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Determination of Polycyclic Aromatic Hydrocarbons and Trace Metals in New Orleans Soils and Sediments

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Soil and sediment samples from New Orleans have been collected and analyzed for contamination by 16 polycyclic aromatic hydrocarbons (PAHs) and 8 trace metals. Total PAH contents were found to vary from 40 μg/kg to 40,000 μg/kg, and concentrations of total metals varied in the range of 80 mg/kg and 7600 mg/kg. Source analysis of PAHs using diagnostic concentration ratios such as phenanthrene/anthracene and fluoranthene/

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pyrene indicated that PAHs found at elevated concentrations in New Orleans soils and sediments were of pyrolytic origins. Spearman rank bivariate correlation analysis revealed significant correlations between soil PAHs and metals ($r = 0.80, p < 0.0001$*) and between sediment PAHs and metals (*$r = 0.62, p < 0.05$*), suggesting common pollution sources for the two groups of environmental pollutants. Strong correlations were also found between Pb and Zn in soils (*$r = 0.93, p < 0.0001$*) as well as in sediments (*$r = 0.65, p < 0.05$*).*

Keywords Soil and sediment contamination, PAHs, metals, accelerated solvent extraction, GC/MS analysis.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are hazardous organic pollutants that are widely distributed in the environment. Several PAHs are known to be potent carcinogens in animals (Heidelberger, 1976). Incomplete combustion of fossil fuels, including petroleum and coal, constitutes the major anthropogenic sources of PAHs. Various PAH concentrations have been found in air particulates, soils, waters, and sediments, largely due to urban runoffs, motor vehicle emission, factory discharge, and accidental petroleum spills (Laflamme and Hites, 1978). PAHs can be rather persistent in the environment, especially in the presence of substances that inhibit PAH degradation processes. For example, Wild *et al*. reported that PAH degradation was significantly slowed in soil amended with Ni-rich sludge (Wild *et al*., 1991). PAHs have often been found to coexist with heavy metals due to similar pollution sources (Bradley *et al*., 1994; Weiss *et al*., 1994; Strnad *et al*., 1994; Kodama *et al*., 1988). Notably, motor vehicle emissions were found the likely source for both PAHs and heavy metals such as lead and cadmium in a municipal refuse dump (Lin *et al*., 1995). Even in agricultural soil, relatively high correlation was found between PAHs and Pb concentrations (Maliszewska-Kordybach *et al*., 1995).

In the mild climate near the Gulf of Mexico, New Orleans residents use limited heating during winter. The preferred fuel is natural gas instead of heating oil. Furthermore, compared to other mid- to large-size cities in the United States, New Orleans is relatively less industrial. The source of PAHs present in New Orleans soils and sediments is therefore more likely to be associated with background PAH contents and other urban activities including use of vehicles. In this study, concentrations of 16 PAHs in urban soils and urban waterway sediments were determined. The results were contrasted against those of rural soils and freshly deposited alluvium samples that are considered to be free of PAH contamination due to urban activities and to represent natural background PAH levels. Because urban activities can contribute significantly to the accumulation of heavy metals in soils and sediments (Mielke *et al*., 2000), several metals were also determined in the same soil and sediment samples. For PAH determinations, a relatively new sample treatment method based on accelerated solvent extraction (ASE) was employed. ASE has a number of advantages including low per-extraction cost, less solvent and time consumption, and simple extraction protocols (Richter *et al*., 1996; Wang *et al*., 1999). Next, gas chromatography-mass spectrometry was used for quantitative analysis of PAHs in the extracts. For metal determinations, acid extracts of soil samples were analyzed by the inductively coupled plasma-atomic emission spectrometry (ICP-AES). The correlation between PAH and metal concentrations as well as the correlation between trace metals were examined by statistical analysis.

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Experimental

Materials and Regents

PAH standard mixtures, 2-fluorodiphenyl, 4,4-difluorobiphenyl, and p-terphenyl-d_{14} were obtained from ChemService (West Chester, PA). The standard mixture contains 16 PAHs listed as EPA priority pollutants (see Table 1 for a list of the 16 PAHs) each at 100 μg/ml in methanol. The calibration standard solutions were prepared by diluting the mixture to concentrations ranging from 0.1 μg/mL to 5.0 μg/mL with methylene chloride. 4,4-difluorobiphenyl and p-terphenyl-d_{14} were used as internal standards, and they were added to the final extracts prior to GC-MS analysis. Florisil (100–200 mesh size), solid phase extraction cartridges, GC grade solvents (hexane, methylene chloride, acetone, and acetonitrile), nitric acid, and Ottawa Sand Standard were all purchased from Aldrich Chemicals (St. Louis, MO). National Institute of Standards and Technology (NIST) traceable metal standards for ICP-AES analysis were purchased from Fisher Scientific (Fair Lawn, NJ).

Apparatus

A Dionex (Sunnyvale, CA) accelerated solvent extractor (ASE 200) was used for all sample extractions of PAHs. A Hewlett-Packard Model 5890 Series II Plus gas chromatograph equipped with an HP 5989B MS detector (Agilent Technologies, Palo Alto, CA) was used for the quantitative determination of PAHs. The instrument was controlled by the HP G1034C ChemStation software. The GC column used was an HP-5MS, crosslinked 5% phenyl methyl siloxane capillary column, 30 m × 0.25 mm id, with film thickness of 0.25 μm. A

Table 1
PAH recovery determined at 2 μg/g Soil Sample Level (n = 3)

PAH	Recovery %
1. Naphthalene	57.9 ± 5
2. Acenaphthylene	86.6 ± 9
3. Acenaphthene	65.3 ± 6
4. Fluorene	83.9 ± 7
5. Phenanthrene	81.2 ± 10
6. Anthracene	72.6 ± 5
7. Fluoranthene	73.5 ± 6
8. Pyrene	79.9 ± 6
9. Benz(a)anthracene	105 ± 5
10. Chrysene	104 ± 7
11. Benzo[b]fluoranthene	106 ± 4
12. Benzo[k]fluoranthene	105 ± 5
13. Benzo(a)pyrene	91.0 ± 9
14. Indeno[1,2,3-cd]pyrene	75.8 ± 7
15. Dibenz[a,h]anthracene	75.5 ± 8
16. Benzo[g,h,i]perylene	68.5 ± 10

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SpectroFlame ICP-AES instrument (Spectro Analytical Instruments, Fitchburg, MA) was used for all metal determinations in soil and sediment samples.

Sample Preparation

Soil samples ($n = 36$) were collected according to methods developed by Mielke *et al*., (Mielke *et al*., 1983; Mielke, 1997). All samples were collected within the top 2.5 cm of the surface and air-dried before extraction. Urban soil samples included those from busy thoroughfare, residential street side, open space, and house drip-line. Alluvium samples ($n = 4$) were collected from the Bonnet Carré Spillway (BCS). Rural soil samples were collected from Jean Laffite National Park. The alluvium and rural samples were used as controls that have minimal effect of traffic. Soil samples were air-dried, ground with a porcelain mortar and pestle, and sieved through a 2.0 mm sieve. The soil samples were divided into two portions, one for PAH analysis and the other for metal determinations, and were stored at room temperature before extraction. The mortar and pestle were cleaned with deionized water between samples.

Bayou St. John (BSJ) sediments were collected with a Wildco-Ekman bottom dredge from bridges along the bayou. To minimize the effect of tide and rain on sediment results, a second batch of sediments was collected three months later at the same sites, and the results were average values of the two batches of samples. For initial sample preparation, all sediments were spread out on glass trays to air dry at room temperature for 10 days. The air-dried sediment samples formed hard lumps of clay that were ground with a porcelain mortar and a pestle that were cleaned with deionized water between samples. All samples were divided into two groups for separate organic and inorganic extraction and analysis.

For PAH recovery studies in soil, 1.0-gram aliquots of clean soil (rural soils that were predetermined to have PAH concentrations below detection limits) were prepared and fortified with 20 μL standard PAH solution to give soil concentration of 2.0 μg/(gram sample) for each PAH. The fortified sample aliquots ($n = 3$) were then mixed with 1.0 g anhydrous Na_2SO_4 before they were transferred into the ASE extraction cells. For analysis of all soil and sediment samples, three 5.0-gram aliquots of each sample were mixed with 5-gram anhydrous Na_2SO_4 and extracted with methylene chloride by ASE.

For metal determinations, 4-gram air-dried soil or sediment samples were suspended in 20-mL 1 M nitric acid and shaken mechanically for two hours. The extracts were centrifuged at 1600x g for 15 minutes. The resulting supernatant was filtered through P4 filter paper (Fisher Scientific) and collected in 20-mL metal-free polyethylene vials for analysis by ICP-AES. The ICP-AES was calibrated with NIST reference standards and diluted to the appropriate range for each metal.

Accelerated Solvent Extraction

Extraction parameters have been previously described (Wang *et al*., 1999; Richter *et al*., 1996). Briefly, a cellulose paper was placed at the bottom of each 11-mL Dionex extraction cell before samples were loaded. The extra space in the cell was filled up with Ottawa Sand Standard before sealing off the top. ASE operation parameters included a 5-min. heating-up time, two sequential 5-min. static extraction periods followed by a 1.5-min. purge time. The extraction pressure was held at 1500 psi within the cell and the temperature was kept at 100°C in the oven. The total extraction volume was 20 mL of methylene chloride. The ASE extracts were collected in 40-mL glass vials with Teflon septum caps.

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Post-Extraction Cleanup Procedures

The extracts were first evaporated to approximately 2 mL under a nitrogen stream. The concentrated extracts were then loaded onto the top of the solid phase extraction cartridges containing 2 g Florisil (Supelco, Bellefonte, PA). The cartridge was allowed to dry for 5 minutes. PAHs were eluted from the column with 10 mL methylene chloride using a Visiprep SPE Vacuum Manifold (Supelco, Bellefonte, PA). The collected eluent was evaporated down to 1 mL followed by addition of internal standards prior to GC-MS analysis. All evaporation and clean-up procedures were carried out in a fume hood to minimize PAH and organic solvent contamination in the laboratory.

Quantitation for PAHs

The GC-MS was operated under the following conditions. The temperature of the injection port and the detector was held at 290°C. The oven temperature was set at 40°C initially (1 min. hold), increased to 250°C at 12°C/min., and to 310°C at a rate of 5°C/min. (3 min. hold). The temperatures of the ion source and the quadrupole mass analyzer were kept at 250 and 100°C, respectively. Helium gas was used as the carrier gas at a constant flow rate of 0.8 mL/min. An automatic sample injector (HP 6890) was used to introduce 1.0 μL of each sample extract in an intermittent standard injection sequence. The retention time of each PAH component was determined by injecting individual PAH solutions under constant GC-MS instrumental conditions. The SIM mode (selected ion monitoring) was then used for quantitation in which three ions were selected for calculating the chromatographic peak area of each PAH (Wang *et al.*, 1999). The response factors of PAHs relative to the two internal standard compounds were determined at five PAH concentrations (from 0.10 to 5.0 μg/mL) to obtain standard calibration curves. For PAH determinations in fortified and all other soil and sediment samples, internal standards were added to the final extracts before GC-MS analysis. A standard reference material from NIST, SRM1941b was analyzed for verification of the quantification method. The recoveries of 14 PAHs certified by NIST ranged from 80% to 125%.

Statistical Analysis

A GraphPad Prism 3.03 software (GraphPad Software, Inc., San Diego, CA) was used for statistical analysis of all PAH and metal data determined in soil and sediment samples.

Results and Discussion

Figure 1 shows gas chromatograms of a 1-ppm PAH solution (A), a spiked soil sample extract (B), and an urban soil sample extract (C). Because elution lasted for about 30 minutes, two internal standards were used to calculate the relative response factors of the PAHs. The internal standard, 4,4′-difluoro-1,1-biphenyl, was used for the eight PAHs that eluted before 20 min., and p-terphenyl-d_{14} was used for the other eight PAHs that eluted after 20 min. PAHs of higher molecular weights had increasingly higher detection limits (up to 0.1 μg/mL), which set the lower end of PAH concentration range that could be determined in this study.

Shown in Table 1 are the recovery data for 16 PAHs obtained from spiked soil samples. The low recovery of naphthalene is likely due to the volatility of this PAH. The recoveries of

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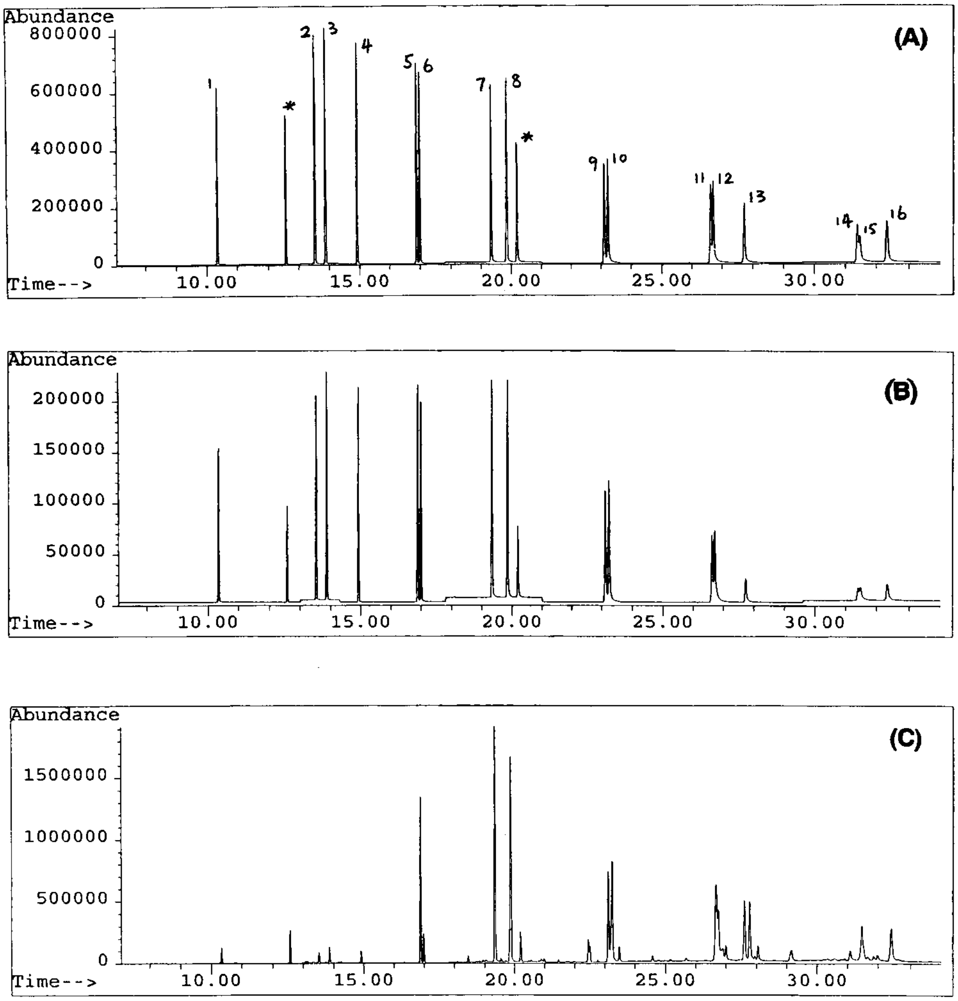

Figure 1. SIM chromatograms of (A) a standard solution containing 1.0 μg/mL PAHs with corresponding peaks labeled as: 1. naphthalene, 2. acenaphthylene, 3. acenaphthene, 4. fluorene, 5. phenanthrene, 6. anthracene, 7. fluoranthene, 8. pyrene, 9. benz[a]anthracene, 10. chrysene, 11. benzo[b]fluoranthene, 12. benzo[k]fluoranthene, 13. benzo[a]pyrene, 14. indeno[1,2,3-cd]pyrene, 15. dibenz[a,h]anthracene, 16. benzo[g,h,i]perylene, and with internal standards labeled as *, (B) an extract of soil sample spiked at 2.0 μg/g, and (C) a soil sample extract.

higher molecular weight PAHs such as benzo[g,h,i]perylene are also relatively low, which may be attributed to lower extraction efficiencies for the larger PAHs.

A brief description of the soil samples taken from New Orleans is given in Table 2. A schematic location map of the city of New Orleans (Figure 2) shows some of the sampling sites. Urban sampling sites include busy streets with heavy traffic (3, 5, 11, 12), streets with moderate traffic (4, 7, 8, 10, 14–17, 21, 22), residential areas such as the open space and backyard around houses (1, 2, 6, 9, 13, 18, 20, 23, 24) and the city park area (28–32) approximately 500 m from a main traffic road. Rural samples include Bonnet Carré Spillway (BCS) alluvium soils (33–36) and soils from Louisiana's Jean Lafitte National Park (25–27) where little residence or traffic exists. Sampling sites for Bayou

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Table 2
Soil sample information

Sample No.	Sample Location	Sample Description
1	Press Ave.	Open space soil
2	Press Ave.	Open space soil
3	N Claiborne Ave.	Busy street soil (heavy traffic)
4	Marais St.	Street soil (moderate traffic)
5	Elysian Fields Ave.	Busy street (heavy traffic)
6	Villere St.	Soil under house drip-line
7	Elysian Fields Ave.	Street soil (moderate traffic)
8	St. Anthony Blvd.	Street soil (moderate traffic)
9	Colombus St.	Open space soil
10	N Johnson Ave.	Street soil (moderate traffic)
11	Canal St.	Busy street soil (heavy traffic)
12	General Diaz St.	Street soil (heavy traffic)
13	Banks Ave.	Soil under house drip-line
14	Gravier St.	Street soil (moderate traffic)
15	LaSalle St.	Street soil (moderate traffic)
16	Toledano St.	Street soil (moderate traffic)
17	Pitt St.	Street soil (moderate traffic)
18	Pitt St.	Garden bare soil
19	Pitt St.	Street soil (light traffic)
20	Pitt St.	Soil under house drip-line
21	Broadway Ave.	Open space soil (light traffic)
22	Broadway Ave.	Open space soil (light traffic)
23	Broadway Ave.	Foundation soil
24	Broadway Ave.	Foundation soil
25	Jean Lafitte National Park	Open space soil (no traffic)
26	Jean Lafitte National Park	Open space soil (no traffic)
27	Jean Lafitte National Park	Open space soil (no traffic)
28–32	City park	Trail side soil (moderate traffic)
33–36	Bonnet Carre Spillway	Alluvium soils (no traffic)

St. John sediments are shown in Figure 3, a schematic location map for Bayou St. John (BSJ) and the bridges under which the sediments were sampled. The location of BSJ can be found in Figure 2 that shows BSJ stretching from urban New Orleans to the Lake Pontchartrain.

PAH concentrations determined in soil and sediment samples are summarized in Table 3 under three categories: urban ($n = 29$), rural ($n = 7$), and Bayou St. John sediment ($n = 11$). Rural soil samples were determined to have low concentrations of PAHs, most of which are below the detection limit. The four alluvium samples show total PAH concentrations in the range of 50 to 600 μg/kg. Low levels of PAHs are also found in soils taken from a rural site, Jean Lafitte National Park, LA, which contain less than 400 μg/kg total PAHs (JL-1, TC-1, and ES-1), comparable to the PAH levels found in BCS alluvium soils. Alluvium is the parent material for all soils of the lower Mississippi River Delta including New Orleans (Hunt, 1972). The Spillway was built after the flood of 1927 to relieve water pressure and

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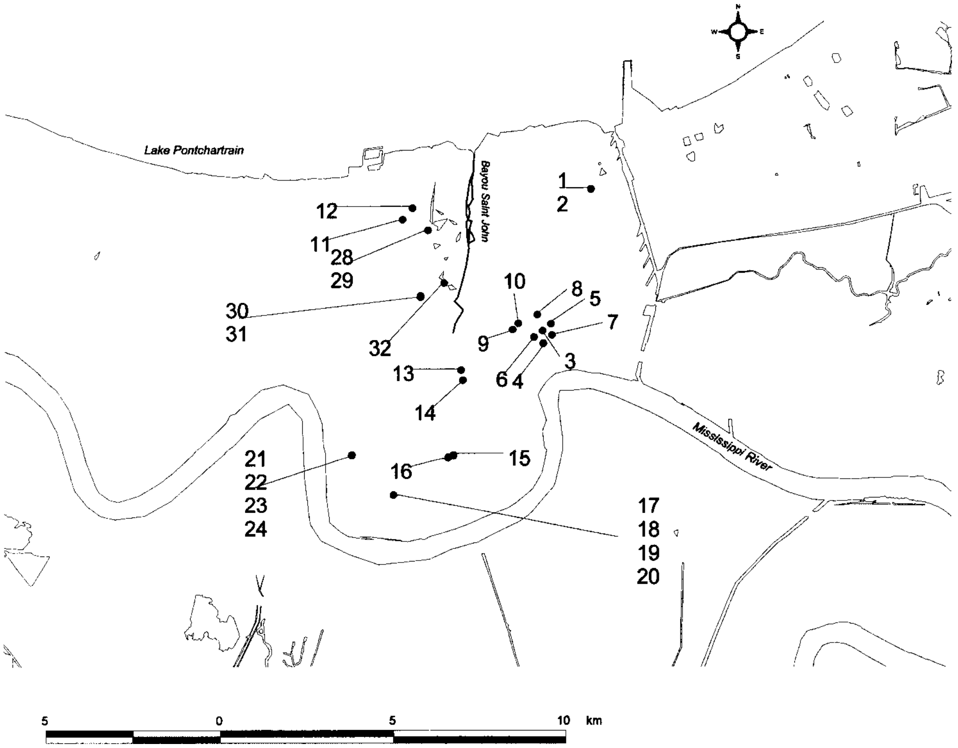

Figure 2. A soil sampling map for the City of New Orleans. Numbers shown in the map correspond to the sample numbers in Table 2. Sample number 25, 26, and 27 are not shown because the collection sites are out of the map range.

damage to the levee system that protects New Orleans from floodwater (Barry, 1997). The Spillway gates were last opened between March 17 and April 18, 1997. Alluvium soils were deposited when the floodwaters from the Mississippi River spread through the Spillway to Lake Pontchatrain. Together, rural and alluvium soils (n = 7, Table 3) provide a point of reference where PAH concentrations are not likely influenced by vehicular emissions or other anthropogenic sources.

In contrast, urban soils were found to contain much greater levels of both individual and total PAHs. All 16 PAHs were detected in most of the 29 urban soil samples. The four PAHs that were not detected in all samples are the most volatile ones, namely naphthalene (detected in 27 samples), acenaphthylene (25), acenaphthene (22), and fluorene (28). These low molecular weight PAHs were also found at lower concentrations than the heavier PAHs, presumably due to their greater volatility (see discussion on sediment PAHs). Soil PAH concentrations showed a wide range, both within the urban category and between urban and rural samples. Total PAH concentration in urban soils varied from 639 μg/kg to 40692 μg/kg, with lower concentrations generally found in sites of light traffic or in open space, and with higher concentrations mostly associated with heavy traffic. Soils sampled from busy street sites with heavy traffic showed the highest total PAH levels with total PAH concentrations up to 40 mg/kg, approximately 100 times higher than levels detected in BCS alluvium soils and Jean Lafitte National Park samples. The average total PAH in urban soils was determined to be 5562 μg/kg, a level about ten times higher than the

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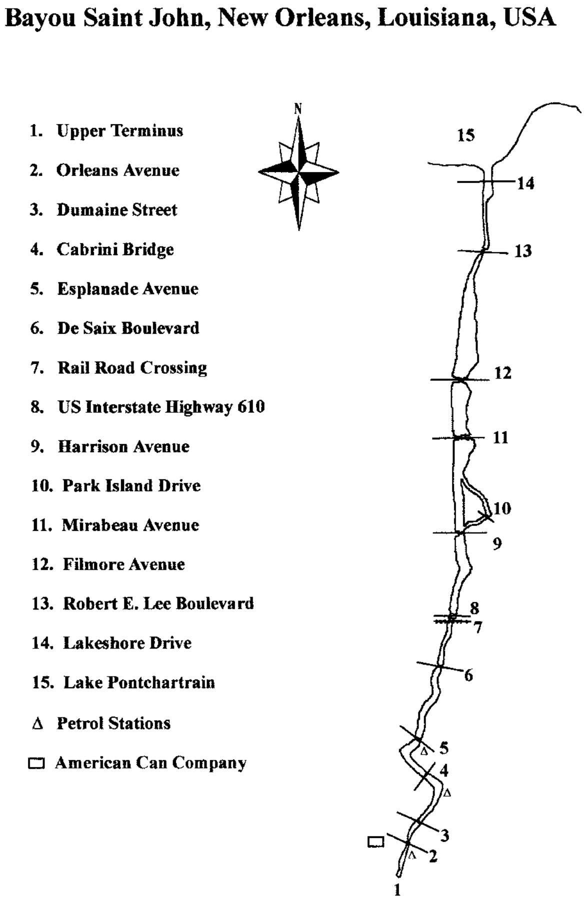

Figure 3. Map of Bayou St. John showing the bridges under which sediments were sampled.

background concentrations in alluvium and rural soils. Of the 16 PAHs examined in urban soils, phenanthrene, fluoranthene, pyrene, benzo[b]fluoranthene, and benzo[a]pyrene were present at the highest concentrations.

PAH levels were also determined in 11 sediment samples taken from Bayou St. John, and the results are summarized under the BSJ sediment group in Table 3. Bayou St. John is an open canal that starts from the urban area of New Orleans and ends at Lake Pontchatrain. During WWII, BSJ was the location of boat manufacturing and testing activities (Strahan, 1994). After WWII, the lower section of the bayou was straightened and dredged by the US Army Corps of Engineers and BSJ has since become a sort of recreational area for city residents. Through Bayou St. John's north to south stretch, eleven bridges cross the bayou that range from two-lane roads to a multi-lane freeway. In addition, diesel powered trains run on railroad tracks that parallel the freeway and cross the bayou. Sediment sampling sites are shown in Figure 3, a schematic location map for Bayou St. John and the bridges under which the sediments were sampled. Of the eleven sediment samples analyzed, the highest total PAH level is 25 mg/kg found in the clay and organic rich sediments under the Esplanade Bridge in the urban section of the bayou, and the lowest is less than 0.04 mg/kg, found in the sandy Lakeside sediments.

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Table 3
PAH levels determined in New Orleans soils and sediments, μg/kg

	Urban Soils, n = 29				Rural and Alluvium Soils, n = 7				BSJ Sediments, n = 11			
PAHs (μg/kg)	# of Detection	Low	High	Average	# of Detection	Low	High	Average	# of Detection	Low	High	Average
1. Naphthalene	27	0	258 ± 31	57 ± 9	3	0	46 ± 8	12 ± 3	11	7 ± 6	1227 ± 65	366 ± 31
2. Acenaphthylene	25	0	158 ± 14	28 ± 4	1	0	5 ± 4	1 ± 1	10	0	207 ± 24	96 ± 12
3. Acenaphthene	22	0	206 ± 15	39 ± 5	1	0	6 ± 3	1 ± 1	10	0	300 ± 27	124 ± 12
4. Fluorene	28	0	182 ± 20	38 ± 3	2	0	14 ± 3	3 ±	10	0	302 ± 18	162 ± 15
5. Phenanthrene	29	51 ± 6	3435 ± 124	377 ± 26	7	10 ± 3	71 ± 12	30 ± 7	11	45 ± 14	2569 ± 117	1070 ± 99
6. Anthracene	29	12 ± 3	890 ± 61	96 ± 7	3	0	10 ± 3	3 ± 1	11	2 ± 3	771 ± 42	369 ± 22
7. Fluoranthene	29	54 ± 4	4558 ± 210	565 ± 29	7	5 ± 3	65 ± 13	28 ± 8	11	83 ± 9	3644 ± 28	1206 ± 121
8. Pyrene	29	116 ± 7	4878 ± 275	692 ± 44	6	0	62 ± 12	25 ± 4	11	82 ± 7	3478 ± 182	1715 ± 119
9. Benz(a)-anthacene	29	91 ± 5	6859 ± 345	797 ± 54	3	0	43 ± 10	16 ± 3	11	48 ± 5	4044 ± 212	1697 ± 95
10. Chrysene	29	46 ± 3	2483 ± 171	354 ± 27	5	0	28 ± 8	9 ± 3	11	35 ± 5	1621 ± 106	842 ± 63
11. Benzo(b)-fluoranthene	29	105 ± 11	4496 ± 438	852 ± 63	4	0	57 ± 13	27 ± 9	11	82 ± 10	4253 ± 316	1726 ± 134
12. Benzo(k)-fluoranthene	29	16 ± 4	1480 ± 109	172 ± 12	4	0	19 ± 8	5 ± 3	11	20 ± 5	822 ± 65	409 ± 38
13. Benzo(a)-pyrene	29	52 ± 5	6103 ± 302	749 ± 45	2	0	54 ± 14	10 ± 4	11	93 ± 17	2078 ± 147	1133 ± 81
14. Indeno-(1,2,3-cd)-pyrene	29	12 ± 3	5578 ± 387	343 ± 29	6	0	120 ± 11	30 ± 7	11	131 ± 12	1301 ± 79	663 ± 62
15. Dibenz(a,h) anthracene	29	9 ± 3	8202 ± 476	405 ± 44	6	0	120 ± 12	33 ± 8	11	76 ± 10	712 ± 74	375 ± 44
16. Benzo(g,h,i) perylene	29	10 ± 4	6760 ± 433	397 ± 41	2	0	30 ± 10	5 ± 2	11	69 ± 12	894 ± 62	433 ± 46
Total PAHs	29	639 ± 83	40692 ± 2703	5562 ± 427	7	43 ± 15	559 ± 89	242 ± 42	11	772 ± 85	27288 ± 1998	12387 ± 973

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Sediment samples from BSJ near New Orleans' downtown area (with heavier traffic) exhibit significantly higher PAHs than those taken from the Bayou section closer to the Lake Pontchartrain. Traffic becomes lighter towards the Lake and a greater extent of transport of sediment and water between the lake and the Bayou may be another factor for the low sediment PAH levels (similar to those in the Lake sediments (Overton *et al*., 1986). In addition, the average total PAH concentration in BSJ sediments is 12 mg/kg, more than twice that of urban soil PAHs, while concentrations of the first 6 PAHs (from naphthalene to anthracene, see Table 3) are on average 3 to 6 times greater than in urban soils. If sediment and soil PAHs share the common pollution source, the higher level of PAHs in sediment may be in part due to lack of degradation by photo-oxidation in sediments compared to soils (Neff, 1979). On the other hand, volatility of lighter PAHs (e.g. naphthalene, acenaphthene) may be responsible for the lower concentrations found in soil than in sediments.

To examine the sources of PAHs in New Orleans soils and sediments that showed a wide range of concentrations, several PAH concentration ratios were calculated and are listed in Table 4. These diagnostic ratios can be used to distinguish different PAH sources, namely pyrolytic and petrogenic. For example, because phenanthrene is the most thermodynamically stable three-ring PAH isomer and the phenanthrene to anthracene concentration ratio is temperature dependent (Alberty and Reif, 1988), PAHs originating from pyrolytic processes such as fuel combustion in automobiles are characterized by low phenanthrene/anthracene ratios (<10). On the other hand, petrogenic PAHs, formed by the slow maturation of organic matter, typically show higher phenanthrene/anthracene ratios (>10) (Baumard *et al*., 1998; Adami *et al*., 2000). Similarly, the concentration ratio of fluoranthene to pyrene can also be indicative of pyrolytic or petrogenic origin of the PAHs (Rogge *et al*., 1993; Ricking and Schulz, 2002; Lipiatou and Saliot, 1991). For New Orleans urban soils and BSJ sediments, the phenanthrene/anthracene ratios were calculated to be 3.93 and 2.90, respectively. These values are well below a ratio of 10, indicating pyrolytic origin of PAHs. The ratio was

Table 4
Molecular diagnostic ratios calculated from average PAH concentrations

Sample Types	$\frac{\text{Phenanthrene}}{\text{Anthracene}}$	$\frac{\text{Fluoranthene}}{\text{Pyrene}}$	$\frac{\text{Indenopyrene}}{\text{Indenopyrene} + \text{Benzoperylene}}$	References
Urban soil (n = 29)	3.93	0.81	0.46	This work
Rural & alluvium soil (n = 7)	10.0	1.12	0.80	This work
Sediments (n = 11)	2.90	0.70	0.60	This work
Mediterranean Sea	2.87–73	0.74–1.30	0.49–0.62	Baumard *et al*., 1997
Sediments	4.88–32	1.17–1.85	0.37–0.59	Lipiatou and Saliot, 1991
Surface sediments, northern Adriatic Sea	0.84–11.19	0.61–1.38	0.10–0.54	Adami *et al*., 2000
Vehicular emission				Rogge *et al*., 1993
Catalyst equipped	8.0	0.80	0.10–0.22	Kavouras *et al*., 2001
Diesel engine	7.6	0.58	0.35–0.70	Sicre *et al*., 1987

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significantly higher in rural and alluvium soils (phenanthrene/anthracene = 10) where total PAH concentrations were found at less than one-twentieth that of urban soils. The average fluoranthene to pyrene ratio was 0.80 for urban soils and 0.70 for BSJ sediments, which is consistent with PAH data from automobile exhaust (Rogge *et al*., 1993), and within the range reported for fluoranthene/pyrene ratios in sediments (Sicre *et al*., 1987; Wang *et al*., 2002) and urban particulate (Kavouras *et al*., 2001). The ratio of indeno[1,2,3-cd]pyrene/(indeno[1,2,3-cd]pyrene+benzo[ghi]perylene) found in this study was 0.46 for urban soils, 0.60 for sediments, and 0.80 for rural soils. These values are comparable with those reported (0.37–0.62) by previous studies (Grimalt *et al*., 1988; Lipiatou and Saliot, 1991) where sources of PAH contaminations were attributed to pyrolytic origins. While these diagnostic ratios of PAHs provide only qualitative information about the source contributions to PAH contamination, our results indicate that the most important source of PAHs is likely fuel combustion in automobiles. This is further supported by the general trend observed in this study, i.e., higher PAH concentrations were normally found at sampling sites with heavier traffic.

Concentrations of eight metals including Pb, Zn, Cd, Mn, Ni, Cu, Cr, and V have also been determined in soil and sediment samples, and are summarized in Table 5. Similar to trends observed in PAH results, urban soils showed significantly higher metal levels (average total metal 1548 mg/kg) than rural and alluvium soils (average total metal 290 mg/kg), except Mn for which the concentration was slightly higher in rural and alluvium soil. The difference in metal concentrations between rural and urban soils was the greatest for Pb (784 mg/kg vs 11 mg/kg) and Zn (504 mg/kg vs 21 mg/kg), indicating anthropogenic sources of Pb and Zn contamination in urban soils. In BSJ sediments, total metal concentrations varied from 21 ppm to 2877 ppm, with low metal levels found in sediments near the Lake Pontchartrain and high metal concentrations present in sediments near central urban areas. In both urban soil and sediment samples, Pb and Zn were the most abundant metal contaminants, consitituting approximately 80% of total metal concentrations determined. Elevated Pb and Zn in urban environments have been widely reported and their sources have been attributed to such anthropogenic activities as automobile exhaust, tire wear (Zn), and

Table 5
Metal levels determined in New Orleans soils and sediments, mg/kg

Metal (mg/kg)	Urban Soils, n = 29			Rural and Alluvium Soils, n = 7			BSJ Sediments, n = 11		
	Low	High	Average	Low	High	Average	Low	High	Average
Pb	31.7	5195	784	4.8	17.3	11	3.2	2156	403
Zn	27.2	3295	504	11.6	36.4	21	11.2	425	234
Cd	0.9	6.7	3	0.3	2	1.4	0.6	5.2	2.5
Mn	47	428	189	128	358	233	43	246	135
Ni	6.7	36.9	13	1	10.5	5.6	1.2	14.8	9.1
Cu	3.8	116	17.6	2.3	14.5	8	1	89.8	46.4
Cr	0.5	9	1.9	0.4	1.7	1.1	0.4	13.9	3.2
V	2	12	4.8	0.8	10.5	3.5	0.7	12.2	7.2
Total metals	197	7613	1548	159	396	290	81.1	2877	843

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building siding (Davis *et al*., 2001; Sheets *et al*., 2001; Kaminski and Landsberger, 2000; Mielke *et al*., 1999; Lin *et al*., 1998; Elhelu *et al*., 1995). Statistic analysis showed strong correlations between Pb and Zn determined in this study. The Spearman correlation was calculated to be $r = 0.93$ ($p < 0.0001$) for soils and $r = 0.65$ ($p < 0.05$) for sediments, providing evidence that elevated Pb and Zn concentrations in urban New Orleans were due to similar pollution sources.

The correlation between PAHs and metals was also determined by calculating the Spearman rank bivariate correlations. The Spearman correlation coefficient (r) between total metals and total PAHs for 36 soil samples including rural and alluvium soils was 0.80 ($p < 0.0001$), indicating a strong correlation between the two groups of pollutants. For BSJ sediment samples, the correlation between metals and PAHs was 0.62 ($p < 0.05$) a significant correlation, yet not as strong as in soil samples. This may be in part due to the few number of sediment samples used for the study. It is thus statistically significant that soil and sediment PAH levels generally increase with increasing total metal concentrations. As seen in Tables 3 and 5 for alluvium and rural soil samples, PAH concentrations were found at the lower end of all soil samples with an average of 242 μg/kg, while the average total metal level was also at a low level of 290 mg/kg. This compares to the average level of total PAHs and metals at 5562 μg/kg and 1548 mg/kg for urban soil samples, respectively. Similarly, in sediments higher levels of total PAHs are also coupled with higher metal concentrations. Overall, the correlation between PAHs and metals suggests they may share similar pollution sources in the urban environment.

Conclusion

Soils and sediments from New Orleans urban areas were found to contain elevated levels of PAHs and trace metals compared to rural soils. The large difference in PAH and metal concentrations between urban and rural soils points to anthropogenic sources of the two groups of pollutants. Source analysis based on diagnostic PAH concentration ratios indicates that PAHs found in urban soils and sediments are of pyrolytic origin. In a city where there is little use of heating oil in the winter season, the most important pyrolytic source of PAHs in urban soils is automobile exhaust. Furthermore, strong correlations were found between PAHs and metals in the samples examined. In Bonnet Carré Spillway and Jean Lafitte National Park soils, both PAHs and total metals were found at or near the lowest levels of all samples studied. The small metal and PAH quantities at these sites reflect the background metal and PAH contents in the absence of urban activities (e.g., traffic and housing). In contrast, much higher levels of metals and PAHs were found in many urban soil samples, especially near busy traffic streets. Although leaded gasoline and lead-based paint are no longer in use, persistence of lead in the environment and the continuing release of zinc via automobile tire wearing may have contributed to the bulk of the current elevated levels of soil and sediment total metals. Together, the pyrolytic origin of the PAHs and the correlation between PAHs and heavy metals found in New Orleans soils provide evidence that urban pollution from internal-combustion-powered traffic contributes to both groups of contaminants that are persistent in the environment. The combined effect of PAH and heavy metal mixtures on the environment and human health needs to be further studied.

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