Report as of FY2006 for 2004IL52G: "Carbonaceous Material Fractions in Sediments and Their Effect on the Sorption and Persistence of Organic Pollutants in Small Urban Watersheds"

Publications

- Conference Proceedings:
  - Yang, Y., C. J. Werth, 2006, Carbonaceous material fractions in sediments and their effect on the sorption and persistence of organic pollutants in small urban watersheds in the 12th Annual Environmental Engineering and Science Spring Symposium, the University of Illinois, Urbana, IL, 49.
  - Yang, Y., C. J. Werth, 2005, Carbonaceous material fractions in sediments and their effect on the sorption and persistence of organic pollutants in small urban watersheds in the11th Annual Environmental Engineering and Science Spring Symposium, the University of Illinois, Urbana, IL, 23.

Report Follows

Illinois Water Resources Center
Annual Report
Spring 2007

Title: Carbonaceous Material Fractions in Sediments and Their Effect on the Sorption and Persistence of Organic Pollutants in Small Urban Watersheds

Principal Investigators: Charles J. Werth, Peter C. Van Metre, and Barbara J. Mahler

Research Categories: Water Quality

Problem and Research Objectives:

Particle-associated contaminants (PACs), including chlorinated organic compounds, trace elements, and polycyclic aromatic hydrocarbons (PAHs), are an important contributor to urban non-point source pollution across the Nation. Occurrence of PACs has resulted in the impairment of thousands of streams, lakes, and reservoirs. In the past decade, researchers at the U.S. Geological Survey (USGS) investigated the extent to which the contaminant concentrations and trends recorded in sediment cores were associated with suspended sediment in influent streams (Van Metre et al., 1997). Van Metre and Mahler (2004) indicated that in small urban watersheds, concentrations of some PACs on suspended sediment in influent streams can greatly exceed those in bed sediment in the downstream reservoir, and that trends may not be preserved in cores for some PACs. Their observations present a problem for effective sediment monitoring and best management practices for mitigating PAC occurrence. Although the significant loss of contaminants during transport and soon after deposition has been attributed to the solubilization of some contaminants, and the solubilization and mineralization of some solid-phase carbonaceous materials (CMs), relatively little is known about the role played by CMs in the transport and fate of PACs in small urban watersheds.

In this research, we focus on one class of PACs, polycyclic aromatic hydrocarbons (PAHs). PAHs have been a major concern regarding public health and environmental impact because of their widespread occurrence in the environment, as well as their carcinogenic and mutagenic properties. Concentrations of PAHs have increased in recent decades in many urban lakes and streams, particularly in areas with rapid urbanization (Van metre and Mahler, 2005). PAHs are strongly sorbed to solid particles and enter receiving water bodies with storm runoff from impervious surfaces or storm sewers in urban watersheds, as well as by atmospheric deposition. We hypothesized that CM particles are the primary carriers of PAHs in urban watersheds and control the persistence of PAHs as they undergo transport from the land surface into receiving water bodies, and deposition and burial as sediments.

The overall objective of this study is to determine how CM fractions affect the persistence of PACs, with a focus on PAHs in small urban watersheds. The specific objectives are 1) to determine the types and amounts of CMs in urban soil and dust particles with storm runoff, in suspended particles during transport, and in lake sediments after settling, accumulation and burial, 2) to identify the sources of CM particles that may concentrate, transport, and redistribute PAHs in urban watersheds, and elucidate the relationships between CM properties and PAH loadings, and 3) to simulate the particle-associated PAH loading in urban waterhsheds.

Methodology: This research project consists of three phases.

Phase I: Sampling and bulk sediment PAC analysis.

Lake Como and Lake Fosdic watersheds in Fort Worth, Texas were chosen to be urban "laboratories". Samples of lake sediments, suspended sediments and bed sediments in influent streams, soils, street dust, and parking lot dust were collected from each watershed. One split of the samples was used for PACs analysis, PAH desorption, and the determination of sediment deposition time at the USGS National Water Quality Lab (NWQL), and the other split is being used for CM fractionation, characterization, and sorption in our laboratory. All Phase I work has been completed.

Phase II: Enrichment and characterization of CM fractions.

All Lake Como and Lake Fosdic samples, except suspended sediments (due to sample mass limitations), were density separated with a sodium polytungstate solution to obtain loose particulate carbonaceous material (LPCM), occluded particulate carbonaceous material (OPCM), and the remaining humified and mineral associated fraction (HFr). The former two fractions for each lake were combined to create light fractions (LFr), and the HFr fractions from Lake Como were subjected to a series of chemical and thermal treatment steps to obtain sub-samples enriched in different CM fractions (Jeong and Werth, 2005). Chemical treatment steps are exposure to HCl and HF to remove inorganic minerals and acid soluble organic materials, exposure to trifluoroacetic acid (TFA) to remove easily hydrolysable organic materials, exposure to NaOH to remove humic and fulvic acids, and exposure to $K_2Cr_2O_7/H_2SO_4$ to remove the more recalcitrant kerogen and humin. Thermal treatment refers to sample oxidation in excess air at 375°C (CTO 375) (Gustafusson et al., 1997), which was used to quantify the soot carbon contents of bulk samples. All Lake Como samples were also evaluated using organic petrography to quantify CM types and amounts. Remaining enrichment and CM characterization work in Phase II involves treating all Lake Como samples with $K_2Cr_2O_7/H_2SO_4$ in order to quantify kerogen and humin, measurement of organic carbon in all samples via elemental analysis, and surface functional group characterization using Fourier-transform infrared spectroscopy.

Native PAH loadings on all light and heavy (LFr and HFr) fractions of Lake Fosdic samples are in the process of being determined using a Dionex accelerated solvent extraction (ASE) system and a Varian gas chromatography/mass spectrometer (GC/MS) following EPA method 3545 and 8270c. As part of Phase II, we also plan to select different types of CM particles from these samples using a microscope, and measure the PAH loadings on these isolated CM particles. This will allow us to determine on what CMs the native PAHs concentrate, and whether this corresponds to the CMs that have the highest sorption capacity. If the two do not correspond, then redistribution of PAHs during transport and burial is likely.

Phase III: Measurement and prediction of sorption for PAHs and modeling of contaminant loading in urban watersheds

Sorption isotherms were measured at 25°C for all Lake Como bulk and acid treated sub-samples except suspended sediments using established batch equilibrium methods (Xia and Ball, 1999). Radio-labeled phenanthrene was used as the sorbate to distinguish spiked sorbate from background contaminants.

Remaining Phase III work involves measuring the sorption isotherms for the Lake Fosdic samples. The sorption isotherms and the surface properties characterized in Phase II will be used to predict PAHs sorption capacities of CM particles and to identify mechanisms that control the persistence of PAHs in urban reservoirs. Although not part of our original proposal, we also plan to use the EPA Storm Water Management Model (SWMM) to estimate the production of pollutant loads associated with the runoff during strom events, and to evaluate the effectiveness of BMPs for reducing pollutant loadings in the Lake Como urban watershed.

Principal Findings and Significance

Total PAH concentrations on Lake Como bulk samples are shown in Figure 1. Results indicate that total PAHs in sealed parking lot dust are 30 times greater than in unsealed parking lot dust, and 80-110 times greater than in lake sediments. The higher PAH concentrations in sealed parking lot dust indicate that coal tar pitch from sealed parking lots may dominate PAH loading in watersheds with commercial and residential land use (Mahler et al., 2005). The asphalt street dust and soil in the residential area have the lowest concentrations of PAHs. Total PAHs in the suspended stream sediment greatly exceed the probable effect concentrations (PEC, 22800 μg/kg) and threshold effect concentrations (TEC, 1610 μg/kg) in consensus-based sediment-quality guidelines (MacDonald et al., 2000), and are 4-6 times greater than in the stream bed sediments and lake sediments where the total PAHs are lower than the PEC. This observation is consistent with the previous published work (Van Metre and Mahler, 2004), indicating that particles with relatively high PAH concentrations are transported to the lake, but that these concentrations decrease during particle transport and burial in the sediments.

Organic carbon contents of all Lake Como samples are shown in Figure 2. Organic carbon contents generally increase with the sediment depth. This corresponds to the trend in PAH concentrations (Figure 1). Total PAH concentrations were normalized to organic carbon contents and results are shown in Figure 3. The normalized PAH concentration in the sealed parking lot material is almost 20 times more than in the sealed parking lot dust, and almost 80 times more than in the remaining samples.

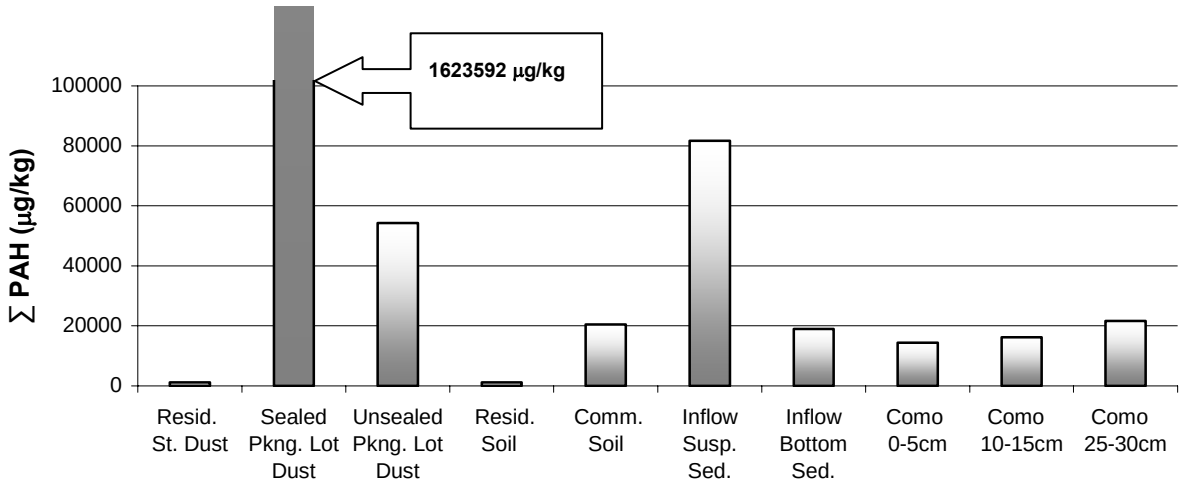


Figure 1. Total PAH concentrations in bulk samples from Lake Como watershed.

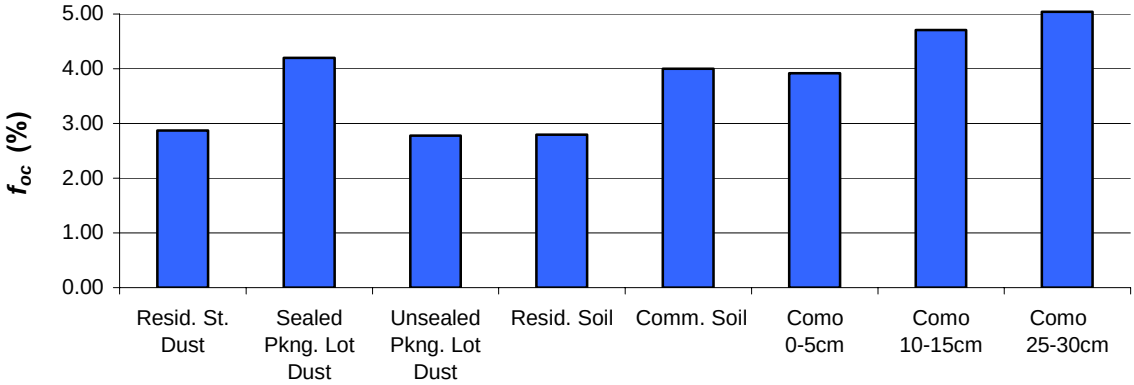


Figure 2. Organic carbon contents (f_{oc}) in bulk samples from Lake Como watershed.

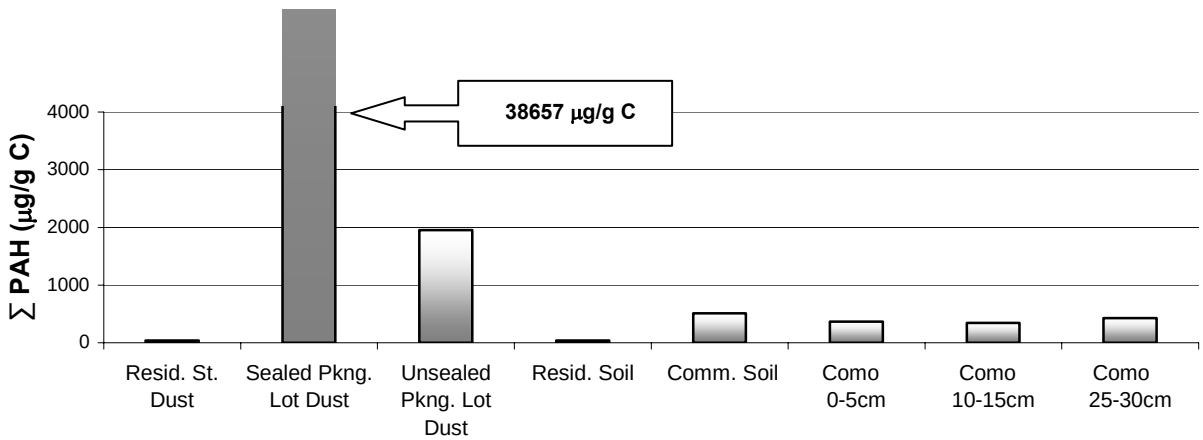


Figure 3. Total PAH concentrations normalized to the organic carbon contents in bulk samples from Lake Como watershed.

Photomicrographs from petrography analysis are shown in Figure 4. Amounts of different CMs determined from the corresponding quantitative analysis are shown in Figure 5. Results indicate that recent organic matter (OM) and OM in ancient sediments dominate CMs in soils and sediments. Asphalt-like and bitumen-like substances are greater in inflow bed sediment than in lake sediments, and greater in top sediment than in deeper sediments. Soot is relatively abundant in lake sediments. Coal tar pitch dominates sealed parking lot dust, while asphalt-like and bitumen-like substances dominate unsealed parking lot dust and street dust. However, relatively little to no coal tar pitch particles was observed in inflow bed sediments and lake sediments by organic petrographic analysis (with a sensitivity of 0.2% for particles greater than 1 to 2 microns). Since PAH levels in coal tar pitch are very high (3.4 to 20 wt %) (Mahler et al., 2005), it takes only a few coal tar pitch particles to elevate the PAH concentrations in sediments. The gradually eroded coal tar particles may be broken down during transport with runoff and diluted by larger CM particles when they get into the streams and lakes, so their concentrations in sediments may be lower than the detection limit of organic petrography. However, due to their great PAH loadings (Figure 1), coal tar particles from sealed parking lot dust may contribute to

PAH contamination in Como sediments. Mass spectroscopy fingerprints of PAHs for coal tar particles, asphalt-like and bitumen-like substances, soot, recent OM and OM in ancient sediments and lake sediments will be compared to assess this assertion.

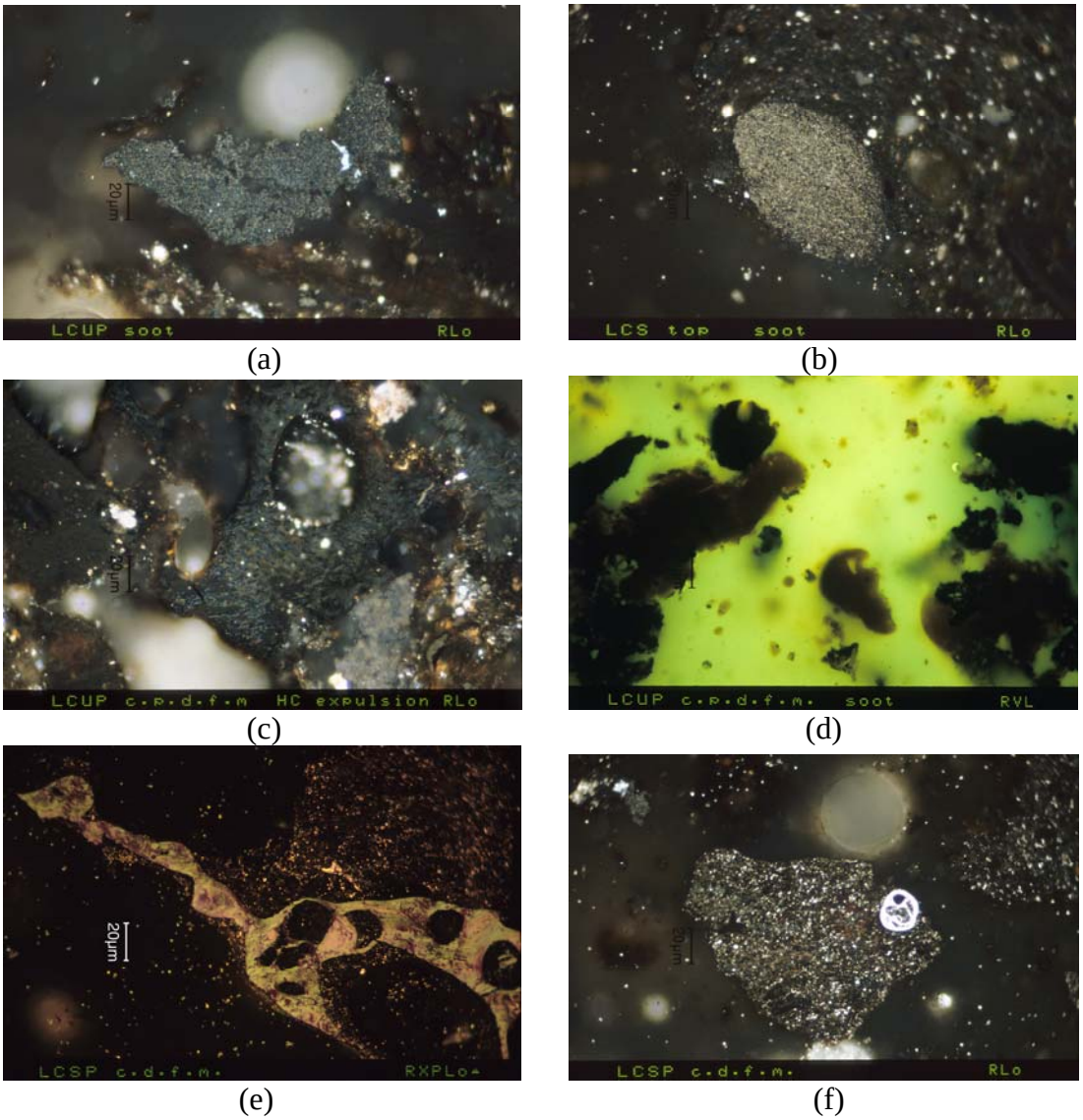
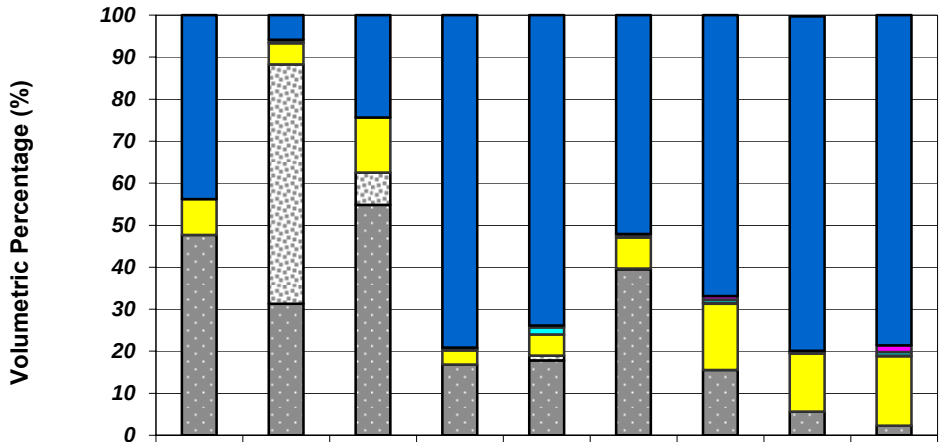


Figure 4. Photomicrographs illustrating the different organic matter present in selected samples: (a) blue grey soot from Lake Como unsealed parking lot dust; (b) rounded soot particle from Lake Como top sediment (0-5 cm); (c) porous asphalt producing a film of oil from Lake Como unsealed parking lot dust; (d) brown fluorescing bitumen & drops related from Lake Como unsealed parking lot dust; e) coal tar pitch with coke particles from Lake Como sealed parking lot dust; f)coal tar pitch with cenosphere from Lake Como sealed parking lot dust. All pictures were taken with a Leitz DMRX-MPVSP microscope photometer in both reflected white-light and UV+violet-light illumination (fluorescence mode), equipped with a WILD MPS48 photoautomat.

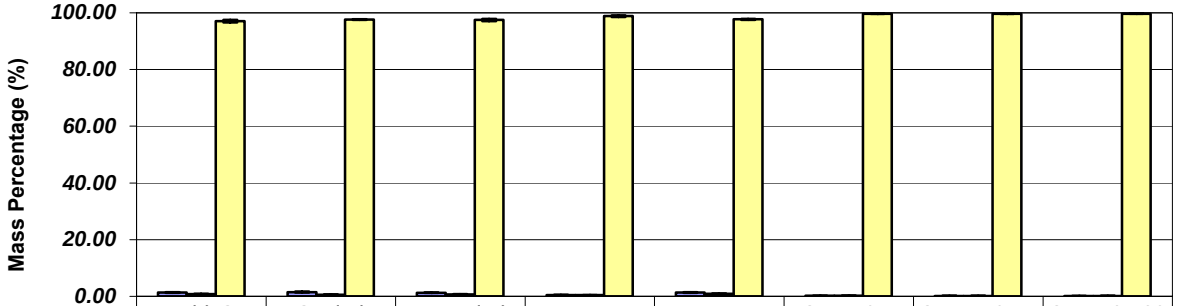


	Resid. St. Dust	Sealed Pkng. Lot Dust	Unsealed Pkng. Lot Dust	Resid. Soil	Comm. Soil	Inflow Bed Sed.	Como 0-5 cm	Como 10-15 cm	Como 25-30 cm
Recent OM and OM in Ancient Sediments	43.8	5.9	24.4	79.1	73.9	52.1	66.9	79.6	78.6
Hard Coal	0	0.6	0	0.2	0.4	0.4	0.8	0.3	1.6
Charcoal	0	0	0	0.3	1.7	0.2	0.8	0.2	0.8
Coke Carbon Forms	0	0.2	0	0.2	0	0.2	0.2	0	0.2
Char	0	0	0	0	0	0	0	0.2	0
Soot	8.5	5	13.1	3.4	5	7.4	15.8	13.8	16.5
Coat Tar Pitch	0	57	7.7	0	1.2	0.2	0	0	0
Asphalt-like and Bitumen-like Substances	47.7	31.3	54.8	16.8	17.8	39.5	15.5	5.6	2.3

Figure 5. Volumetric percentages of various CMs in bulk samples from Lake Como watershed determined by organic petrography.

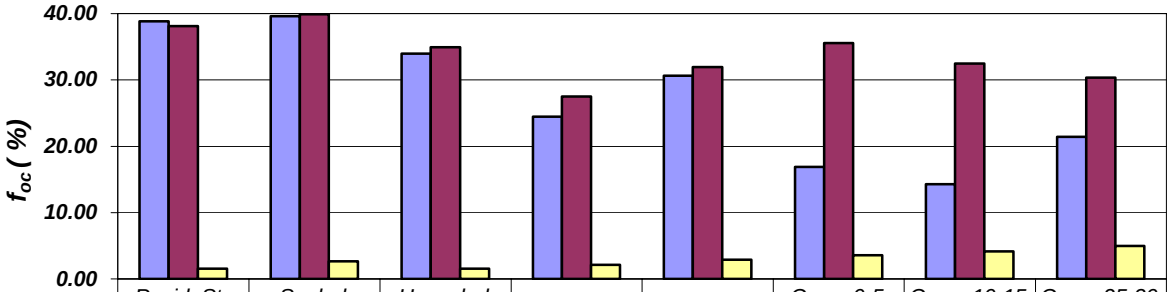
The mass percentages of density-separated fractions are presented in Figure 6, and the organic carbon contents of these fractions are shown in Figure 7. The HFr fractions dominate the mass contents of all bulk samples, ranging from 97.8% to 99.7%. Although the organic carbon contents of the LPCM and OPCM fractions are much greater than that those of the HFr fractions (Figure 7), the majority of CMs are associated with the HFr fractions (>52%) due to the dominant mass contents.

The remaining mass percentages of the different HFr fractions after sequential chemical treatment are presented in Figure 8, and the remaining carbon contents of these fractions after sequential chemical treatment are shown in Figure 9. The significant mass loss of the HFr fractions after the HCl/HF acidification (89.5-95.7%) indicates that minerals (carbonates and silicates) are the major contents of particles in urban runoff (Figure 8). The most recalcitrant CMs are in sealed parking lot dust, which only lost about 32% of the total carbon after sequential chemical treatment (Figure 9). The fact that the resistance of CMs to the chemical treatment slightly increases with the sediment depth suggests the maturity of sediment CMs, which are subjected to years of chemical and biological reactions after deposition and burial.



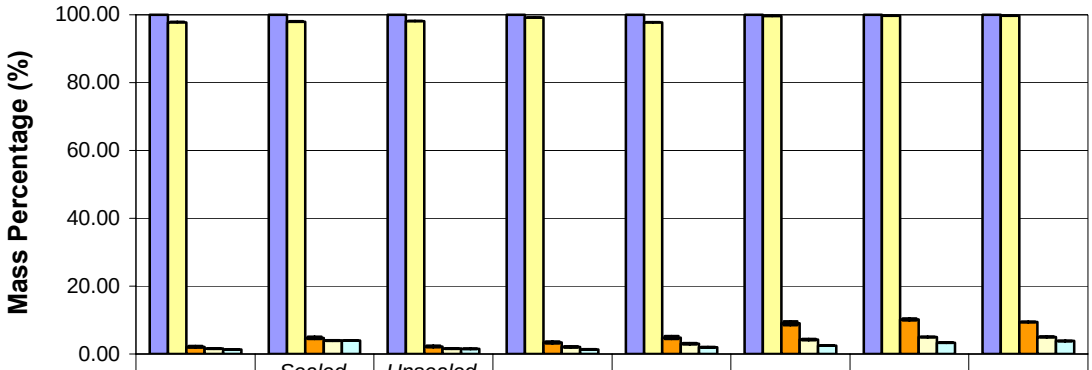
	Resid. St. Dust	Sealed Pkng. Lot	Unsealed Pkng. Lot	Resid. Soil	Comm. Soil	Como 0-5 cm	Como 10-15 cm	Como 25-30 cm
LPCM	1.40	1.52	1.26	0.48	1.38	0.18	0.15	0.13
OPCM	0.83	0.58	0.65	0.40	0.87	0.18	0.17	0.17
HFr	97.07	97.68	97.47	98.82	97.71	99.64	99.68	99.71

Figure 6. Mass percentages of density-separated fractions of Lake Como samples.



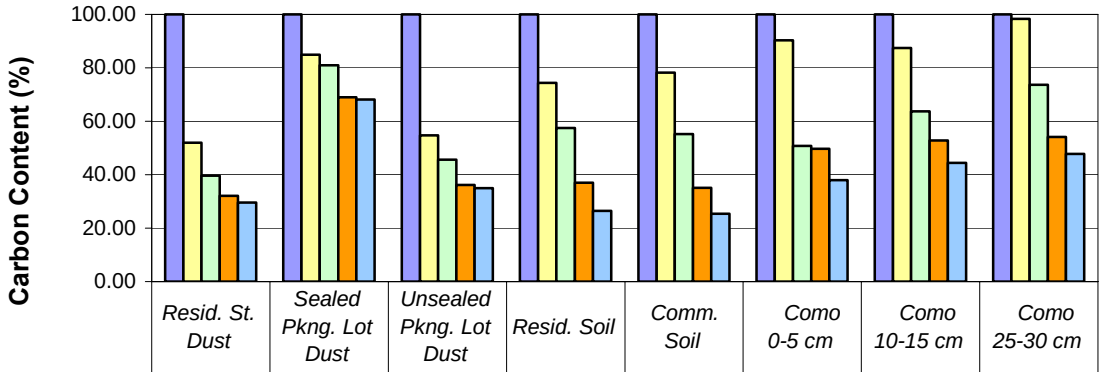
	Resid. St. Dust	Sealed Pkng. Lot	Unsealed Pkng. Lot	Resid. Soil	Comm. Soil	Como 0-5 cm	Como 10-15 cm	Como 25-30 cm
LPCM	38.83	39.63	33.97	24.46	30.66	16.86	14.30	21.42
OPCM	38.14	39.92	34.95	27.52	31.92	35.56	32.49	30.36
HFr	1.53	2.64	1.55	2.10	2.90	3.55	4.13	4.99

Figure 7. Organic carbon contents (f_{oc}) of bulk samples and density-separated samples from Lake Como watershed.



	Resid. St. Dust	Sealed Pkng. Lot Dust	Unsealed Pkng. Lot Dust	Resid. Soil	Comm. Soil	Como 0-5 cm	Como 10-15 cm	Como 25-30 cm
Bulk	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
HFr	97.78	97.91	98.09	99.12	97.75	99.64	99.68	99.71
HCl/HF-treated HFr	2.12	4.76	2.18	3.40	4.85	9.05	10.19	9.43
TFA-treated HFr	1.58	3.99	1.58	2.07	2.98	4.24	5.00	5.02
NaOH-extracted HFr	1.34	3.95	1.48	1.36	1.98	2.49	3.33	3.83

Figure 8. Remaining mass percentages of density-separated HFr fractions after the sequential chemical treatment.



	Resid. St. Dust	Sealed Pkng. Lot Dust	Unsealed Pkng. Lot Dust	Resid. Soil	Comm. Soil	Como 0-5 cm	Como 10-15 cm	Como 25-30 cm
Bulk	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
HFr	52.01	84.85	54.71	74.43	78.20	90.28	87.44	98.32
HCl/HF-treated HFr	39.62	80.96	45.67	57.49	55.22	50.84	63.71	73.64
TFA-treated HFr	32.12	69.04	36.14	36.97	35.15	49.66	52.84	54.15
NaOH-extracted HFr	29.57	68.16	34.93	26.43	25.38	37.96	44.47	47.80

Figure 9. Remaining carbon contents in density-separated HFr fractions after the sequential chemical treatment.

All sorption isotherms are nearly linear, with Freundlich exponents, n, greater than 0.90 (Table 1). Freundlich constants (K_f) of LFr fractions are greater than those of HFr and bulk samples due to the high organic carbon content in LFr.

Table 1. Parameters of sorption isotherms and organic carbon contents (f_{oc}) in Lake Como samples.

		K_f (ug/L)/(ug/g)^n	n	f_{oc} (%)	log Koc (L/kgC)
	Bulk	2.01	0.91	3.92	4.43
Como 0-5cm Sediment	HFr	1.74	0.93	3.55	4.48
	LFr	18.08	0.91	26.20	4.66
	Bulk	2.38	0.97	4.71	4.63
Como 10-15cm Sediment	HFr	2.18	0.95	4.13	4.55
	LFr	19.20	0.91	23.90	4.74
Como 25-30cm Sediment	Bulk	2.68	0.96	4.93	4.65
	HFr	2.29	0.98	4.99	4.62
	LFr	17.01	0.92	27.00	4.56
	Bulk	1.35	0.93	2.87	4.54
Resid. St. Dust	HFr	1.28	0.93	1.53	4.76
	LFr	7.84	0.99	38.58	4.45
	Bulk	3.76	0.94	3.53	4.86
Sealed Pkng. Lot Dust	HFr	2.97	0.94	2.64	4.97
	LFr	15.77	0.94	39.71	4.50
	Bulk	0.92	1.00	2.78	4.51
Unsealed Pkng. Lot Dust	HFr	1.11	0.97	1.55	4.81
	LFr	11.49	0.95	34.30	4.53
	Bulk	0.62	0.95	2.80	4.25
Resid. Soil	HFr	0.81	0.90	2.10	4.43
	LFr	7.21	0.93	26.14	4.23
	Bulk	0.92	0.94	2.92	4.44
Comm. Soil	HFr	1.00	0.93	2.90	4.56
	LFr	6.69	0.96	31.14	4.42

Organic carbon normalized sorption coefficients are presented in Figure 10. Previous research has revealed that in addition to the organic carbon content, the nature or quality of the CMs has a significant impact on sorption capacity (Rutherford et al., 1992). For soil and dust samples, K_{oc} values are higher in HFr fractions than in LFr fractions, indicating more geologically mature CMs may be associated with HFr fractions (Kleineidam et al, 1999). The greater K_{oc} values for the bulk and HFr fraction of the sealed parking lot dust could also account for the higher PAH concentrations in this sample, in addition to the original contributions from the coal tar pitch sealcoat (Figure 3).

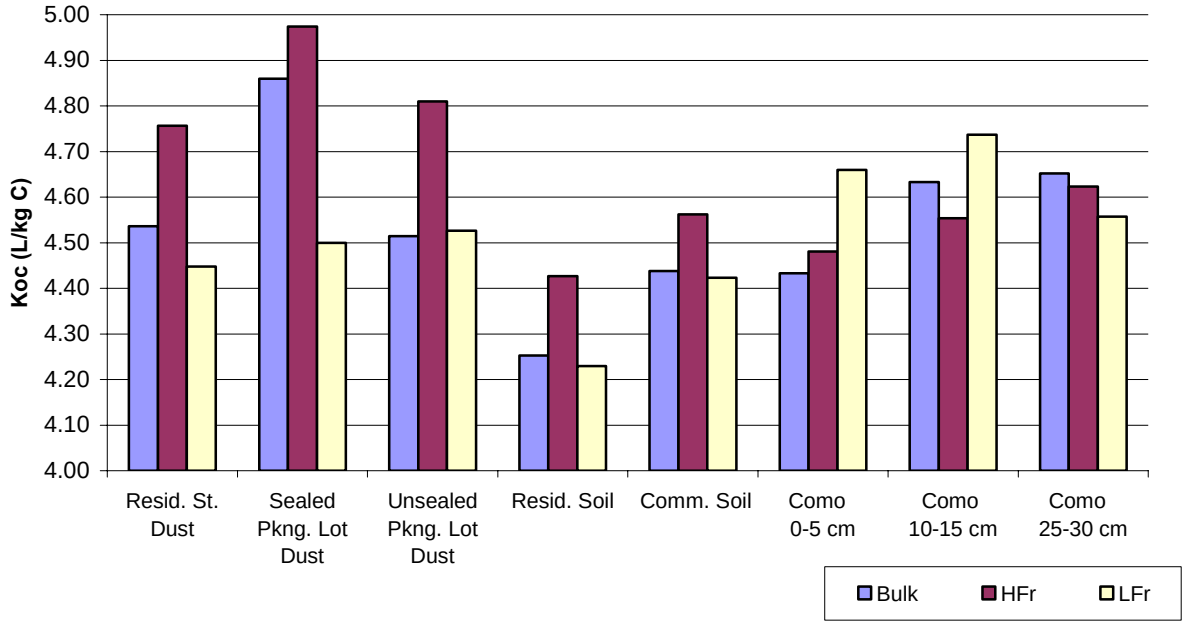


Figure 10. Calculated organic carbon normalized partition coefficient (K_{oc}) in all samples.

Assuming that, at a fixed aqueous concentration, the mass sorbed to the density separated fraction *i* is the same when this fraction is alone, or is part of the bulk sample, relative sorption contribution of fraction *i* at a given concentration *C* can be defined as:

$$Relative \quad Sorption \quad Contribution \quad of \quad Fraction \quad i = \frac{q_i}{\Sigma q_i} \times 100\%$$

where $q_i = K_F C^n \times m_i$

and m_i is the mass percentage of fraction i in bulk samples.

The relative sorption contribution of LFr and HFr fractions of all samples at the equilibrium concentration of 0.1 ppm are shown in Figure 11. The HFr fractions dominate the sorption of phenanthrene relative to the LFr fractions, due to their considerable mass contents. PAHs loadings on these two density-separated fractions will be analyzed to verify that the CMs associated with HFr fractions are the primary carriers of PAHs in urban watershed.

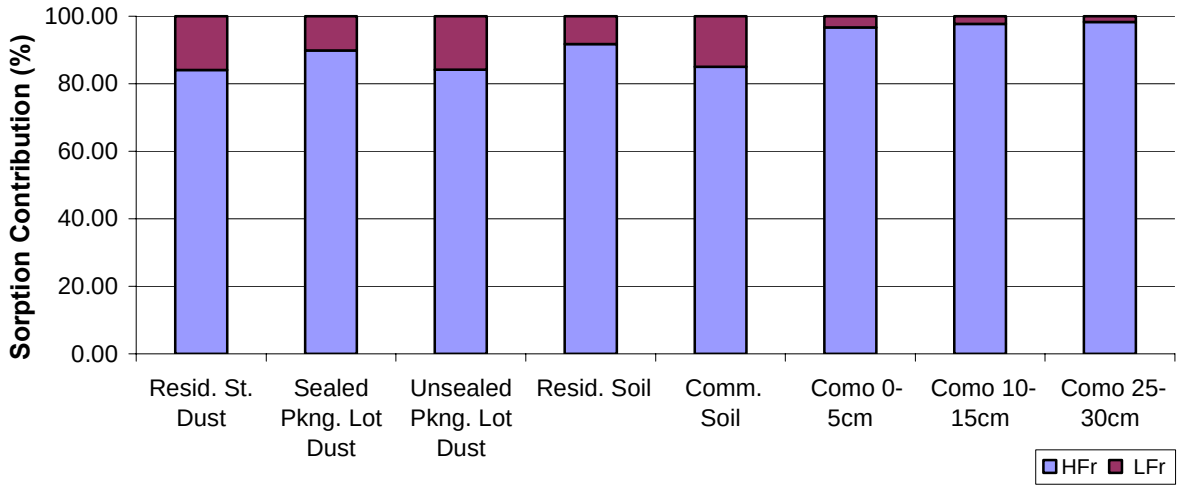


Figure 11. Relative sorption contribution of Lake Como samples at the equilibrium concentration of 0.1 ppm.

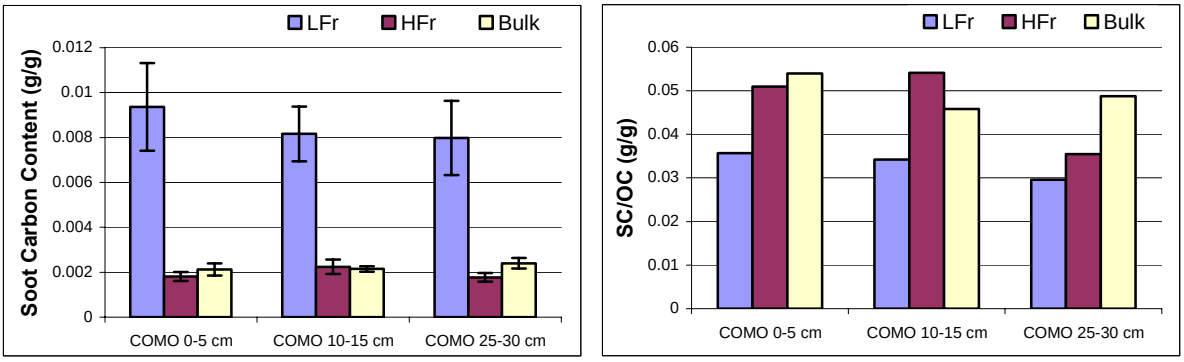


Figure 12. Soot carbon (SC) contents in density-separated fractions of Lake Como sediments quantified by CTO 375 method: (a) SC contents; (b) ratio of SC to organic carbon (OC).

Soot carbon (SC) contents of Lake Como sediments are listed in Figure 12 (a). The LFr fractions contain up to 4 times more SC than the HFr fractions; however, the ratio of SC/OC is lower in the LFr fractions than in the HFr fractions due to the greater amounts of total organic carbon in the LFr fractions (Figure 12 (b)). This ratio reflects the dominance of SC in the organic carbon pool. The small values of SC/OC (<0.055) suggest the dominant amounts of other types of OM in sediments, which can be the recent OM and OM in ancient sediments revealed by organic petrography (Figure 5).

Graduate Students Supported with Funding
Yaning Yang, a PhD student, has been supported on this project for the past three years.

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Department of Civil and Environmental Engineering
College of Engineering
University of Illinois at Urbana-Champaign
Ph.D. student (degree expected in 2008)

Multiple undergraduates have also worked on the project. These are Bushra Dinkha in year 2, Bushra Dinkha and Karina Lairet in year 3, and Ben Dukes in the summer of 2007.

We presently have funds remaining on the project and request a one-year no-cost extension to complete the project work and write the associated manuscripts for publication in peer-reviewed journals. The no-cost extension will also allow Yaning Yang to complete her PhD thesis and graduate.

Publications and Presentations
Yang, Y., C. J. Werth, P.C. Van Metre, B.J. Mahler, J.T. Wilson, B. Ligouis, M. Razzaque, 2007, The role of carbonaceous materials in the fate of PAHs in an urban watershed in European Geosciences Union General Assembly 2007, Vienna, Austria.

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Notable Achievements
Coal tar particles from sealed parking lot dust may be the major source of PAH contamination in lake sediments due to their great PAH loadings.

Related and Seed Projects
N/A

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