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DIFFERENCES IN SEDIMENT ORGANIC MATTER COMPOSITION AND PAH WEATHERING BETWEEN NON-VEGETATED AND RECENTLY VEGETATED FUEL OILED SEDIMENTS

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We examined polycyclic aromatic hydrocarbon (PAH) attenuation in contaminated field sediments after only 2 years of plant growth. We collected sediments from vegetated and non-vegetated areas at the Indiana Harbor Canal (IHC), an industrialized area with historic petroleum contamination of soils and sediments. PAH concentrations, PAH weathering indices, and organic matter composition in sediments colonized by Phragmites, cattails, or willow trees were compared to the same indices for non-vegetated sediments. We hypothesized that bulk sediment and humin fractions with measurable increases in plant organic matter content would show measurable changes to PAH attenuation as indicated by more weathered PAH diagnostic ratios or reduced PAH concentrations. Carbon-normalized PAH concentrations were lower in vegetated bulk sediments but higher in vegetated humin fractions relative to non-vegetated sediment fractions. Total organic carbon content was not indicative of more weathered N_3/P_2 ratios or reduced PAH concentrations in vegetated sediment fractions. More weathered N_3/P_2 ratios were observed with increased modern carbon (plant carbon) content of vegetated sediment fractions. Phragmites sediments contained more modern carbon (plant carbon) and more weathered PAH ratios [C_3 -naphthalenes and C_2 -phenanthrenes (N_3/P_2)] than willow, cattail, and non-vegetated sediments.

KEYWORDS polycyclic aromatic hydrocarbon (PAH), ^{14}C accelerator mass spectrometry (AMS), *Phragmites*, cattails, willow trees

INTRODUCTION

Field and laboratory studies of polycyclic aromatic hydrocarbons (PAHs) phytoremediation have yielded mixed results with regard to PAH degradation. Most short-term studies evaluated PAH attenuation within a single growing season after vegetated and non-vegetated soils were amended with specific PAH analytes. Some of these studies showed that vegetation did not significantly degrade PAHs relative to non-vegetated controls (Lalande *et al.*, 2003; Muellerand Shann, 2006). Other studies did show significant reductions in PAH concentrations within a few months (Aprill and Sims, 1990; Spriggs, Banks, and Schwab, 2005; Maila, Randima, and Cloete, 2005; Alvarez-Bernal *et al.*, 2007; Jouanneau

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et al., 2005). Over a 4-week growing period, Corgié, Beguiristain, and Leyval. (2004) observed lower concentrations of pyrene in the soil directly adjacent to plant roots relative to soil away from vegetation. Banks, Lee, and Schwab (1999) also observed significant reductions in labeled PAH concentrations in planted soils versus non-planted soils; their tracer studies also showed that loss of PAH was not the result of abiotic sorption to root structures. Miya and Firestone (2001) proposed that enhanced PAH degradation in soils impacted by root exudates and root debris resulted from rhizo-stimulated heterotrophic, bacteria populations that are capable of PAH degradation. However, Jouanneau *et al.* (2005) observed less pyrene mineralization in soils amended with both plants, *Phragmites australis*, and a pyrene-degrading *Mycobacterium* bacteria as compared to soils amended with only pyrene-degrading *Mycobacterium* bacteria.

A long-term study reported significant PAH reductions in the presence of mixed vegetation after 12 years' exposure in field lysimeters (Doick *et al.*, 2005). Significant declines in PAH concentrations were also observed after 3–4 years of hybrid poplar growth at a former creosote facility field site (Marr *et al.*, 2006; Widdowson *et al.*, 2005; Pitterle *et al.*, 2005), but declines in PAH concentrations were observed only for two- and three-ring PAH analytes (Widdowson *et al.*, 2005). When mulberry root extracts were added to sediments aged with ^{14}C -phenanthrene for 518 days, root-amended soils mineralized more phenanthrene and sequestered more ^{14}C label in humin relative to sterile controls (Kamath, Schnoor, and Alvarez, 2005). The authors proposed that the continuous addition of organic matter (mulberry exudates) enhanced phenanthrene dissipation by two possible mechanisms: 1) enhanced microbial populations that increased PAH biodegradation and/or 2) increased phenanthrene bioavailability and partitioning into more available organic matter (OM) compartments via destabilization of the humic matrix.

Plant-derived materials demonstrate different sorptive affinities for PAHs (Salloum, Chefetz, and Hatcher, 2002; Chen *et al.*, 2005; Chefetz *et al.*, 2000). Plant cuticle, an aliphatic biopolymer, has greater sorption coefficients (Log K_{oc} values) for PAHs than lignin or cellulose (Salloum *et al.*, 2002; Chefetz *et al.*, 2000). Mao *et al.* (2002) observed that the sorption capacity of some cuticular, aliphatic plant materials correlated well with PAH sorption capacity in soils. Kukkonen *et al.* (2003) observed a positive correlation between rapid PAH desorption from sediment and the presence of plant materials such as lipids and lignin. Rockne *et al.* (2002) observed that sediment fractions containing coarse plant detrital material had greater log K_{oc} values for PAHs and desorbed more PAHs than other sediment fractions. Interestingly, greater desorption was observed for larger PAH analytes such as pyrene, chrysene, and benzo[a]pyrene as well as two- and three-ring PAHs in sediments containing plant detrital material (Shor *et al.*, 2003).

We previously reported significant reductions of total PAH concentrations [TPAH] and more weathered diagnostic PAH ratios for refinery distillate waste colonized by *Phragmites australis* (Gregory *et al.*, 2005). At the refinery distillate waste site, several decades of *Phragmites*' colonization and propagation altered the sediment organic matter (SOM) composition and increased PAH weathering in both bulk sediment and humin fractions. Reductions of TPAH and modern carbon content, or plant carbon content, were as great if not greater in *Phragmites* humin fractions as *Phragmites* bulk sediments. Would similar changes occur after only 2 years of plant growth in fuel-oiled sediments?

The purpose of this study was to better understand changes to PAH attenuation in contaminated field sediments after only a few years of plant growth. We collected sediments from vegetated and non-vegetated areas at a site with historic fuel-oil contamination. PAH

concentrations, PAH weathering indices, and organic matter composition in sediments colonized by *Phragmites*, cattails, or willow trees were compared to the same indices for non-vegetated sediments. We hypothesized that sediment fractions with measurable increases in plant organic matter content would show measurable changes to PAH attenuation, as indicated by more weathered PAH diagnostic ratios or reduced PAH concentrations.

MATERIALS AND METHODS

Site Description and Sampling Methods

The IHC is a heavily industrialized area with historic petroleum contamination of soils and sediments. Diesel fuel is the predominant petrogenic contaminant source at the site and workers have reported a persistent petroleum sheen in canal waters for decades (Sand Creek Consultants, Inc., 2002). Total petroleum hydrocarbon (TPH) concentrations range from 2% to 43% of sediment mass. In 2001, eight samples of oiled-shore sediments had mean PAH concentrations of 4100 ppm (Sand Creek Consultants, Inc., 2002). In 2002, several varieties of hybrid poplars and willows trees (*Salix exigua*) were planted in riparian soils and oiled-shore sediments as part of a phytoremediation treatability study. Sediment analyses at the site indicated that PAH contamination for oiled-shore sediments was greatest in the first 5 inches of sediment (personal communication, Steve Rock, USEPA). Disturbance of the site in 2002 resulted in colonization by *Phragmites australis*, the common reed plant, and *Typha latifolia*, cattails.

Sediment samples were collected by removing approximately 10 cm of sediment by hand trowel or shovel within a 2-m diameter circle of vegetated or non-vegetated sediments. Sediment samples were collected at six to nine locations for each plant species and three locations of non-vegetated sediments. Non-vegetated sediments were composited at the site prior to storage and transport. In vegetated areas, plant litter and debris were removed from the sediment surface, after which time sediments with plants roots were removed *in toto*. Visible plant roots and plant material were removed from sediments prior to mixing sediments together for each plant species. Sediments were transported in plastic bags at 0°C. Prior to chemical fractionation and analyses, small visual root residuals were removed and sediments were 2-mm sieved and homogenized again in ceramic bowls.

Sediment Fractionation

The original composite sediments samples are referred to as bulk sediment fractions. Aliquots of bulk sediments (10–15 g) were first freeze-dried then chemically fractionated to obtain humin and de-ashed humin fractions according to previously described methods in Gregory *et al.* (2005). Briefly, sediments were lipid-extracted twice then extracted with sodium hydroxide under a nitrogen headspace to remove humic and fulvic acids. Humin was de-ashed using hydrochloric acid (HCl) and hydrofluoric acid (HF). A preferential loss of larger alkylated PAH homologues due to the chemical fractionation procedure of sediment has been evaluated and discussed previously (Gregory *et al.*, 2005). Humin represents the sediment organic matrix after extraction with dichloromethane (DCM) and alkaline salts to remove lipids and humic/fulvic acids, respectively. De-ashed humin represents humin after extraction with HF/HCl to remove the mineral matrix.

OM Composition. Replicate aliquots of bulk sediment, humin, and de-ashed humin fractions were analyzed for percent total organic carbon (% TOC) using an SOP NC 2100 CHN Analyzer (Thermo Electron S.p.A., Milan, Italy). Sediment samples were sent to The Lawrence Livermore National Laboratory (Livermore, CA, USA) for standard radiocarbon dating analysis. Sediment fractions were combusted to CO₂ then reacted with a Fe/H₂ catalyst to form graphite. Samples were analyzed by accelerator mass spectrometry (AMS) with standards (NBS Oxalic Acid I and II; NIST-SRM-4990, 4990c) and blanks for organic carbon samples (Johnson-Mathey 99.9999% graphite powder). Splits of combusted samples were taken for ¹³C analysis to correct AMS values (Stuiver and Polach, 1997). Data are expressed as the percent modern carbon (¹⁴C PMC) determined from the measurement of fraction modern that is the deviation of the ¹⁴C/C ratio of a sample from “modern” (Stuiver and Polach, 1997). Petroleum contains very little ¹⁴C activity (¹⁴C PMC ~ 0%) because of its ancient origin, whereas modern plant carbon and recent humification of modern plant carbon will reflect modern ¹⁴C activity (¹⁴C PMC ~ 100%) from atmospheric ¹⁴CO₂.

Gas Chromatography/Mass Spectrometry (GC/MS) select ion monitoring (SIM). DCM extracts of bulk sediment, humin, and de-ashed humin were first loaded onto neutral activated alumina columns prior to analysis by GC/MS. Extracts were concentrated to 5 mL and spiked with deuterated phenanthrene (*d*₁₀, 500 ng/mL) and benzo[*a*]pyrene (*d*₈, 505 ng/mL) as internal standards. Extracts were analyzed for 42 PAHs using a modified method of EPA 8270 (US EPA, 1986) similar to that employed by Luellen and Shea (2002). GC/MS SIM mode analyses were conducted on a HP5890 Series II GC equipped with electronic pressure control connected to an HP5970 or HP5972 MSD using a Restek 30 m × 0.25 mm Rtx-5 (film thickness 0.25 μm) MS w/Integra-Guard column.

Statistical Analyses

Statistical significance was determined by either a student *t*-test when comparing two sample means, or Dunnett’s analysis of variance (ANOVA) ($P < 0.05$) (Dunnett, 1955, 1964) by which multiple means of vegetated data sets were compared against non-vegetated controls. Unless otherwise noted, triplicate samples were used to determine the averaged recoveries of PAHs in sediment extracts and total organic carbon (TOC) present in sediment samples. Values in tables represent the mean of measurements ± one standard deviation.

RESULTS AND DISCUSSION

PAH Concentrations in Sediment Fractions

Mean concentrations of 42 alkylated and non-alkylated PAHs (TPAH) for our collected sediments were similar to TPAH concentrations of fuel oiled sediments (4100 ppm) collected in the same area and reported by Sand Creek Consultants in 2001 (Sand Creek Consultants, Inc., 2002). Mean TPAH and 16 Environmental Protection Agency (EPA) priority PAH concentrations of *Phragmites* and willow tree bulk sediments were significantly lower than non-vegetated bulk sediments (Table 1) (Dunnett’s ANOVA, $P < 0.05$). TPAH and 16 EPA PAH concentrations for cattails bulk and humin fractions were significantly greater than all other sediments (Table 1) (Dunnett’s ANOVA, $P < 0.05$). TPAH concentrations showed no significant differences between non-vegetated *Phragmites* and willow tree humin fractions and non-carbon normalized PAH concentrations in de-ashed humin fractions were similar for all sediment fractions.

Table 1 Mean PAH concentrations^{a,b} (± 1 standard deviation)^c for vegetated and non-vegetated Indiana Harbor sediment fractions. Bold-face means and standard deviations are significantly different than other means for that PAH analysis

	Non-Vegetated	<i>Phragmites</i>	Cattails	Willow Trees
Bulk Sediment				
[TPAH] ^a ($\mu\text{g/g}$ soil)	4796 \pm 602.4	3,713 \pm 185.1 ^A	5701 \pm 613.2	3,490 \pm 555.5 ^A
[16 PAH] ^b ($\mu\text{g/g}$ soil)	1205 \pm 124.7	942 \pm 62.94 ^A	1421 \pm 51.89	890 \pm 53.5 ^A
[TPAH] ($\mu\text{g/g}$ OC)	33,500 \pm 6,450	26,900 \pm 1,610 ^A	16,600 \pm 2,340 ^A	16,000 \pm 3,554 ^A
Humin				
[TPAH] ($\mu\text{g/g}$ soil)	13.3 \pm 4.50 ^A	16.2 \pm 4.47 ^A	38.6 \pm 3.20	11.4 \pm 0.811 ^A
[16 PAH] ($\mu\text{g/g}$ soil)	4.22 \pm 1.25 ^A	3.81 \pm 0.602 ^A	12.0 \pm 0.645	4.47 \pm 0.163 ^A
[TPAH] ($\mu\text{g/g}$ OC)	253 \pm 96.3 ^A	482 \pm 143 ^A	640 \pm 75.9	159 \pm 17.5 ^A
De-ashed Humin				
[TPAH] ($\mu\text{g/g}$ soil) ^a	3.88 \pm 0.337 ^A	8.37 \pm 2.30 ^A	4.54 \pm 0.320 ^A	4.57 \pm 1.76 ^A
[16 PAH] ($\mu\text{g/g}$ soil) ^b	1.61 \pm 0.790 ^A	2.54 \pm 0.304 ^A	1.66 \pm 0.165 ^A	1.76 \pm 0.511 ^A
[TPAH] ($\mu\text{g/g}$ OC)	81.2 \pm 9.88 ^A	192 \pm 2.92	95.5 \pm 18.7 ^A	146 \pm 27.3 ^A

^aTotal alkylated and non-alkylated PAH (TPAH) ($n = 42$) concentrations of lipid extracts from sediment fractions analyzed at North Carolina State University (NCSU).

^bMean values of the sum of concentrations of the 16 EPA Priority PAH pollutants in lipid extracts from sediment fractions analyzed at NCSU.

^c Values are mean \pm one standard deviation ($n = 3$).

^AMean values that are not significantly different (Dunnnett's ANOVA, $P < 0.05$) (Dunnnett, 1955, 1964).

Greater PAH concentrations in cattail bulk sediments may be attributed to site heterogeneity and variant PAH concentration distributions. Percent TOC and modern plant carbon (PMC) content of bulk sediments would support this explanation (Figure 1). Cattail bulk sediment has the highest %TOC content of all bulk sediments analyzed, but a PMC mean similar to non-vegetated and willow tree bulk sediment (Figure 1). Only about 8% of the TOC content of cattail bulk sediment can be attributed to plant carbon, whereas 21% of the TOC content in *Phragmites* bulk sediment is plant carbon. Fuel oil represents a smaller percent of TOC content for *Phragmites* sediments and, as reported in Table 1, TPAH concentrations were lower in *Phragmites* bulk sediments than cattail bulk sediments. Our data suggest that the high TOC content of cattails bulk sediment reflects greater fuel oil content.

To account for lower PAH recovery due to carbon dilution from plant carbon inputs, TPAH concentrations were carbon normalized (TPAH/OC) in each sediment fraction (Table 1). We previously observed significantly lower PAH concentrations in *Phragmites* carbon-normalized sediment fractions relative to non-vegetated sediment fractions at a site where *Phragmites* had colonized refinery distillate waste for several decades (Gregory *et al.*, 2005). At the IHC site, TPAH/OC concentrations were significantly lower in all vegetated bulk sediments relative to non-vegetated bulk sediments. However, TPAH/OC for cattails humin and *Phragmites* de-ashed humin were significantly greater than non-vegetated humin fractions (Dunnnett's ANOVA, $P < 0.05$; Table 1).

PAH concentrations in vegetated humin fractions were not related to increased % TOC but were related to PMC content or plant carbon content. Percent TOC did not increase with TPAH/OC concentrations for vegetated humin fractions (Table 1, Figure 1). Rockne *et al.* (2002) observed similar results and could not correlate TOC content to increased TPAH concentrations in estuarine sediments fractions that contained plant detrital material.

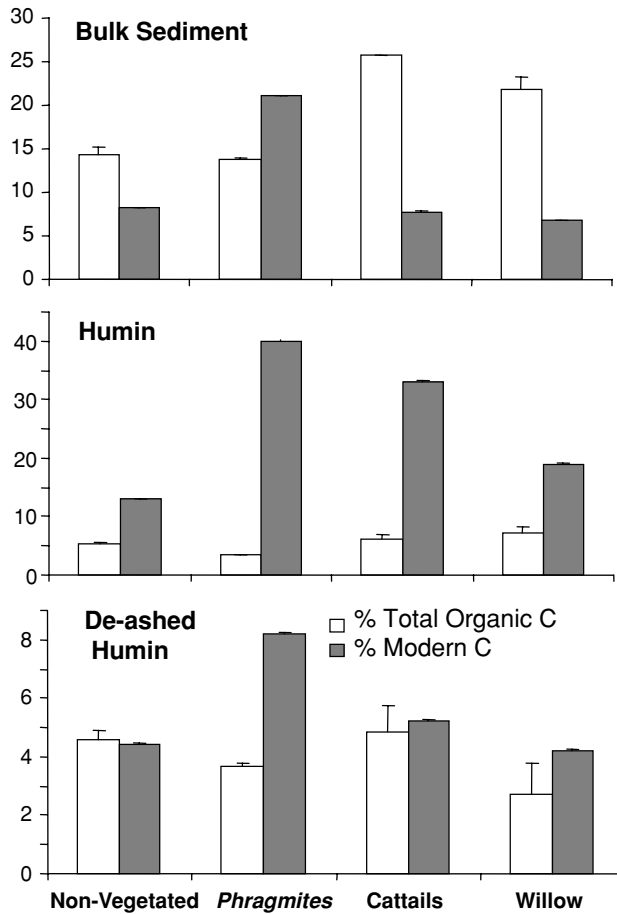


Figure 1 Total organic carbon (% TOC) and PMC (% PMC) for bulk sediment and humin fractions of vegetated and non-vegetated sediments at the IHC site. Values are means \pm one standard deviation.

TPAH concentrations were significantly greater in cattail humin and TPAH/OC *Phragmites* de-ashed humin. These fractions contained significantly greater plant carbon content (PMC) than non-vegetated humin fractions, but %TOC was not significantly different (Figure 1; Dunnett's ANOVA, $P < 0.05$). A second explanation for greater TPAH concentrations in these vegetated humin fractions is the accumulation of PAHs in plant carbon materials. Rockne *et al.* (2002) observed more TPAHs (> 85%) in estuarine sediment fractions that contained plant detritus than fractions that did not contain plant detritus. TPAH concentrations were greater in detrital sediment fractions although these fractions comprised only 4% of the total sediment mass. Rockne *et al.* (2002) used equilibrium aqueous–solid partitioning data to show that sediment fractions with plant detrital material were stronger, preferential sorbents for PAH sequestration and partitioning than sediment fractions without plant materials. The authors speculated that as PAHs partition from various organic matter-rich regions in sediments aggregates, they reversibly partitioned into sediment material that is rich in plant vascular debris. Thus, greater PAH concentrations

in cattail humin and *Phragmites* de-ashed humin may result from PAH sequestration and partitioning into plant-derived materials in vegetated fuel-oiled sediments.

PAH Weathering and Sediment Composition

Alkylated PAH ratios provide a quantitative measure of PAH weathering and can be used: 1) to describe the degree of weathering and biodegradation of spilled oil and 2) to predict and monitor the effectiveness of remediation activities (Douglas *et al.*, 1996). The ratio of C₃-naphthalenes and C₂-phenanthrenes (N₃/P₂) is used for diesel fuel and crude oil in the early stages of weathering as the tri-alkylated naphthalenes have a shorter lifespan in relation to many other PAHs. C₃-dibenzothiophenes vs. C₃-chrysenes (D₃/C₃) ratios can be used to detect later stages of weathering for diesel and crude oils (Douglas *et al.*, 1996). Biodegradation is often the primary mechanism for PAH weathering, but volatilization and leaching may also weather the lighter PAHs as plants physically disturb the petroleum distillate matrix (Widdowson *et al.*, 2005; Marr *et al.*, 2006). We did not observe more weathered D₃/C₃ ratios for any vegetated sediment fractions relative to the non-vegetated sediment fractions. This outcome is not unexpected given the short exposure of sediment to vegetation (2 years).

Figure 2 shows cross plots of N₃/P₂ weathering ratios to %TOC for all sediment fractions. More weathered ratios are observed for *Phragmites* bulk sediment and humin fractions and willow tree humin relative to non-vegetated fractions. N₃/P₂ ratios for all samples in de-ashed humin were similar; this is not unexpected given the refractory nature of de-ashed humin and the short period of exposure to vegetation. Relationships between %TOC and N₃/P₂ ratios for non-vegetated and *Phragmites* bulk sediment and humin fractions are not apparent. In fact, there is no consistent pattern between N₃/P₂ ratios and %TOC for either non-vegetated or vegetated sediment fractions. Previously, we observed increased N₃/P₂ weathering with increased %TOC in distillate refinery waste colonized by *Phragmites* and other trees and shrubs after 30 years of plant growth (Gregory *et al.*, 2005). This trend is not evident in vegetated IHC sediments after only 2 years of plant growth. The substantial amount of fuel oil present in sediments may prohibit detection of plant carbon contributions to TOC by %TOC analyses. Our results show that %TOC content of sediment fractions is not indicative of PAH dissipation or even the presence and absence of vegetation.

Figure 3 shows a more consistent relationship between N₃/P₂ weathering ratios and PMC measurements. For bulk sediment and humin fractions, the most weathered ratios are observed in *Phragmites* fractions that contain more ¹⁴C activity, or modern carbon, than all other sediment fractions (Figure 1). Willow trees also had more weathered N₃/P₂ ratios in humin fractions and more modern carbon than non-vegetated humin. All three vegetated de-ashed humin fractions were more weathered than non-vegetated de-ashed humin, but only cattails and *Phragmites* contained more modern carbon than non-vegetated de-ashed humin.

Interestingly, all three vegetated humin fractions contain more modern carbon than non-vegetated humin (Figure 1; Dunnett's ANOVA, $P < 0.05$). This trend is not observed in bulk sediment fractions and is less apparent in de-ashed humin fractions. Increased modern carbon content for *Phragmites* and cattails humin (Figure 1) is related to greater carbon-normalized TPAH concentrations (Table 1), but only *Phragmites* humin shows a relationship between increased modern carbon and more weathered N₃/P₂ ratios. Rockne *et al.* (2002) and Shor *et al.*, (2003) observed that sediment fractions with plant detrital

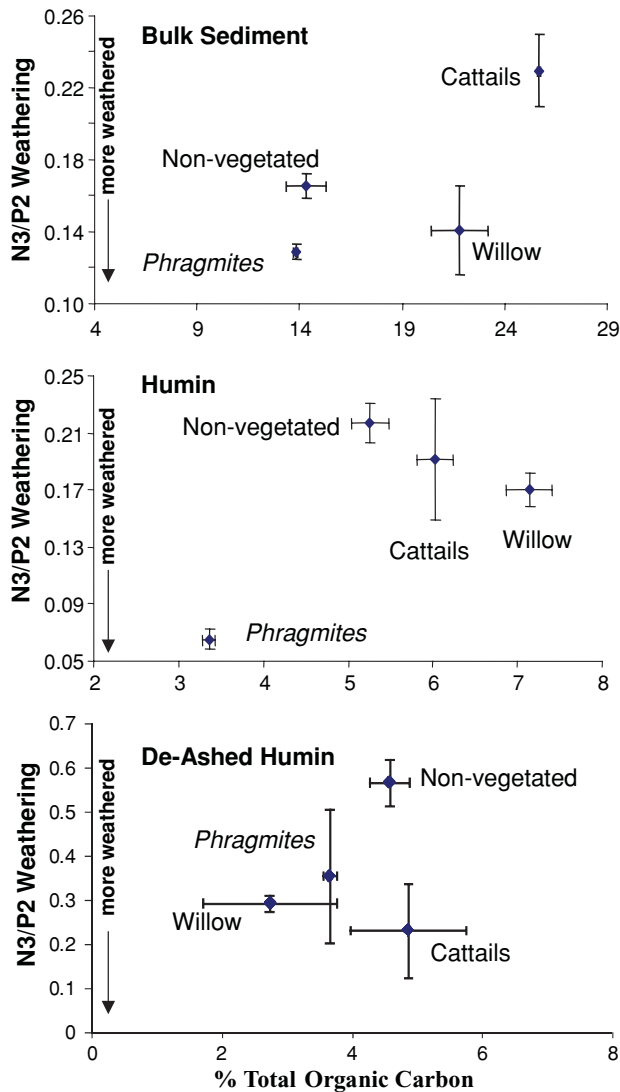


Figure 2 Cross-plots of C₃-naphthalenes to C₂-phenanthrenes (N₃/P₂) alkylated PAH homologues to %TOC for sediment and humin fractions of vegetated and non-vegetated sediments at the IHC site. Values are means \pm one standard deviation.

material and high PAH concentrations disproportionately impacted high molecular weight PAH desorption and more extensively desorbed all PAHs than sediment fractions without detrital material. These authors stressed the important role of plant material as a preferential sorbent in sediments in which other geosorbents such as soot are not the primary source of PAHs to sediments.

Phragmites australis is considered an invasive species, but it is also a useful model plant to study because of its tolerance to anthropogenic contamination and physiological characteristics. *Phragmites australis* is known for its translocation of oxygen and carbon from plant shoots/leaves to sediments *via* its roots (Minchinton, 2002). Nearly 50% of

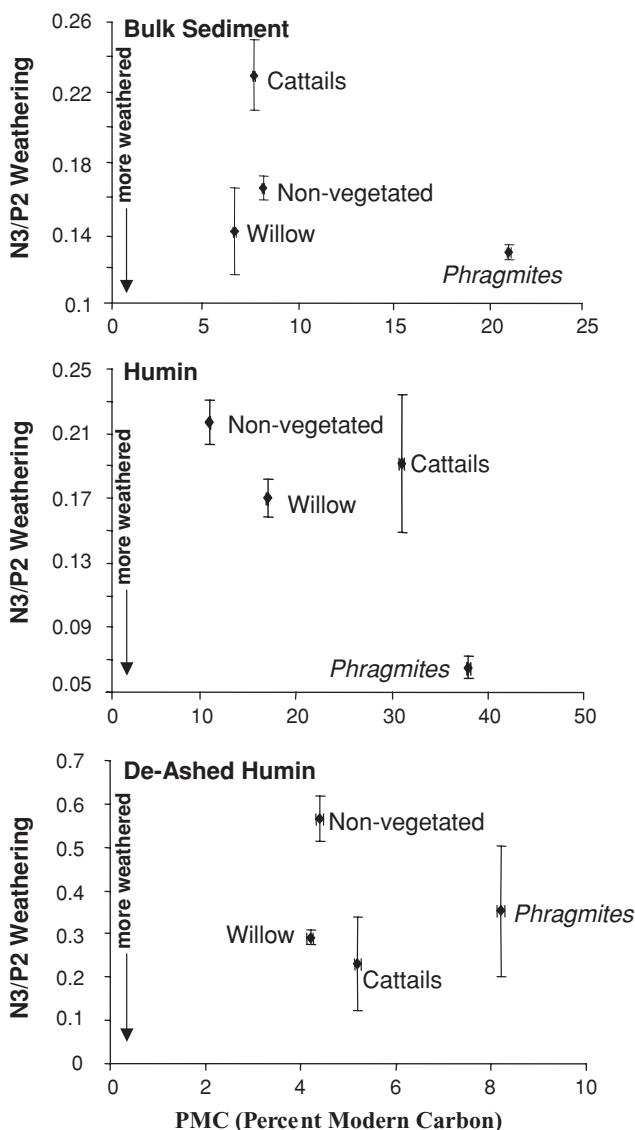


Figure 3 Cross-plots of C₃-naphthalenes to C₂-phenanthrenes (N₃/P₂) alkylated PAH homologues to PMC for sediment and humin fractions of vegetated and non-vegetated sediments at the IHC. Values are means ± one standard deviation.

its litter becomes substrate material for soils and sediments and the majority of its biomass is non-grazed (Asaeda *et al.*, 2002). Total organic acid concentrations in pore water of both deep water and land stands of *Phragmites australis* average 1100–1600 $\mu\text{mol/L}$, and are predominantly acetic, citric, tartaric, and malic acids (Cizkova *et al.*, 1999). These attributes, no doubt, contribute to *Phragmites*' success and tolerance of saturated (Armstrong and Armstrong, 2001), metal-contaminated (Ye *et al.*, 2003), saline (Chambers, Mozdzer, and Ambrose, 1998), and eutrophic environments (Lin *et al.*, 2002).



Courtesy of Steve Rock, USEPA

Figure 4 *Phragmites australis* and cattails (*Typha angustifolia*) growth in greenhouse containers. Plants were rooted in clean soil that was placed on top of IHC sediment. *Phragmites* grew around and into the oiled sediment, whereas cattails did not. (Courtesy of Steve Rock.)

Likewise, these characteristics may explain the increased amounts of plant carbon present in *Phragmites* sediments.

Visual differences between plant colonization of IHC sediments are presented in Figure 4. IHC sediments were planted with either cattails or *Phragmites* that had been harvested from the IHC site during sediment collection. Plants were rooted in clean soil on top of IHC sediment; the two sediments (clean and IHC) were separated by burlap material. As is evident in Figure 4, *Phragmites* roots grew around the burlap material and into the IHC sediment. Cattails roots did not penetrate IHC sediment and remained in the clean soil. Such distinct differences may readily explain the observed differences in plant carbon

accumulation and PAH weathering between *Phragmites* and cattail sediment fractions in our study.

CONCLUSION

This study shows the alteration of sediment composition in bulk and humin sediment fractions after 2 years of plant growth in fuel oiled sediments. Mass normalized TPAH concentrations did not decline in vegetated sediments relative to non-vegetated sediments. Carbon-normalized TPAH concentrations were significantly lower in vegetated bulk sediments, but higher in humin fractions. Percent TOC data was not a useful indicator of PAH concentrations, modern carbon (plant carbon) accumulation, or PAH weathering in vegetated sediment fractions relative to non-vegetated sediments. Significant increases in PMC content were observed with greater N_3/P_2 weathering in vegetated sediment fractions. *Phragmites* sediments contained more plant carbon and more weathered PAHs ratios than cattails or willow trees. This study highlights that other “qualities,” such as overall carbon transfer from plant to soils/sediments, may impact the efficacy and rate of PAH attenuation in engineered, plant–soil systems. The extent of carbon deposition from plant to sediment/soil appears to be species specific to plants.

Another interesting observation is the measurable increase of plant carbon in sediment humin after only 2 years of plant growth. Our results suggest that sequestration of biogenic carbon in more refractory portions of the sediment matrix may occur at faster rates than anticipated. Thus, using naturally abundant radiocarbon measurements to study plant and PAH carbon cycling at sites with significant petrogenic pollution may yield more interesting insights into carbon and contaminant cycling in sediments and soils.

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