PAH bioremediation using compost. Because all PAHs were found to have a small but significant bioavailable fraction, it is likely that the microbial PAH degradation potential for four to six ring PAHs was the limiting factor in PAH biodegradation. Bioremediation of low concentration PAH contaminated stormwater pond sediments using compost was not effective in significantly reducing PAH concentrations using the experimental setup developed for this experiment.

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Appendix: Summary of Concentration data

Table A.1. Concentrations of PAHs in the un-amended sediment (mg/kg-dry)

	PAH	sediment (st dev)
acenaphthene	0.16	0.02
acenaphthylene	0.05	0.01
fluorene	0.32	0.07
phenanthrene	4.33	0.85
anthracene	0.60	0.16
pyrene	5.64	1.32
fluoranthene	7.16	1.79
chrysene	4.72	0.95
benz[a]anthracene	4.30	1.49
benzo[bjk]fluoranthene	7.12	2.10
benzo[a]pyrene	3.85	0.98
benzo[ghi]perylene	2.01	0.36
indeno[cd123]pyrene	1.72	0.32
dibenzo[ah]anthracene	0.68	0.13

Table A.2. Concentrations of PAHs partitioned on to XAD over 1,2 and 14 days (mg/kg-dry)

	1 day	2 day	14 day
acenaphthene	0.00	0.00	0.00
acenaphthylene	0.03	0.05	0.11
fluorene	0.03	0.04	0.10
phenanthrene	0.61	0.73	2.60
anthracene	0.19	0.27	0.55
pyrene	0.66	1.52	5.10
fluoranthene	0.47	1.13	3.16
chrysene	0.02	0.08	0.73
benz[a]anthracene	0.12	0.36	0.96
benzo[bjk]fluoranthene	0.04	0.17	1.40
benzo[a]pyrene	0.00	0.02	0.61
benzo[ghi]perylene	0.00	0.00	0.09
indeno[cd123]pyrene	0.00	0.00	0.25
dibenzo[ah]anthracene	0.00	0.00	0.33

Table A.3. Concentrations of PAHs for the 75% sediment glass bottle reactor. (mg/kg-ash)

	Time=0 day	Time=60 day	Standard Deviation day 0	Standard Deviation day 60
acenaphthene	0.16	0.08	0.04	0.05
acenaphthylene	0.04	0.04	0.02	0.01
fluorene	0.29	0.09	0.06	0.09
phenanthrene	5.11	2.65	0.50	1.04
anthracene	0.79	0.57	0.15	0.22
pyrene	7.51	6.77	2.01	1.93
fluoranthene	10.41	9.30	2.75	2.82
chrysene	4.75	5.93	1.34	3.72
benz[a]anthracene	3.96	5.89	0.98	2.11
benzo[bjk]fluoranthene	6.60	8.95	2.12	1.87
benzo[a]pyrene	3.92	6.69	1.11	1.71
benzo[ghi]perylene	3.08	5.10	1.11	0.99
indeno[cd123]pyrene	2.67	4.49	0.97	0.95
dibenzo[ah]anthracene	0.93	1.57	0.39	0.36

Table A.4. Concentrations of PAHs for the 85% sediment glass bottle reactor. (mg/kg-ash)

	time=0 day	time=60 day	standard deviation day 0	standard deviation day 60
acenaphthene	0.16	0.08	0.04	0.05
acenaphthylene	0.04	0.04	0.02	0.01
fluorene	0.29	0.09	0.06	0.09
phenanthrene	5.11	2.65	0.50	1.04
anthracene	0.79	0.57	0.15	0.22
pyrene	7.51	6.77	2.01	1.93
fluoranthene	10.41	9.30	2.75	2.82
chrysene	4.75	5.93	1.34	3.72
benz[a]anthracene	3.96	5.89	0.98	2.11
benzo[bjk]fluoranthene	6.60	8.95	2.12	1.87
benzo[a]pyrene	3.92	6.69	1.11	1.71
benzo[ghi]perylene	3.08	5.10	1.11	0.99
indeno[cd123]pyrene	2.67	4.49	0.97	0.95
dibenzo[ah]anthracene	0.93	1.57	0.39	0.36

Table A.5. Concentrations of PAHs for the 85% sediment adiabatic reactor. (mg/kg-ash)

	time=0 day	time=90 day	standard deviation day 0	standard deviation day 90
acenaphthene	0.18	0.14	0.01	0.01
acenaphthylene	0.05	0.05	0.02	0.02
fluorene	0.32	0.24	0.07	0.02
phenanthrene	5.12	3.83	0.30	0.51
anthracene	0.59	0.62	0.19	0.16
pyrene	5.20	6.05	1.25	0.61
fluoranthene	7.22	8.01	0.64	1.03
chrysene	4.78	5.04	1.21	0.86
benz[a]anthracene	4.02	4.57	1.25	1.58
benzo[bjk]fluoranthene	7.73	8.27	2.74	1.72
benzo[a]pyrene	3.80	4.05	1.09	0.98
benzo[ghi]perylene	2.06	2.09	0.48	0.37
indeno[cd123]pyrene	1.69	1.77	0.41	0.30
dibenzo[ah]anthracene	0.67	0.70	0.14	0.09

Table A.6. Concentrations of PAHs for the 75% sediment adiabatic reactor. (mg/kg-ash)

	time=0 day	time=90 day	standard deviation day 0	standard deviation day 90
acenaphthene	0.16	0.13	0.03	0.02
acenaphthylene	0.05	0.05	0.02	0.02
fluorene	0.34	0.26	0.07	0.07
phenanthrene	4.64	3.39	0.44	0.30
anthracene	0.56	0.50	0.16	0.10
pyrene	5.37	4.73	1.61	0.21
fluoranthene	6.87	6.25	0.25	0.34
chrysene	4.40	4.04	0.99	0.57
benz[a]anthracene	4.06	3.76	1.63	1.50
benzo[bjk]fluoranthene	7.23	6.00	2.90	2.13
benzo[a]pyrene	3.86	3.98	1.20	1.01
benzo[ghi]perylene	1.93	1.75	0.52	0.23
indeno[cd123]pyrene	1.68	1.44	0.39	0.19
dibenzo[ah]anthracene	0.66	0.55	0.17	0.06

Table A.7. Concentrations of PAHs for the 60% sediment adiabatic reactor. (mg/kg-ash)

	time=0 day	time=90 day	standard deviation day 0	standard deviation day 90
acenaphthene	0.10	0.12	0.03	0.03
acenaphthylene	0.04	0.02	0.02	0.02
fluorene	0.26	0.21	0.06	0.04
phenanthrene	4.46	2.65	0.81	0.52
anthracene	0.48	0.35	0.23	0.05
pyrene	4.15	4.79	1.16	1.35
fluoranthene	5.24	6.70	0.48	0.88
chrysene	3.88	3.70	0.81	0.41
benz[a]anthracene	4.16	3.43	0.94	0.65
benzo[bjk]fluoranthene	6.23	5.28	1.15	0.57
benzo[a]pyrene	3.10	2.90	1.11	0.47
benzo[ghi]perylene	1.47	1.64	0.56	0.34
indeno[cd123]pyrene	1.30	1.60	0.27	0.28
dibenzo[ah]anthracene	0.58	0.60	0.12	0.05