Polycyclic Aromatic Hydrocarbons in Soil of the Canadian River Floodplain in Oklahoma

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The accumulation of polycyclic aromatic hydrocarbons (PAH) in soil, plants, and water may impart negative effects on ecosystem and human health. We quantified the concentration and distribution of 41 PAH (n = 32), organic C, total N, and S (n = 140) and investigated PAH sources using a chronosequence of floodplain soils under a natural vegetation succession. Soil samples were collected between 0- and 260-cm depth in bare land (the control), wetland, forest, and grassland areas near a closed municipal landfill and an active asphalt plant (the contaminant sources) in the north bank of the Canadian River near Norman, OK. Principal component, cluster, and correlation analyses were used to investigate the spatial distribution of PAH, in combination with diagnostic ratios to distinguish pyrogenic vs. petrogenic PAH suites. Total PAH concentration (ΣPAH) had a mean of 1300 ng g^{-1}, minimum of 16 ng g^{-1}, and maximum of 12,000 ng g^{-1}. At 0- to 20-cm depth, ΣPAH was 3500 ± 1600 ng g^{-1} (mean ± 1 SE) near the contaminant sources. The most common compounds were nonalkylated, high molecular weight PAH of pyrogenic origin, i.e., fluoranthene (17%), pyrene (14%), phenanthrene (9%), benzo(b)fluoranthene (7%), chrysene (6%), and benzo(a)anthracene (5%). ΣPAH in the control (130 ± 23 ng g^{-1}) was comparable to reported concentrations for the rural Great Plains. Perylene had a unique distribution pattern suggesting biological inputs. The main PAH contamination mechanisms were likely atmospheric deposition due to asphalt production at the 0- to 20-cm depth and past landfill operations at deeper depths.

Most PAH are toxic, carcinogenic, and persistent hydrophobic organic contaminants that are found ubiquitously in the environment due primarily to anthropogenic activities, such as incomplete combustion of fossil fuels and oil spills. These contaminants are harmful to humans and ecosystem health because they enter the food chain and may persist in the environment for decades (Sporstol et al., 1983; Jones et al., 1989b). There is concern that continuous anthropogenic activities may lead over time to an accumulation of PAH in soil, plants, and water (Trapido, 1999; Wilcke, 2007; Desaules et al., 2008). A long-term study on archived soils at the Rothamsted Experimental Station in southeast England, for example, showed a fourfold increase in PAH burden of the plow layer from the mid-1800s to the 1980s (Jones et al., 1989a). In terrestrial environments, PAH that are formed naturally are on average <10% of the total PAH pool, but they do occur in plants and are produced during forest or prairie fires or volcanic activities. They may be synthesized by algae, plants, or bacteria. A typical range for natural PAH in soil is 0 to 10 ng g^{-1} (Edwards, 1983).

By analyzing distributions of PAH compounds and their relative concentrations in soil, water, air, plant, or animal samples, it is possible to distinguish between PAH of pyrogenic origin, that is, compounds formed during combustion processes, and those of petrogenic origin, that is, those derived from petroleum sources such as oil spills (Youngblood and Blumer, 1975; Sporstol et al., 1983; Pies et al., 2008; Bu et al., 2009). Three PAH, naphthalene, anthracene, and fluoranthene, have been detected in groundwater near the closed municipal landfill at Norman, OK, suggesting the possible PAH migration from surface soils and sediments or buried waste materials into groundwater. The landfill is located on

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Abbreviations: ALKYL, alkylated polycyclic aromatic hydrocarbons; COMB, combustion polycyclic aromatic hydrocarbons; DIBENZ, dibenzothiophenes; Fluo/Pyr, fluoranthene to pyrene; MF/F, methyl-fluoranthenes and methyl-pyrenes to fluoranthene; MP/P, methyl-phenanthrenes and methyl-anthracenes to phenanthrene; P/A, phenanthrene to anthracene; PAH, polycyclic aromatic hydrocarbons; PCA, principal component analysis; PHPAH, parent high molecular weight polycyclic aromatic hydrocarbons; PLPAH, parent low molecular weight polycyclic aromatic hydrocarbons; QA–QC, quality assurance–quality control; SOC, soil organic carbon; SRM, standard reference material; UTM, Universal Transverse Mercator; ΣEPA16, sum of concentrations for the 16 PAH on the USEPA priority list.

an active floodplain of the Canadian River—its channel had shifted through time—and is representative of how cities in the United States have used floodplains for waste disposal (Barnes et al., 2004).

Previous investigations quantified organic compounds in landfill leachate and groundwater samples (Schlottmann, 2001; Eganhouse et al., 2001) and in newsprint samples from the inside of the landfill main cells (Chen et al., 2004). Little is known about possible presence and sources of PAH in soils and sediments. Thus, the objectives of this work were (i) to quantify the concentration, distribution, and composition of PAH suites in soil at the Norman landfill site and (ii) to infer information about possible PAH sources. In an effort to gather information on past land uses, we compared the PAH burden in soil under a natural vegetation succession that has been developing since landfill closure about 25 yr ago. Most previous studies that quantified PAH concentrations in soil measured primarily the 16 (nonalkylated) PAH on the USEPA priority list (EPA16). In this study, we analyzed a broad PAH suite composed of 41 PAH, including alkylated PAH (ALKYL), which may also comprise many carcinogenic PAH, and provide more complete information about PAH origin. The ALKYL of triaromatic compounds (e.g., phenanthrene and anthracene) are often used to distinguish between a pyrogenic and a petrogenic origin of PAH suites (Youngblood and Blumer, 1975; Yunker et al., 2002; Neff et al., 2005; Pies et al., 2008).

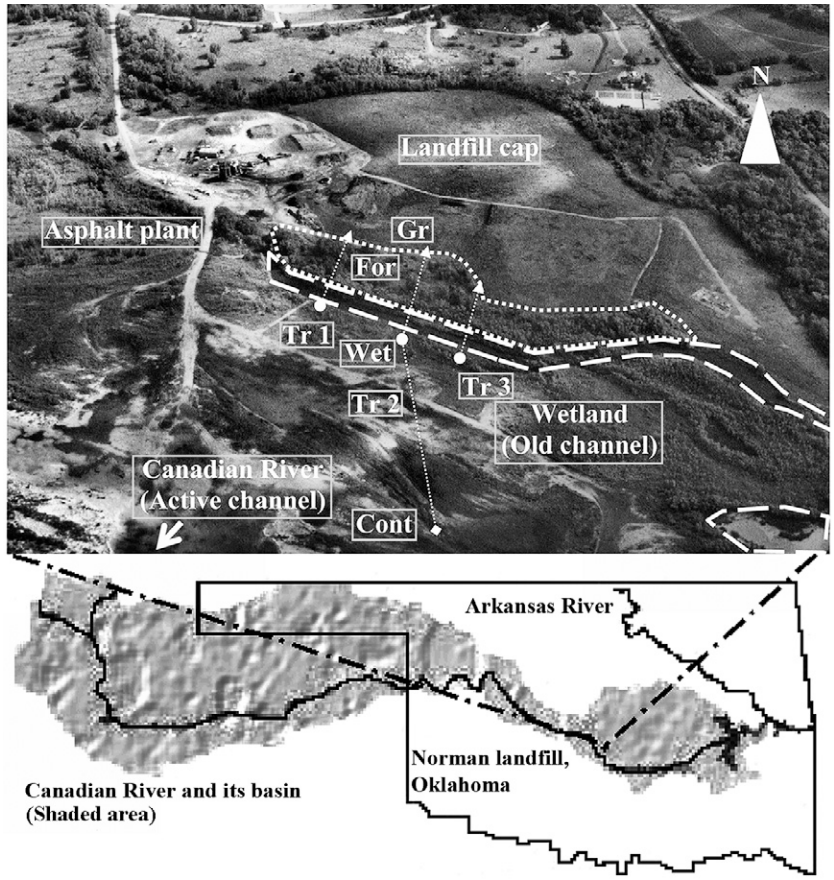


Fig. 1. Aerial view of the sampling areas near the closed municipal landfill at Norman, Oklahoma, in the south central Unites States: An asphalt plant in operation since the 1970s is located immediately north of a wetland that represents a remnant of the old Canadian River channel. Sampling areas within transects (Tr) 1, 2, and 3: Cont, control (square) nearest to the active channel; Wet, areas (circles) near the wetland (dashed contour) under common reed; For, sampling areas within transect direction and under arboreal vegetation (dotted contour); and Gr, areas (triangles) under grass vegetation.

Materials and Methods

Research Site

The study area is located along the Canadian River in Cleveland County, central Oklahoma (35°10′6″ N, 97°26′41″ W; Fig. 1). The climate of this region is moist, subhumid, and continental and is characterized by high-intensity rainfall (Soil Survey Staff, 1987). Mean annual precipitation is 955 mm, with a minimum of 38 mm in January and maximum of 135 mm in May; mean annual temperature is 15.6°C, with a minimum of 2.4°C in January and maximum of 27.8°C in July (1971–2000, Oklahoma Climatological Survey, 2009).

Topography consists of gently rolling plains with slopes <5%. Soils are quaternary alluvium on terrace deposits that lay over the Hennessey group, a lower Permian mudstone and shale unit. The most common soil type of the study area is the Gracemore soil series (sandy, mixed, thermic Oxyaquic Udifluvents). The typical soil profile has a loamy fine sand A horizon, from the surface to about 30-cm depth, and a fine sand C horizon, from 30- to 180-cm depth (Soil Survey Staff, 1987). Soil pH in a 1:1 soil mass to water volume ratio ranges 7.5 to 8.7, whereas soil pH in a 1:2 soil mass to 0.01 M $CaCl_2$ volume ratio ranges 7.2 to 7.9 (Sartori, unpublished data, 2009).

The water table near the active channel ranges from 0.15 to 1 m below the surface (Soil Survey Staff, 1987), and from <1 to about 4 m, moving north from the wetland area. In the study area (Fig. 1), the river channel moved approximately 500 m southward to its present location after two significant floods in 1986 and 1987 (Curtis and Whitney, 2003). A natural wetland has remained since that migration, encompassing a remnant of the old Canadian River channel (Eganhouse et al., 2001). Common reed [*Phragmites australis* (Cav.) Trin. ex Steud.] occurs in monotypic stands near the wetland and decreases in abundance moving north from the Canadian River active channel. Forested areas (i.e., uneven-aged stands) occur north of the wetland area near the landfill cap and derive from a natural vegetation succession (tree age ranges from 1 to ~25–30 yr old). Most common woody species include eastern cottonwood (*Populus deltoides* Bart. ex Marsh.), narrowleaf willow (*Salix exigua* Nutt.), and salt cedar (*Tamarix gallica* L.) (Burgess, 2006).

The site has been heavily disturbed by a variety of land uses, including the abandoned Norman Municipal Landfill, which operated in varying forms from the 1920s until 1985 on the north bank of the Canadian River (Fig. 1). The landfill covers a

total area of approximately 350,000 m^2 of the active floodplain, including unmitigated areas where waste was buried before 1970 and the unlined, clay-capped landfill, where most waste was buried from 1970 to 1985. It contains primarily residential and commercial solid waste, although accidents of hazardous waste disposal were also reported. Throughout the site, open burning was routinely and legally practiced during the time of operation as "open dump" (1920s–1971), without restrictions on the type of material being discarded (Curtis and Whitney, 2003). Beginning in 1960, the operators of the landfill excavated trenches to the water table and buried wastes beneath a 15-cm layer of sand (Schlottmann, 2001). Trenches were abandoned in 1971, when the City of Norman leased the property to the Norman Asphalt plant, for operation of a sanitary landfill (Curtis and Whitney, 2003), and wastes were deposited on lifts of sand 0.6 m above the water table. The landfill was closed in 1985 and covered with a low-permeability cap and revegetated with Bermudagrass (*Cynodon* spp.), leaving two mounds rising about 12 m above the surrounding land surface (Schlottmann, 2001). Major impacts of the asphalt plant on the floodplain area include sand quarrying near the Canadian River active channel and atmospheric emissions during asphalt production from 1970s to present.

Soil and Sediment Sampling

Soil and sediment samples were collected during September 2007 and June to July 2008, following a stratified random sampling with vegetation type as substratum (Fig. 1), within which soil samples were collected at depths ranging from 0 to 260 cm and split into 20-cm-depth increments (n = 140). Along transects 1 to 3, 17 sampling points were randomly selected and geo-referenced within the control (in two points for the 0–140 cm depth increment), wetland (five for the 0–200 cm depth increment), forest (six for 0–260 cm), and grassland areas (four for 0–200 cm). Forest areas were unmitigated with clear indication of past landfill operations because buried "trash" was often found during sampling. Intensity of sampling was highest in these areas and lowest in the control and wetland areas, where there was a lower variability in soil C and no signs of past landfill operations.

In the sampled areas under forest, the soil profile typically lacked a well-developed forest floor layer. The low stand density and canopy closure had favored the presence of a dense understory vegetation with rapidly decomposing plant litter. A stainless steel auger with extension (8.3-cm diam.; AMS, American Falls, ID) was used for collecting mineral soil samples for chemical analyses in areas under forest and in all other areas for depths <160 cm, after gentle removal of the understory vegetation; a Geoprobe 540UD direct push soil probing unit (4.0-cm diam., Geoprobe, Salina, KS) mounted on a 1-ton pickup truck was used in all other locations and for depths >160 cm. Samples were kept in closed plastic bags under ice and stored in a nearby storage facility during sampling. They were returned to an air-conditioned laboratory in ice and kept in open bags to air dry for 3 wk. To minimize cross-contamination after air-drying, the dried samples were carefully mixed, passed through a 2-mm sieve, and stored in closed bags until analysis. During these phases, there may be losses of the most volatile organic compounds (e.g., up to 45% for naphthalene). Losses of other, less-volatile compounds may also occur but are generally within the margins of the analytical error (Krauss et al., 2000; Wilcke and Amelung, 2000).

Analysis of PAH

For the quantification of PAH concentrations, a subset (n = 32) of the original samples was selected for the control, wetland areas along transects 1 and 2, and the forest and grassland areas along all three transects (Fig. 1). Samples represented the soil surface (0–20 cm depth increment, n = 9), medium (40–60 cm, n = 8; 60–80 cm, n = 7; and 80–100 cm, n = 1), and deep layers (160–180 cm, n = 1; 160–200 cm, n = 5; and 240–260 cm, n = 1). Polycyclic aromatic hydrocarbon analysis followed the NOAA NS&T methods (Denoux et al., 1998; Qian et al., 1998). Briefly, weighed aliquots (~10 g) of air-dried soil samples were extracted in extraction cells with HPLC grade dichloromethane (Burdick and Jackson, Muskegon, MI) using an ASE 200 Accelerated Solvent Extractor (Dionex, Houston, TX), after addition of surrogate standards, i.e., deuterated PAH (d8-Naphthalene, d10-Acenaphthene, 10-Phenanthrene, d12-Chrysene, and d12-Perylene) (ULTRA Scientific, North Kingston, RI). The extracts were concentrated in a water bath at 60°C to ~1 to 2 mL, purified by Si/Al column chromatography, and analyzed using gas chromatography–mass spectrometry. Just before analysis, the extracts were spiked with a solution containing the gas chromatography internal standards (i.e., d10-Fluorene and d12-Benzo(a)pyrene). The quality assurance–quality control (QA–QC) samples included a method blank, a duplicate sample, a matrix spike sample, and a standard reference material (SRM) (NIST 1944, Gaithersburg, MD) per batch of 20 samples or fewer. The QA–QC parameters included the percentage difference between the original and duplicate sample relative to their average, the matrix spike recovery, analytes within the 95% confidence interval for the SRM, and the recoveries of surrogate standards. The recoveries of the surrogates were monitored in each sample using the relative response factor of the surrogate to the gas chromatography internal standard. The QA–QC samples were processed and analyzed with every analytical batch.

The purified extracts were analyzed on a Hewlett-Packard 5890/5970 gas chromatography–mass spectrometer (Hewlett-Packard, Boise, ID), using a selective ion monitoring detection technique, after the addition of internal standards. The calibration was performed with known concentrations of analytes at five different concentration levels, and the average response factors of the analytes were used for PAH concentration determination relatively to the added surrogates. The 41 analyzed PAH are listed in Table 1 and include 7 parent (i.e., nonalkylated) low molecular weight (PLPAH), 12 parent high molecular weight (PHPAH), 4 dibenzothiophenes (DIBENZ), and 18 alkylated PAH (ALKYL). ALKYL include compounds with C1- (= methyl-), C2-, C3-, and C4-alkyl groups (chains of hydrocarbons) that contain one, two, three, and four carbons, respectively.

Soil Organic Carbon, Nitrogen, and Sulfur

Soil total C, N, and S concentrations were measured (n = 140) after pulverization by a dry combustion technique (Nelson and Sommers, 1996), using a Vario EL *III* CHNOS elemen-

Table 1. Comparison among concentrations (mean ± 1 SE) of polycyclic aromatic hydrocarbons (PAH) in soil extracts by depth and vegetation type. Soil samples were collected (0- to 200-cm depth) from alluvial soils (Oxyaquic Udifluvents) under a natural vegetation succession of the Canadian River floodplain in Oklahoma, near an active asphalt plant and a closed municipal landfill, during September 2007 and June to July 2008. Samples collected under different vegetation types were grouped based on similarities in PAH suites using cluster analysis.

List of PAH†	Groups by soil depth and vegetation type‡					
	0–20 cm		40–60 cm		60–80 cm	160–200 cm
	Control–wetland	Forest–grassland	Control–grassland	Forest–wetland	Overall mean	Overall mean
	ng g^{-1}					
ΣPAH	130 ± 23	3500 ± 1600	48 ± 11	3900 ± 2700	770 ± 360	50 ± 14
ΣPLPAH	44 ± 3.6	460 ± 260	17 ± 4.4	450 ± 310	110 ± 48	9.7 ± 2.3
ΣPHPAH	36 ± 18	2400 ± 1000	9.0 ± 3.0	2800 ± 2000	440 ± 220	13 ± 8.4
ΣDIBENZ	3.9 ± 0.30	39 ± 24	1.6 ± 0.26	30 ± 15	17 ± 11	1.3 ± 0.31
ΣALKYL	42 ± 5.3	630 ± 290	21 ± 4.1	640 ± 370	210 ± 110	26 ± 7.9
ΣCOMB	33 ± 17	2300 ± 1000	7.4 ± 2.1	2600 ± 1900	410 ± 210	7.8 ± 4.2
ΣEPA16	74 ± 16	2600 ± 1200	23 ± 5.9	2900 ± 2100	480 ± 230	16 ± 5.0
PLPAH						
Acenaphthene	1.5 ± 0.39	30 ± 19	0.40 ± 0.057	34 ± 27	4.2 ± 2.0	0.40 ± 0.082
Acenaphthylene	0.50 ± 0.18	6.5 ± 2.1	0.19 ± 0.057	11 ± 8.0	3.5 ± 2.3	0.19 ± 0.045
Anthracene	0.99 ± 0.39	51 ± 34	0.26 ± 0.043	51 ± 41	7.0 ± 3.6	0.30 ± 0.13
Biphenyl	1.4 ± 0.11	4.9 ± 1.2	0.52 ± 0.065	7.9 ± 2.7	6.1 ± 4.1	0.68 ± 0.16
Fluorene	3.4 ± 0.47	27 ± 16	0.69 ± 0.14	30 ± 22	5.3 ± 2.5	0.67 ± 0.10
Naphthalene	15 ± 6.3	24 ± 5.3	11 ± 3.8	39 ± 12	36 ± 14	3.6 ± 2.0
Phenanthrene	21 ± 3.1	310 ± 190	4.1 ± 0.58	280 ± 210	48 ± 22	3.9 ± 0.78
PHPAH						
Benzo(a)anthracene	2.3 ± 1.3	170 ± 74	0.44 ± 0.13	230 ± 180	32 ± 18	0.53 ± 0.28
Benzo(a)pyrene	2.2 ± 1.3	160 ± 66	0.57 ± 0.26	210 ± 140	33 ± 19	0.70 ± 0.35
Benzo(b)fluoranthene	4.0 ± 2.2	250 ± 93	0.71 ± 0.19	330 ± 220	56 ± 29	0.99 ± 0.54
Benzo(e)pyrene	2.5 ± 1.3	140 ± 47	0.87 ± 0.32	190 ± 120	41 ± 22	0.75 ± 0.42
Benzo(k)fluoranthene	1.6 ± 0.84	89 ± 32	0.37 ± 0.10	110 ± 74	19 ± 9.7	0.50 ± 0.23
Benzo(g,h,i)perylene	1.9 ± 0.80	110 ± 35	0.86 ± 0.28	170 ± 96	35 ± 19	0.49 ± 0.38
Chrysene	3.6 ± 1.9	210 ± 78	0.91 ± 0.30	260 ± 180	47 ± 24	0.86 ± 0.46
Dibenzo(a,h)anthracene	0.30 ± 0.18	20 ± 7.2	ND§	37 ± 25	7.0 ± 4.1	0.056 ± 0.056
Fluoranthene	7.5 ± 3.5	570 ± 310	1.2 ± 0.21	540 ± 430	64 ± 32	1.3 ± 0.58
Indeno(1,2,3–c,d)pyrene	1.7 ± 0.67	110 ± 40	0.48 ± 0.25	180 ± 120	32 ± 17	0.46 ± 0.34
Perylene	2.1 ± 0.66	52 ± 22	1.6 ± 1.3	69 ± 46	18 ± 6.9	5.4 ± 4.2
Pyrene	6.0 ± 3.2	470 ± 250	0.96 ± 0.23	440 ± 340	52 ± 27	1.2 ± 0.61
DIBENZ						
C1-Dibenzothiophenes	1.1 ± 0.088	7.0 ± 3.9	0.42 ± 0.056	7.2 ± 3.4	3.9 ± 2.4	0.40 ± 0.047
C2-Dibenzothiophenes	1.2 ± 0.17	8.9 ± 5.1	0.53 ± 0.10	6.3 ± 2.4	5.7 ± 4.1	0.36 ± 0.12
C3-Dibenzothiophenes	0.52 ± 0.015	8.5 ± 6.2	0.40 ± 0.12	4.4 ± 1.8	4.7 ± 3.6	0.24 ± 0.12
Dibenzothiophene	1.0 ± 0.073	15 ± 9.1	0.24 ± 0.032	12 ± 8.7	2.7 ± 1.4	0.28 ± 0.037

tal analyzer (Elementar Americas, Inc., Mt. Laurel, NJ). Soil inorganic C concentration was determined through gasometric determination of calcite and dolomite concentration (n = 140) (Loeppert and Suarez, 1996). Soil organic C (SOC), that is, the mass of C in soil organic matter, was computed as the difference between total and inorganic C.

Statistical Analyses

Multivariate statistical methods were used for the screening, data reduction, and analysis of the variance–covariance relationships among all 41 PAH. Principal component analysis (PCA) was evaluated via SAS PROC PRINCOMP (SAS Institute, 1999) for different soil depths and types of variable transformations, including all 32 samples and 41 PAH, based on diagnostics procedures suggested by Johnson and Wichern (1998, p. 458–513). The most satisfactory analysis was based on a two-stage transformation of original variables (n = 32), including only the EPA16 plus perylene. The concentration of each PAH was first divided by the corresponding total PAH concentration, $\sum_{i=1}^{41} \mathrm{PAH}_i$ (i.e., the sum of concentrations for 41 compounds), and then standardized to a normal distribution, with mean of 0 and variance of 1, to account for large differences in variance among variables. For interpretation of the first principal components, Pearson's correlations of PAH with principal component scores were considered. The final step of the multivariate analysis included cluster analysis conducted on the first four principal components by soil depth, to identify similarities among individual samples by depth and gather information about PAH distribution across the landscape.

Spearman's correlation analysis was used as a nonparametric measure of correlation between sampling position and PAH concentrations by soil depth, to test the effect of distance from

Table 1 continued.

List of PAH†	Groups by soil depth and vegetation type‡					
	0–20 cm		40–60 cm		60–80 cm	160–200 cm
	Control–wetland	Forest–grassland	Control–grassland	Forest–wetland	Overall mean	Overall mean
	ng g^{-1}					
ALKYL						
C1-Chrysenes	1.7 ± 0.52	86 ± 31	0.96 ± 0.60	97 ± 63	24 ± 12	0.66 ± 0.45
C1-Fluoranthenes and pyrenes	1.8 ± 0.76	110 ± 59	0.69 ± 0.22	120 ± 90	18 ± 8.6	0.45 ± 0.34
C1-Fluorenes	2.6 ± 0.36	10 ± 3.9	1.1 ± 0.18	10 ± 5.2	3.9 ± 1.7	1.0 ± 0.11
C1-Naphthalenes	5.6 ± 1.6	26 ± 5.2	2.2 ± 0.46	33 ± 12	22 ± 16	6.5 ± 3.1
C1-Phenanthrenes and anthracenes	5.5 ± 0.88	77 ± 40	1.8 ± 0.29	75 ± 51	19 ± 9.2	1.5 ± 0.29
C2-Chrysenes	0.43 ± 0.26	35 ± 16	0.65 ± 0.58	34 ± 18	14 ± 8.5	0.21 ± 0.21
C2-Fluoranthenes and pyrenes	1.2 ± 0.097	51 ± 28	0.80 ± 0.30	96 ± 74	17 ± 8.5	0.38 ± 0.25
C2-Fluorenes	3.0 ± 0.36	7.8 ± 2.5	1.7 ± 0.47	8.5 ± 2.6	5.0 ± 2.4	0.95 ± 0.13
C2-Naphthalenes	4.8 ± 0.81	19 ± 3.9	2.2 ± 0.43	23 ± 7.0	15 ± 10	6.9 ± 3.9
C2-Phenanthrenes and anthracenes	2.9 ± 0.45	51 ± 29	1.4 ± 0.25	39 ± 21	16 ± 9.2	1.2 ± 0.30
C3-Chrysenes	0.29 ± 0.19	23 ± 12	0.43 ± 0.32	12 ± 5.5	7.4 ± 5.1	0.26 ± 0.26
C3-Fluoranthenes and pyrenes	0.43 ± 0.24	32 ± 18	0.51 ± 0.30	30 ± 18	8.9 ± 4.7	0.22 ± 0.16
C3-Fluorenes	2.2 ± 0.54	6.7 ± 3.5	1.4 ± 0.37	6.4 ± 2.3	4.3 ± 2.4	0.41 ± 0.26
C3-Naphthalenes	5.1 ± 0.70	18 ± 3.7	2.6 ± 0.43	18 ± 5.0	12 ± 7.6	3.8 ± 1.1
C3-Phenanthrenes and anthracenes	1.3 ± 0.27	36 ± 24	0.93 ± 0.22	26 ± 12	10 ± 6.5	0.56 ± 0.26
C4-Chrysenes	0.33 ± 0.17	9.4 ± 6.5	0.37 ± 0.21	7.0 ± 2.7	3.9 ± 2.5	ND
C4-Naphthalenes	2.6 ± 0.22	7.1 ± 1.5	1.1 ± 0.15	7.1 ± 2.2	5.8 ± 3.6	0.92 ± 0.26
C4-Phenanthrenes and anthracenes	0.28 ± 0.17	18 ± 15	0.34 ± 0.087	4.7 ± 1.8	2.1 ± 1.0	0.12 ± 0.078

† Soil samples were air-dried and extracted in extraction cells with dichloromethane. The extracts were purified by column chromatography and analyzed using gas chromatography/mass spectrometry. The sum (Σ) of concentrations is reported for all 41 PAH analyzed (ΣPAH, total PAH concentration), parent (i.e., nonalkylated) low molecular weight PAH (ΣPLPAH), parent high molecular weight PAH (ΣPHPAH), dibenzothiophenes (ΣDIBENZ), and alkylated PAH (ΣALKYL). The sum of concentrations for the 10 combustion PAH (ΣCOMB) (Prahl and Carpenter, 1983) and the 16 PAH that are on the USEPA priority list (ΣEPA16) are also reported. C1-, C2-, C3-, and C4- indicate alkyl groups (chains of hydrocarbons) that contain one, two, three, and four carbons, respectively.

‡ Only the overall means across all vegetation types are reported for the 60- to 80- and 160- to 200-cm depth increments.

§ ND, not detected.

the asphalt plant–landfill on PAH concentrations. Position was expressed as Universal Transverse Mercator (UTM) northing and easting. Included in these analyses were $\sum_{i=1}^{41}\mathrm{PAH}_i$, the concentration of parent low molecular weight ($\sum_{i=1}^{7}\mathrm{PLPAH}_i$), parent high molecular weight ($\sum_{i=1}^{12}\mathrm{PHPAH}_i$), dibenzothiophenes ($\sum_{i=1}^{4}\mathrm{DIBENZ}_i$), alkylated ($\sum_{i=1}^{18}\mathrm{ALKYL}_i$), and combustion PAH ($\sum_{i=1}^{10}\mathrm{COMB}_i$). The sum of concentrations for the EPA16 ($\sum_{i=1}^{16}\mathrm{EPA16}_i$) was excluded from this analysis because the EPA16 correspond to the parent PAH listed in Table 1, with the exception of biphenyl, perylene, and benzo(e)pyrene. (Sub- and superscripts are omitted in the remainder of the text.) ΣCOMB is the sum of concentrations for fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, ideno(1,2,3–cd)pyrene, and benzo(g,h,i)perylene (Prahl and Carpenter, 1983). Similarly, Spearman's correlation analysis between soil depth, SOC, total N, and S concentration and proportion of different PAH was conducted including all samples (n = 32) and by vegetation type only for forest and grassland (n = 12), to identify the relative distributions of PAH with depth and their relationship with soil organic matter. These proportions were computed as the ratios of ΣPLPAH, ΣPHPAH, ΣDIBENZ, ΣALKYL, and ΣCOMB to ΣPAH.

One-way MANOVAs were conducted by depth using SAS PROC GLM (SAS Institute, 1999) for the log-transformed concentration of SOC, total N, and S, as response variables, and vegetation, as predictor variable. If MANOVA was significant (α = 0.05) based on Wilks' Lambda test, we then considered the individual ANOVAs (α = 0.1) by variable and constructed a set of orthogonal contrasts of interest to test differences due to vegetation type: (A) forest vs. other vegetation types, (B) grassland vs. control and wetland, and (C) control vs. wetland.

PAH Diagnostic Ratios

Ratios were computed between pairs of parent PAH to interpret PAH sources on the basis of the concept of heat of formation (H_f), the difference between the energy of formation of a certain PAH isomer and the energy of formation of its corresponding, thermodynamically most stable isomer (Budzinski et al., 1997). The reference value of zero, H_f = 0 in joules per mole, is typically assigned to the most stable isomer and is referred as the *reference isomer*. The concentration of a reference isomer in any given PAH suite remains relatively stable despite changes in temperature during a fire or other combustion processes (Budzinski et al., 1997; Yunker et al., 2002).

The selected ratio for molar mass 178 g mol^{-1} was phenanthrene (i.e., the reference isomer) to anthracene (P/A) with H_f = 23.0 kJ mol^{-1}: P/A is <10 for PAH suites of pyrogenic origin and >10 for petrogenic origin. The ratio of fluoranthene (H_f = 86.1 kJ mol^{-1}) to pyrene (i.e., the reference isomer) (Fluo/Pyr) for molar mass 202 g mol^{-1} is >1 for pyrogenic origin and vice versa for petrogenic origin (Yunker et al., 2002). We also computed the ratio of methyl-phenanthrenes and methyl-anthracenes to phenanthrene (MP/P), and methyl-fluoranthenes and methyl-pyrenes to fluoranthene (MF/F). These ratios are based on the findings that there is an inverse relationship between the temperature of formation and the abundance of alkyl carbons in pyrogenic PAH suites. A pyrogenic origin is assumed when these ratios are <1 and vice versa for petrogenic origin (Sporstol et al., 1983; Masclet et al., 1987; Neff et al., 2005). The ΣCOMB to ΣPAH ratio was also considered to describe the distribution of COMB with depth.

Results

PAH Concentration and Distribution

No analytes were detected in the method blank at concentrations greater than three times the analytical method detection limits. The percentage difference between the original and duplicate sample was on average 24.6%. Recoveries of the spiked analytes and of surrogate standards were in the range of 40 to 120%. All analytes were within the 95% confidence interval for each SRM target compound that is provided with the NIST certification. ΣPAH had a mean value of 1300 ng g^{-1}, median of 140 ng g^{-1}, minimum of 16 ng g^{-1}, and maximum of 12,000 ng g^{-1} (Table 2). The five samples with the lowest ΣPAH (16–32 ng g^{-1}) were found in the subsurface under all vegetation types, except under forest: in the control at 40 to 80 cm depth, in the grassland at 160 to 200, and wetland area at 80 to 100 along transect 2. Instead, the five samples with the highest ΣPAH (2200–12,000 ng g^{-1}) were all at shallower depths under forest and grassland areas (three samples at 0- to 20-, one at 40- to 60-, and one at 60- to 80-cm depth).

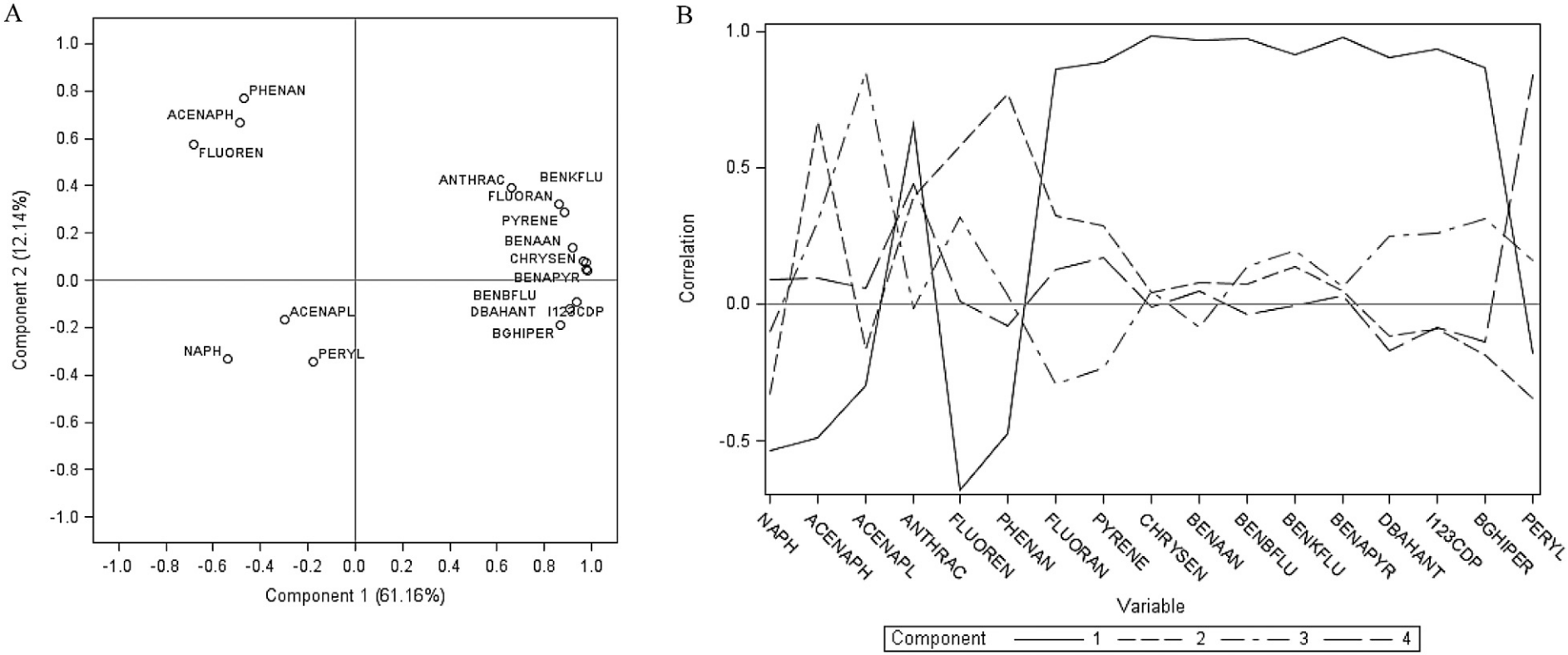
Results from PCA showed that PHPAH played a major role in explaining the variability in the data. The original variables were reduced to four principal components that explained 87.6% of the total variance and had eigenvalues >1. The PHPAH were all grouped in the right side of the pattern plot shown in Fig. 2A, indicating a positive and significant correlation with the first principal component. All PHPAH with the exception of perylene had r ranging from 0.86 (fluoranthene) to 0.98 (chrysene) ($p < 0.001$). Most PLPAH with the exception of anthracene were distributed in the left side of the pattern plot (Fig. 2A), indicating either a negative correlation with the first principal component and/or positive and significant correlations with the second or other remaining components. Anthracene was the only PLPAH highly correlated with the first principal component ($r = 0.66$, $p < 0.0001$), in addition to being correlated with the second and fourth components ($r = 0.4$, $p < 0.05$) (Fig. 2B). Phenanthrene, acenaphthene, and fluorene had positive and significant correlations with the second and third principal components—their correlation with the first principal component was negative. Perylene was the only variable significantly correlated with the fourth component ($r = 0.84$, $p < 0.0001$, Fig. 2B) and had no correlation with the first two components as indicated by its location near the center in Fig. 2A.

Cluster analysis within the 0- to 20-cm depth (Fig. 3) identified two major groups of samples, whose averages are reported in Table 1. ΣPAH was approximately 30-fold greater or more in samples collected under the forest–grassland areas (3500 ± 1600 ng g^{-1}) than those from the control and wetland areas (130 ± 23 ng g^{-1}). The only sample of the forest–grassland group with relatively low ΣPAH was from the grassland area of transect 3 (Gr3) located to the east of the asphalt plant (Fig. 3 and Table 2). The six prevalent compounds for the control–wetland group (Table 1) were phenanthrene (17%), naphthalene (12%), fluoranthene (12%), pyrene (6%), C1-naphthalenes (5%), and C1-phenanthrenes and C1-anthracenes (5%), whereas the forest/grassland group contained more PHPAH, i.e., fluoranthene (17%), pyrene (14%), phenanthrene (9%), benzo(b)fluoranthene (7%), chrysene (6%), and benzo(a) anthracene (5%).

A similar clustering structure occurred within the 40- to 60-cm depth. Concentrations for the group composed mainly of forest samples (3900 ± 2700 ng g^{-1}) were about 80-fold greater than those for the control–grassland group (48 ± 11 ng g^{-1}). The most abundant PAH for the control–grassland group were naphthalene (22%), phenanthrene (9%), C3-naphthalenes (5%), C2-naphthalenes (5%), C1-naphthalenes (5%), and C1-phenanthrenes and C1-anthracenes (4%); the group composed mainly of samples from the forest areas included fluoranthene (14%), pyrene (11%), benzo(b)fluoranthene (8%), phenanthrene (7%), chrysene (7%), and benzo(a)anthracene (6%).

At depths >60 cm, the main groups identified by cluster analysis had negligible differences in concentrations and did not show any correspondence between concentration and distance from the main contaminant sources. Therefore, only grand averages for these subsurface layers were reported in Table 1. The most abundant compounds for the 60- to 80-cm depth were fluoranthene (8%), benzo(b)fluoranthene (7%), pyrene (7%), phenanthrene (6%), chrysene (6%), and benzo(e)pyrene (5%); the most abundant compounds within the 160- to 200-cm depth were C2-naphthalenes (14%), C1-naphthalenes (13%), perylene (11%), phenanthrene (8%), C3-naphthalenes (8%), and naphthalene (7%).

Results of Spearman's correlation analysis for the 0- to 20-cm depth showed a positive correlation ($r = 0.65$, $p < 0.1$) between ΣPAH and UTM northing: the highest correlations were for the individual groups, ΣPHPAH and ΣCOMB ($r = 0.73$, $p < 0.05$), followed by ΣDIBENZ ($r = 0.67$, $p < 0.05$), ΣALKYL ($r = 0.65$, $p < 0.1$), and ΣPLPAH ($r = 0.65$, $p < 0.1$). Spearman's correlation analysis ($n = 32$) showed a negative correlation between soil depth and the proportion of PHPAH or COMB ($r = -0.4$, $p < 0.05$) and a positive correlation between soil depth and the proportion of ALKYL ($r = 0.45$, $p < 0.01$). Results of correlation analysis by vegetation type ($n = 12$) showed a negative correlation between the proportion of PHPAH or COMB and soil depth under forest ($r = -0.7$, $p < 0.01$). Soil organic carbon was positively correlated with the proportion of



Parent low molecular weight PAH:
ACENAPH, Acenaphthene; ACENAPL, Acenaphthylene; ANTHRAC, Anthracene; FLUOREN, Fluorene; NAPH, Naphthalene; PHENAN, Phenanthrene.

Parent high molecular weight PAH:
BENAAN, Benzo(a)anthracene; BENAPYR, Benzo(a)pyrene; BENBFLU, Benzo(b)fluoranthene; BENKFLU, Benzo(k)fluoranthene; BGHIPER, Benzo(g,h,i)perylene; CHRYSEN, Chrysene; DBAHANT, Dibenzo(a,h)anthracene; FLUORAN, Fluoranthene; I123CDP, Indeno(1,2,3–c,d)pyrene; PERYL, Perylene; PYRENE, Pyrene.

Fig. 2. (A) Pattern plot of principal component 1 by component 2 with percentages of variance explained by each component (in parenthesis) and (B) component pattern profiles for the 16 polycyclic aromatic hydrocarbons (PAH) that are on the USEPA priority list plus perylene (n = 32). The scale is Pearson's correlation coefficient between components and individual variables.

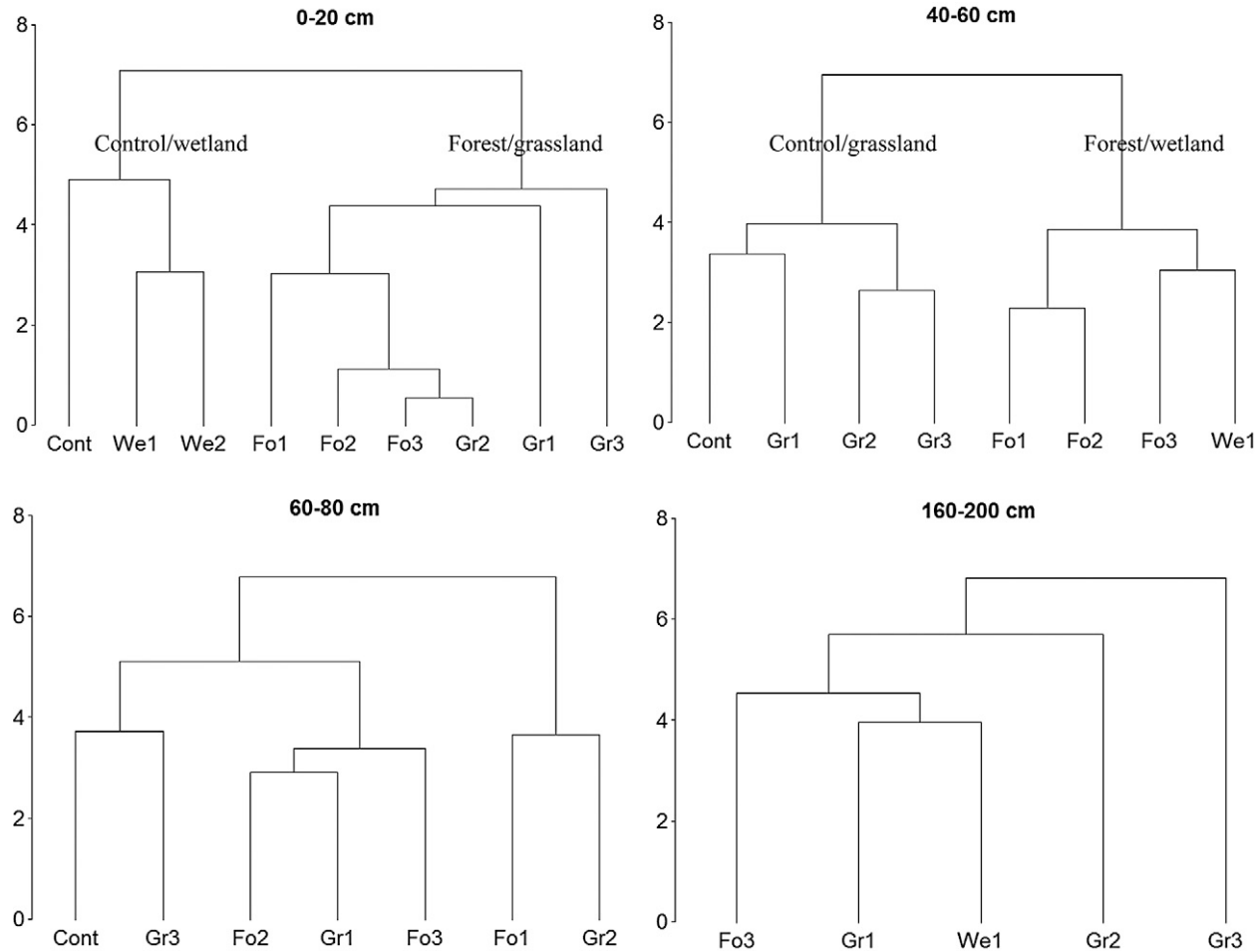


Fig. 3. Dendrograms from cluster analysis by depth increment to investigate the spatial distribution of polycyclic aromatic hydrocarbons (PAH) in alluvial soils (Oxyaquic Udifluvents). Samples were collected at 20-cm-depth increments (within 0–200 cm) along a riparian vegetation succession of the Canadian River floodplain in Oklahoma, near an active asphalt plant and a closed municipal landfill, during September 2007 and June to July 2008. Abbreviations indicate the vegetation type (Cont, control area; We, wetland areas; Fo, areas with arboreal vegetation; or Gr, grassland) and the transect number (1, 2, or 3) of the sampled areas. Vertical axes represent the average distance between clusters.

PHPAH (r = 0.68, p < 0.001) and COMB (r = 0.66, p < 0.001), and negatively correlated with the proportion of PLPAH (r = −0.52, p < 0.01), DIBENZ (r = −0.52, p < 0.05), and ALKYL (r = −0.51, p < 0.01).

Origin of PAH

Most samples were dominated by PAH suites of pyrogenic origin with P/A < 10, Fluo/Pyr > 1, MP/P < 1, and MF/F < 1 (Table 2). This first category corresponds to the forest–grassland (0- to 20-cm depth) and forest–wetland (40- to 60-cm depth) samples that were identified using cluster analysis. Samples with P/A > 10 and/or Fluo/Pyr ≤ 1 likely had a mixed composition of both pyrogenic and petrogenic origin, as indicated also by the corresponding ratios with alkylated compounds. This second category of mixed origin included samples from the control–wetland group at 0- to 20-cm and control–grassland group at 40- to 60-cm depth with P/A > 10. In addition, PAH suites of the grassland area along transect 3 (i.e., Gr3 samples) at 40- to 60- and 60- to 80-cm depths also were of mixed origin, with MP/P ≥ 0.4, MF/F ≥ 1.0, and lowest proportion of combustion PAH (i.e., 10%).

Soil Organic Carbon, Nitrogen, and Sulfur

There was a significant difference in SOC concentration between forest and other vegetation types at 40- to 60-cm depth (p < 0.05) (Fig. 4). Differences in total N concentration were for forest vs. other vegetation types at 0- to 60-cm (p < 0.05), grassland vs. control and wetland at 20- to 40-cm (p < 0.1), and control vs. wetland at 0- to 20- (p < 0.05) and 20- to 40-cm depths (p < 0.1). Sulfur concentration differed for forest vs. other vegetation types at 0 to 80 cm (p < 0.05) and grassland vs. control at 20- to 40-cm depth (p < 0.1).

Discussion

PAH Concentration and Distribution

Almost all samples under forest and/or grassland for the 0- to 20- and 40- to 60-cm-depth increments had ΣPAH or ΣEPA16 > 1000 ng g^{-1} (Tables 1–2), indicating the presence of point source contamination (Desaules et al., 2008): High ΣPAH for samples of the forest–grassland and forest–wetland groups, as identified by cluster analysis (Fig. 3), indicated an abrupt forest-to-wetland transition, although these areas lie within ~300 m from the asphalt plant and probably have similar atmospheric deposition rates.

Table 2. Diagnostic ratios and indices for polycyclic aromatic hydrocarbons (PAH) in soil samples grouped by depth increment. Samples were collected from alluvial soils (Oxyaquic Udifluvents) under a natural vegetation succession of the Canadian River floodplain in Oklahoma, near an active asphalt plant and a closed municipal landfill, during September 2007 and June to July 2008.

Depth (cm)	Sample ID†	P/A‡	Fluo/Pyr	MP/P	MF/F	ΣCOMB/ΣPAH	ΣEPA16	ΣPAH
							ng g^{-1}	
0–20	Cont	36.3	1.7	0.3	0.4	0.1	58	110
	We1	26.6	1.4	0.2	0.2	0.2	59	100
	We2	15.6	1.2	0.3	0.2	0.4	110	170
	Fo1	6.7	1.1	0.4	0.3	0.5	690	1,100
	Fo2	6.8	1.3	0.3	0.1	0.7	1,500	2,100
	Fo3	6.1	1.2	0.3	0.2	0.7	1,900	2,400
	Gr2	9.1	1.2	0.3	0.2	0.7	3,100	3,900
	Gr1	5.6	1.2	0.2	0.2	0.6	8,400	11,000
	Gr3	9.1	1.1	0.3	0.3	0.5	110	170
40–60	Cont	21.8	2.2	0.6	0.4	0.1	9.2	32
	Gr1	11.8	1.3	0.4	0.4	0.1	17	34
	Gr2	17.4	1.2	0.4	0.4	0.2	30	51
	Gr3	14.5	0.9	0.4	1.2	0.1	35	78
	Fo1	6	1.2	0.3	0.2	0.7	1,200	1,600
	Fo2	8.9	1.2	0.3	0.2	0.6	1,200	1,900
	Fo3	5.2	1.3	0.3	0.2	0.7	9,300	12,000
	We1	8.7	1.2	0.3	0.2	0.5	150	220
60–80	Cont	ND§	2.4	0.5	0	0.1	4.5	16
	Fo1	3.7	1.2	0.4	0.3	0.7	1,600	2,200
	Fo2	14	1.2	0.4	0.4	0.4	990	2,000
	Fo3	6.2	1.2	0.4	0.2	0.3	64	89
	Gr1	6.5	1.2	0.3	0.2	0.4	35	55
	Gr2	6.3	1.3	0.3	0.2	0.7	640	830
	Gr3	13.6	1.0	0.5	1.2	0.1	59	170
160–200	Fo3	9.6	1.3	0.4	0	0	7.9	64
	Gr1	ND	1.3	0.5	0	0.1	9.6	27
	We1	13.9	1.3	0.4	0.4	0.1	22	46
	Gr2	13.9	1.3	0.3	0	0.2	8.4	19
	Gr3	8.7	1.0	0.4	0.5	0.3	34	95
80–100	We2	ND	1.5	0.3	0	0.1	4.3	17
160–180	Fo1	8.1	1.2	0.3	0.3	0.5	240	400
240–260	Fo2	9.7	1.2	0.3	0.2	0.5	53	88

† Within each depth increment group, samples are ordered based on results of cluster analysis. The ID abbreviations indicate the vegetation type (Cont, control area; We, wetland areas; Fo, areas with arboreal vegetation; or Gr, grassland) and the transect number (1, 2, or 3) of the sampled areas.

‡ Diagnostic ratios: P/A, phenanthrene to anthracene; Fluo/Pyr, fluoranthene to pyrene; MP/P, methyl-phenanthrenes and methyl-anthracenes to phenanthrene; MF/F, methyl-fluoranthenes and pyrenes to fluoranthene. ΣCOMB/ΣPAH, sum of combustion PAH concentrations to total PAH concentration (ΣPAH); ΣEPA16, Sum of concentrations for the 16 PAH that are on the USEPA priority list.

§ ND, compound at the denominator not detected.

Researchers have quantified PAH contamination due to atmospheric deposition at the soil surface (commonly within the 0- to 10-cm-depth increment) in rural or remote regions for comparison with more polluted, industrial and urban centers. Most studies have reported values for rural regions that correspond to ΣEPA16. Wilcke and Amelung (2000) estimated a PAH burden of 63 to 321 ng g^{-1} for rural areas of the Great Plains, Trapido (1999) 100 ng g^{-1} for Estonia, Jones et al. (1989b) 600 ng g^{-1} for Wales, and Desaules et al. (2008) 163 ng g^{-1} for Switzerland. These values are comparable to average ΣPAH and ΣEPA16 at 0- to 20-cm depth for the control and wetland areas of this study at the Norman landfill site.

The positive correlation between ΣPAH and UTM northing for the 0- to 20-cm depth and the negative correlation between soil depth and proportion of COMB also indicate that asphalt production have contaminated the nearby soils. Asphalts are complex mixtures of organic compounds that include PAH and are produced by further processing of the residual product of petroleum distillation (Nahorniak and Booksh, 2006). The main PAH contamination is very likely through atmospheric deposition in the form of emissions from the plant, although some PAH contamination in liquid or solid form might also occur in the grassland areas nearest to the plant (i.e., transect 1 and 2). Polycyclic aromatic hydrocarbons can be leached from storage piles and transported during rainfall events to areas at lower elevations than the plant within the grassland areas. During asphalt production processes, dust can also be generated from, for example, the loading machineries, storage piles, conveyors, and conveyor drop points.

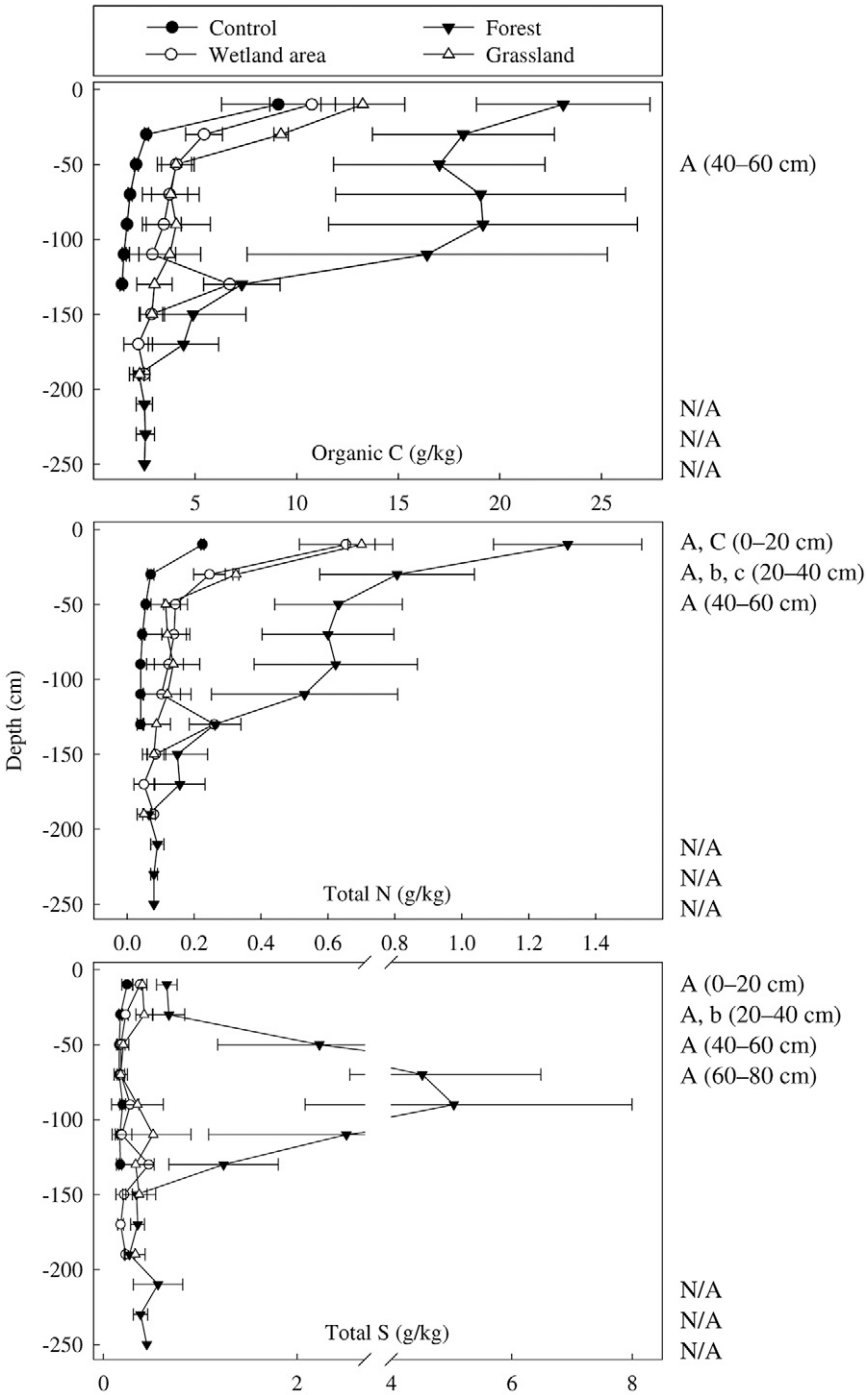


Fig. 4. Patterns of soil organic C, total N, and total S (mean ± 1 SE) concentrations with depth. Mineral soil samples (*n* = 140) were collected from soils (0–260 cm) under a riparian vegetation succession of the Canadian River floodplain in Oklahoma, near an active asphalt plant and a closed municipal landfill, during September 2007 and June to July 2008. Letters indicate significant at $\alpha = 0.05$ (Capitals) and $\alpha = 0.1$ (lowercase) probability levels for orthogonal contrasts: (A) forest vs. all other vegetation types, (B) grassland vs. control and wetland, and (C) control vs. wetland. Contrasts not shown were not significant. N/A, not applicable.

The denser vegetation of the forest and grassland areas likely enhanced PAH sorption and accumulation in soil through canopy interception, stemflow, throughfall, litterfall, and litter decomposition. This speculation is supported by the greater proportion of COMB or PHPAH at the soil surface under forest and grassland and their positive correlation with UTM northing. High concentrations below 20-cm depth under forest may indicate PAH translocation from canopies and understory vegetation into the mineral soil but also point source contamination due to past landfill operations.

Atmospheric deposition alone due to asphalt production could not explain all patterns in PAH concentration with depth because other possible sources likely enhanced PAH accumulation at depths >20 cm. The presence of trash indicates that landfill activities may have increased PAH concentrations in the subsoil under forest more than under other vegetation types. The high ΣPAH concentrations (>1000 ng g^{-1}) and ΣCOMB/ΣPAH ratios (>0.5) at 40- to 60- and 60- to 80-cm depths (Table 2) and the greater S concentrations at 0- to 60-cm depth (Fig. 4) support this speculation. High S concentrations may indicate the presence of construction waste materials common in municipal landfills such as gypsum wallboards.

Origin of PAH

Although the exact nature of the waste materials discarded within the sampled areas remains unknown, the analysis of PAH suites combined with field observations and past historical record provides a valid tool to interpret PAH origin. The high correlation between PHPAH and the first principal component underscores the importance of pyrogenesis, because the first principal component can be interpreted as representative of pyrogenic PAH (Fig. 2). The PCA pattern, with PHPAH grouped to the right in Fig. 2A, is quite similar to that observed by Aichner et al. (2007), who investigated the origin of 20 PAH in 39 sites (0- to 5-cm depth) in the Katmandu urban area, Nepal. These authors found that combustion of fossil fuels was the main source of PAH in soil. The fourth component may be interpreted as the perylene component because of its high and unique correlation with perylene (Fig. 2B). Perylene is believed to have a biogenic origin particularly in anaerobic environments (Krauss et al., 2005; Aichner et al., 2007). Such speculation is also supported by the high perylene percentages observed within the 160- to 200-cm depth (Table 1), where periodic saturation may occur due to seasonal variations in groundwater depth and create anaerobic conditions. The lack of high correlations for PLPAH, including naphthalene and phenanthrene, supports speculations that naphthalene and phenanthrene in soil may have both a biogenic and pyrogenic origin (Krauss et al., 2005). Evidence for pyrogenic origin of certain PLPAH was provided by Ruokojärvi et al.

(1995), who found that phenanthrene, fluoranthene, and pyrene were the most abundant compounds generated in air and waste samples during controlled and spontaneous burning experiments in Finnish landfills. Results by Ruokojärvi et al. (1995) agree with our findings about the abundance of phenanthrene, fluoranthene, and pyrene within the 0- to 60-cm depth increment of contaminated soils under forest and grassland vegetation.

During combustion of organic matter, such as wood or fossil fuels, organic compounds are partially cracked into smaller and unstable fragments (pyrolysis). These fragments are highly reactive free radicals with a very short lifetime and are converted into more stable PAH (pyrosynthesis). Polycyclic aromatic hydrocarbon suites that form at temperatures >1000°C have generally a greater proportion of PHPAH. Pyrogenic PAH produced by incomplete combustion at high temperature have two to six rings and less alkylated substitution, whereas petrogenic PAH, which are produced at relatively low temperature, have preferentially two to three rings and predominance of alkyl groups (Sporstol et al., 1983; Masclet et al., 1987; Hwang et al., 2003).

Diagnostic ratios supported the conclusions of a pyrogenic origin for most PAH suites. High concentrations of PHPAH in the forest and grassland areas indicated the presence of C-rich fractions formed under elevated temperatures. High anthracene and fluoranthene concentrations relative to the corresponding concentrations of their reference isomers, phenanthrene and pyrene, respectively (i.e., P/A < 10 and Fluo/Pyr > 1), indicate PAH suites of a pyrogenic origin (Budzinski et al., 1997; Yunker et al., 2002). Once in soils, some PLPAH (e.g., phenanthrene or anthracene) may undergo aging processes (e.g., degradation, volatilization, or transfer to the biosphere) that change the relative composition of PAH suites. Therefore a sound approach is to apply a combination of ratios or methods when inferring information on PAH sources, including ratios based on PHPAH and PCA, to better account for possible confounding factors (Neff et al., 2005; Pies et al., 2008; Bu et al., 2009).

Results on the presence of mixed suites at the base of the landfill, as indicated by the MP/P and MF/F ratios (Table 2), should be interpreted with some caution because sample size was too small to draw conclusions and the exact source of petrogenic PAH remains unknown. Despite these limitations, other investigations show that that solvents, petroleum products, coal and coke materials, resins, or paints were possible petrogenic sources discarded at the site (Eganhouse et al., 2001). Several anthropogenic activities that produce PAH suites of petrogenic origin cannot be ruled out because of past and present landfill and asphalt plant operations. Petrogenic PAH suites may also derive from unburned diesel fuels from machineries or through atmospheric deposition from the nearby city of Norman. In fact, it has been shown that petrogenic PAH can accumulate in soils (Bu et al., 2009) or pine needles (Hwang et al., 2003) due to atmospheric deposition. Similar compositions in PAH suites (i.e., pyrogenic and mixed origin) were also observed by Pies et al. (2008) in floodplain soils (0- to 200-cm depth) along the Mosel and Saar River, Germany; and Bu et al. (2009) in urban soils (0- to 100-cm depth) of Beijing, China. Pies et al. (2008) used a combination of similar methods to identify PAH sources in sites far from potential point-source contamination. They concluded that the source of pyrogenic PAH was probably coal mining at most sites, whereas the source of petrogenic PAH at one site was lubricating oil.

Summary and Conclusions

Past landfill operations and/or emissions from the adjacent asphalt plant have increased the PAH burden to levels of highly polluted urban areas—up to 12,000 ng g^{-1}—in surface and subsurface soils near the closed municipal landfill at Norman, OK. The contamination due to atmospheric deposition only (ΣPAH of 130 ± 23 ng g^{-1}) near the Canadian River active channel was comparable to that of the rural Great Plains. Parent high molecular weight polycyclic aromatic hydrocarbons played a major role in controlling the variability in the data and were the most abundant compounds in contaminated areas. Perylene had a unique distribution pattern suggesting biological inputs.

The main PAH contamination mechanisms were probably atmospheric deposition due to asphalt production at the soil surface and past landfill operations in the subsurface. Most sampled areas had PAH of pyrogenic origin, indicating that combustion of petroleum products for asphalt production or biomass that was buried during past landfill operations were the most likely sources of PAH in soil. These results also support the hypothesis that PAH persist in soil, following aging and immobilization processes that reduce their bioavailability.

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