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Introduction

The Illinois Water Resources Center is located on the University of Illinois Campus in Urbana-Champaign and serves people throughout Illinois. The state spans from the highly urban Chicago metro region in the northeast to rural southern Illinois and touches many of the central US's major water ways including the Great Lakes, the Mississippi and Ohio Rivers.

In 2008, IWRC researchers, with funding from 104B and 104G sources, completed 2 projects and continued working on an additional 3. Outreach and technology transfer activities included two conferences, publications of a newsletter and web site, and interactions with agencies through the Midwest Technology Assistance Center, the State Water Supply Task Force and many others.

Research Program Introduction

None.

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

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Chapter 1

1.1 Introduction

Long-term non-point source pollution caused by particle-associated contaminants (PACs) in urban lakes and streams is a common problem in the United States. PACs, including chlorinated organic compounds, trace elements, and polycyclic aromatic hydrocarbons (PAHs), are a major concern regarding public health and environmental impact because many of them are persistent, bioaccumulative and (or) toxic. The strong binding of PACs to particles and their subsequent slow release impact the bioavailability of contaminants, sediment quality, surface water quality, and remediation efforts. The occurrence of PACs has resulted in the impairment of thousands of streams, lakes, and reservoirs: PACs were responsible for fish-consumption advisories for 23 percent of total lake acreage and 9.3 percent of total river mileage in the United States in 2000 (USEPA, 2001), and PACs comprise more than 20 percent of total maximum daily loads (TMDLs) nationwide (USEPA, 2003).

Since 1991, the United States Geological Survey (USGS) National Water Quality Assessment (NAWQA) Program has been using sediment cores from reservoirs and lakes to define historical trends of PACs in urban and reference settings across the country, and investigating 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, 2004). 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 sediments in the downstream reservoir, and that trend may not be preserved in cores for some PACs. Their observations present a problem for

effective sediment monitoring and highlight the difficulties encountered in using sediment cores to infer stream water quality. 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.

PACs of concern in this study are polycyclic aromatic hydrocarbons (PAHs) because of their high concentrations and widespread occurrence in the environment, as well as carcinogenic and mutagenic properties. Over the past 25 years, concentrations of PAHs have increased in many urban lakes and streams, particularly in areas with rapid urbanization (Van Metre et al., 1997, 2000; Van Metre and Mahler, 2005). PAHs strongly sorb 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 hypothesize 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 CMs affect the fate and persistence of PACs in small urban watersheds, with a focus on PAHs. This will be achieved by correlation of the amount, type, and PAH sorption properties of CMs found in terrestrial and lake sediment particles of a watershed, where the former, via runoff, are a primary source of CMs and PAHs in lake sediments. Herein, terrestrial particles include street dust, sealed and unsealed parking lot dust, and residential and commercial soils.

This report contains a complete documentation of the research activities and outcomes. **Chapter 2** describes the sample collection, PAH concentrations in samples, and the distribution of CMs in urban watershed determined by organic petrography. The correlation between PAHs and CMs and the potential contribution of coal tar to PAHs are also presented. **Chapter 3** presents the results of chemical and thermal oxidation of field samples, and reference asphalt and coal tar materials, and compares the black carbon contents from these methods to those determined by organic petrography. **Chapter 4** presents the results of CM characterization in terms of element composition, surface functional groups, and specific surface area, and the sorption of phenanthrene to samples and subsamples. The main body of the report is followed by Appendices A, B, and C.

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Chapter 2

The Influence of Coal-Tar Sealant and Other Carbonaceous Materials on Polycyclic Aromatic Hydrocarbon Loads in an Urban Watershed

2.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are common contaminants in the environment. Many PAHs and their metabolites are toxic, mutagenic, and/or carcinogenic, and adversely affect human health and aquatic ecosystems. Over the past 30 years, total PAH concentrations (∑PAH) in urban fresh-water sediments generally have increased (Mahler et al., 2005; Van Metre and Mahler, 2005; Chalmers et al., 2007) and increasing ∑PAH are correlated with increases in urban land-use intensity (Van Metre and Mahler, 2005; Chalmers et al., 2007). Numerous urban sources of PAHs have been identified, including the combustion of fossil fuels, forest fires, motor oil, tire debris, roofing tar, asphalt pavement, and coal tar (Wakeham et al., 1980; Rogge et al., 1993a, 1993b, 1997, 1998; Breedveld et al., 2007). Surface runoff is the most important pathway for the introduction of PAHs into aquatic environments in small urban watersheds (Van Metre and Mahler, 2004; Kimbrough and Dickhut, 2006; Chalmers et al., 2007) and the majority of PAHs in runoff are associated with carbonaceous material (CM) particles (Motelay-Massei et al., 2006). However, the role of CM particles as PAH sources and carriers in urban streams and lakes remains unclear.

CM particles in urban runoff originate from different land-use settings, including residential and commercial soils, rooftops, roads, parking lots, and construction sites. They are derived from heterogeneous source materials, for example, recently accumulated organic debris of plants and animals, partially humified materials,

geopolymers such as kerogen and coal, various types of char and soot from combustion of fuel and biomass, and coal and petroleum byproducts (Murakami et al., 2005; Jeong et al., 2008). The latter can be released from vehicles and industries and by the wear of tires and of asphalt-paved and coal-tar-sealed infrastructure surfaces (Mahler et al., 2005, Murakami et al., 2005). All of these source materials can be altered in the environment by physical, chemical, and biological processes. In recent years, efforts have been made to measure PAH concentrations in a variety of CM particles, including combustion-derived soot (Gustafsson et al., 1997; Jonker et al., 2005) and charcoal (Jonker et al., 2005), and coal-and-petroleum-derived CMs such as coal (Jonker et al., 2005), coke (Khalili et al., 1995), coal tar (Khalil et al., 2006), and asphalt (Wakeham et al., 1980). Several particulate CMs have been found to be important sources of PAHs in urban environments. Boonyatumanond et al. (2007) reported that tire debris was the major contributor of PAHs to street dust in Bangkok, Thailand. Murakami et al. (2008) found that pyrogenic CM particles including diesel exhaust were the dominant source of PAHs in runoff from Chuo Highway in Tokyo, Japan. Because methods used in source apportionment are generally limited to PAH profile measurements with statistical analysis, the types, amounts, and origins of PAH-associated CM particles in urban stream and lake sediments are unknown.

Mahler et al. (2005) found that particles in simulated runoff from parking lots treated with coal-tar-based sealcoat had an average 65-times higher ∑PAH (mean of 3,500 mg/kg) than those from unsealed asphalt and concrete parking lots. Similarly, Van Metre et al. (2009) found that PAH concentrations in dust swept from sealed parking lots in the central and eastern U.S., where coal-tar sealcoat is used, were about 1,000 times

higher than those in dust swept from sealed parking lots in western U.S., where asphalt-based sealcoat is used (median concentrations of 2,200 and 2.1 mg/kg, respectively). The concentrations in particles from coal-tar-sealed pavements were one to two orders of magnitude higher than those in tire wear particles in Bangkok (Boonyatumanond et al., 2007), and about 15 times higher than those in diesel vehicle exhaust particles in Tokyo (Murakami et al., 2008). To our knowledge, coal-tar sealants are not in use in Japan or Thailand. Values for national use of coal-tar sealcoat in the U.S. are not available, but the sealcoat industry estimates that in the State of Texas, 225 million L of refined coal-tar-based sealcoat are applied annually (Scoggins et al., 2007 and references therein), and the New York Academy of Sciences reported estimated annual use of coal-tar-based sealcoat in the New York harbor watershed of approximately 5.3 million L (Valle, 2007). Mass balance estimates and PAH assemblages indicate that runoff from parking lots treated with coal-tar sealcoat is a major source of PAHs in the urban watersheds studied (Mahler et al., 2005). Although it is clear that coal-tar sealcoat contributes to PAHs in urban stream and lake sediments, there remains considerable uncertainty regarding the specific contributions of this CM to PAH loadings, and to the fate of PAHs associated with coal tar sealcoats.

In this study, for the Lake Como watershed in Fort Worth, Texas, we characterized CM particles and PAHs in soils and in dust from paved surfaces that likely are mobilized by runoff, and in sediment from the reservoir and its influent stream. CM particles were characterized using organic petrography, and these characteristics were compared to PAH concentrations to identify the types of CMs that are the principal contributors to PAH loadings in the urban reservoir. The objectives are to identify the

sources and distribution of CM particles in this small urban watershed and to determine which CMs are the dominant sources of PAHs in the lake and stream sediments, with a focus on the role of coal-tar sealants used on parking lots. Information on the association of PAHs with CM particles in urban runoff will contribute to the assessment of the fate of PAHs and their influence on aquatic environments and the development of watershed management strategies to control PAH contamination and improve water quality.

2.2 Materials and Methods

Details of sampling and analytical methods and all PAH data are presented in Wilson et al. (2006), and are summarized briefly here. Note that only residential soil #1 reported in Wilson et al. (2006) was used in our study.

2.2.1 Sample Collection

Samples of sediment, soil, and pavement dust were collected in October 2004 from the Lake Como watershed in Fort Worth, Texas (Figure A1, Appendix A). The watershed is 2.75 km^2 in area, of which 90.4% is urbanized. About one-half of the developed land is residential (47.6%) and one- half is commercial, industrial, and transportation (Van Metre et al., 2003 and references therein). Three sediment cores were collected from a single site in Lake Como using a box corer. The site corresponds to the lower lake site in Van Metre et al. (2003), and cores were taken several meters apart to avoid sampling of disturbed sediment. The cores were vertically extended and sliced at 5-cm intervals, and subsamples from similar depths (depth from the top: 0-5 cm, 10-15 cm, and 25-30 cm) were combined from the three cores to create three large-volume samples.

Influent suspended-sediment samples were obtained by filtering 75 L of stormwater collected from the influent stream during a runoff event through a 0.45-µm PTFE-membrane (Mahler and Van Metre, 2003). The sampling site is the same as was monitored for suspended-sediment chemistry and loads by Van Metre et al. (2003). Influent streambed sediment samples were collected with a stainless steel scoop at the same locations as the suspended-sediment three days following the storm event during which the suspended-sediment samples had been collected. Streambed sediment samples were collected from areas of the channel where fine-grained sediment had accumulated by scooping the soft, relatively fine-grained top sediment. Numerous scoops were combined to obtain a composite sample. Two composite surface soil samples, one from a residential neighborhood and the other from a commercial area, were collected by random sampling at approximately 40 locations near roads, sidewalks, and driveways using stainless steel scoops. One composite residential street dust sample was collected from three asphalt-paved residential streets using nylon push brooms and stainless steel dust pans. Two composite parking lot dust samples were collected; one was composited from dust from three coal-tar-sealed commercial parking lots and the other was composited from dust from three unsealed asphalt or cement commercial parking lots. Each sample of streambed sediment, soil, and pavement dust was homogenized and split after passing through a 1-mm sieve; one part was sent to the University of Illinois at Urbana-Champaign (UIUC) and the other part was sent to the USGS laboratory in Denver, Colorado.

2.2.2 Sample Characterization

Sediment deposition dates for lake sediment samples were estimated on the basis of the sedimentation rate in an age-dated core collected at the same location in 2001 (Van Metre et al., 2003). Total CM contents were estimated by measuring weight loss after heating samples at 550ºC for 4 h in a Thermolyne F62700 muffle furnace (Barnstead International) (Heiri et al., 2001). Total organic carbon (TOC) contents were determined with a CE 440 CHN analyzer (Exeter Analytical, Inc.) in the Microanalysis Laboratory at UIUC.

2.2.3 Organic Petrography

Quantitative petrographic analysis was performed on all samples except the suspended-sediment (because of insufficient sample mass) after the removal of carbonate and silicate minerals by treatment with HCl/HF. CM-enriched samples first were embedded on the surface of a liquid epoxy resin, which was subsequently hardened. Resin surfaces were polished and the embedded CMs were observed with a Leitz DMRX-MPVSP photometer microscope using reflected white light and UV+violet-light illumination (fluorescence mode). CM particles were identified and classified according to maceral groups and their subgroups as defined by Taylor et al. (1998). Maceral volume fractions in each sample were determined by point counting of at least 500 macerals using a multi-point cross-hair ocular. The overall accuracy has been determined to be approximately ±2% (Taylor et al., 1998). Three types of CM particles were physically separated by picking with tweezers from representative samples for microscale PAH extraction and analysis: recent organic matter (OM) from residential soil, asphalt- and bitumen-like substances from unsealed parking lot dust, and coal-tar pitch from sealed

parking lot dust. The latter two particle types could not reasonably be picked from other samples because of their small volume fractions.

2.2.4 PAH Analysis

Eighteen parent PAHs, nine specific alkyl-PAHs, and the homologous series of alkyl-PAHs in bulk samples were determined at the USGS laboratory (Olson et al., 2003). Briefly, samples were extracted overnight with dichloromethane in a Soxhlet apparatus. The extracts were injected into a polystyrene-divinylbenzene gel permeation column and eluted with dichloromethane to remove sulfur and partially isolate the target analytes. PAHs and alkyl-PAHs were analyzed by gas chromatography (GC) with mass spectrometry (MS). Separated CM particles were extracted with acetone and dichromathane by accelerated solvent extraction (ASE) at UIUC (EPA method 3545). The extract was cleaned with silica gel (EPA method 3630c), and 16 EPA priority PAHs were analyzed with GC/MS following EPA method 8270c. Quality assurance was provided by analyzing duplicate samples, laboratory blanks, and spiked reagent samples, and monitoring recovery of surrogate compounds. The sum of 13 PAHs in bulk samples ($\sum_{13} \mathrm{PAH}$) are reported here to compare with the consensus-based sediment-quality-guideline (SQG) probable effect concentration (PEC) (MacDonald et al., 2000). For consistency with literature values of PAHs on specific CM particles, the sum of 11 PAHs ($\sum_{11} \mathrm{PAH}$) on separated particles was used.

2.2.5 Data Analysis

Mass percentages of different CMs in each sample were estimated from measured volume fractions and densities determined from the literature or in our laboratory. Organic carbon (OC) contributions of different CMs in each sample were estimated from the calculated mass percentages, OC contents of CMs determined from the literature or in our laboratory, and the measured TOC of bulk samples. Potential PAH loading from coal-tar pitch and the distribution of PAHs among all types of CMs were calculated using PAH concentrations in CM particles determined from the literature or measured in our laboratory. The uncertainty analysis for predicted parameters was estimated by Monte Carlo simulation with Crystal Ball 2000 (Oracle Corp.). The resulting distribution of simulated output was analyzed by least trimmed squares regression with Systat 12 (Systat Software, Inc.) to eliminate the outliers. The estimated means are reported. Details of the risk analysis are in the Appendix A.

2.3 Results and Discussion

2.3.1 PAH Concentrations

Concentrations of $\sum_{13} \mathrm{PAH}$ varied over about three orders of magnitude, with the largest concentrations in the dust from sealed parking lots (Figure 2.1). The $\sum_{13} \mathrm{PAH}$ concentration in that sample (980 mg/kg) greatly exceeds concentrations in all other urban dust and soils; it is about 2000 times greater than that in residential soil (0.49 mg/kg), 1500 times greater than in residential street dust (0.65 mg/kg), and 30 times

greater than in unsealed parking lot dust (32 mg/kg). Stream and lake sediments show a pattern similar to previous studies (Van Metre and Mahler, 2004), with the suspended-sediment concentration of $\sum_{13} \mathrm{PAH}$ (43 mg/kg) higher than streambed sediment (11 mg/kg), and streambed sediment higher than lake sediments (5.7 to 10 mg/kg). This relation likely results from the loss of PAHs to desorption and solubilization of OM during transport and early diagenesis and the dilution of bottom sediment by cleaner coarser material (especially in the streambed). For comparison, the consensus-based sediment-quality-guideline probable effect concentration (PEC) for $\sum_{13} \mathrm{PAH}$ in fresh water aquatic sediments, i.e., the level above which adverse biological effects are expected to occur, is 22.8 mg/kg (MacDonald et al., 2000).

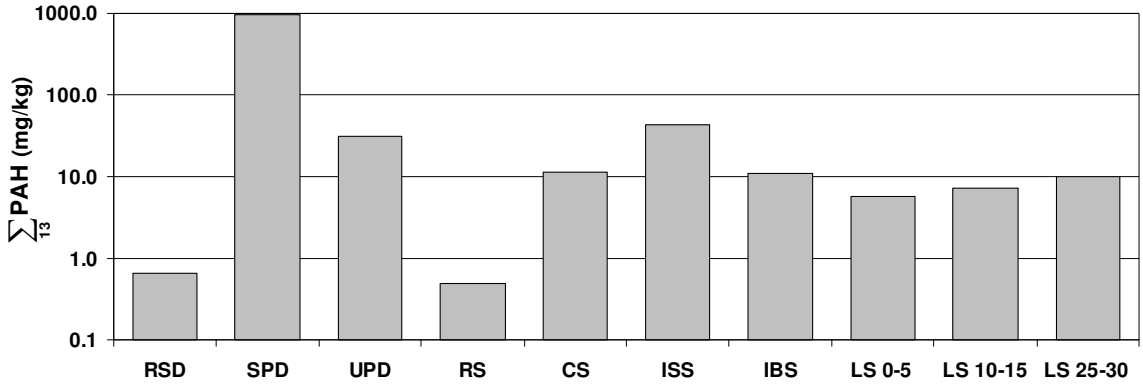


Figure 2.1. Total PAH concentrations in Lake Como watershed samples. Samples include residential street dust (RSD), sealed parking lot dust (SPD), unsealed parking lot dust (UPD), residential soil (RS), commercial soil (CS), influent suspended-sediment (ISS), influent bed sediment (IBS), lake sediment from 0-5 cm depth (LS 0-5), lake sediment from 10-15 cm depth (LS 15-20), and lake sediment from 25-30 cm depth (LS 25-30). ($\sum_{13} \mathrm{PAH}$ as used here is the sum of the detected and estimated concentrations of 13 PAHs as used in the consensus based SQG (MacDonald et al., 2000): naphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, 9H-fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, dibenzo(a,h)anthracene, and benzo(a)pyrene.)

The $\sum_{13} \text{PAH}$ concentrations increase in lake sediments with depth, meaning they are lower in recent years; the 25-30 cm interval is estimated to be about 6 years old (deposited in about 1998). The decrease in PAH concentrations over the past several years might indicate a decrease in PAH load from the watershed but also could be caused by an increase in erosion of cleaner sediment from the watershed (dilution).

The $\sum_{11} \text{PAH}$ concentration in recent OM particles separated from residential soil is 68 mg/kg (Table A3, Appendix A), which is lower than that measured by Ahn et al. (2005) (170 mg/kg) and Khalil et al. (2006) (990 mg/kg), who analyzed particles from contaminated coke oven site soil and manufactured gas plant (MGP) site sediment, respectively. PAHs in separated asphalt- and bitumen-like substances and coal-tar pitch are 2,850 and 75,000 mg/kg, respectively, similar to those detected in asphalt-based and coal-tar-based sealant (2,900 and 87,000 mg/kg, respectively) (Mahler et al., 2005) and coal tar particles from the MGP site (53,000 mg/kg) (Khalil et al., 2006).

2.3.2 Organic Petrography

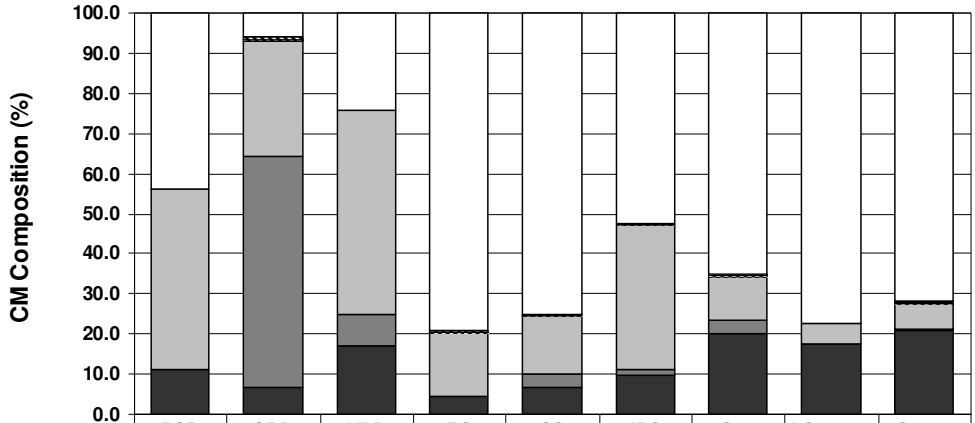
Identified macerals in samples, which consist of multiple subgroups with different physical appearance and volume fractions, are classified into two categories: Recent OM and CMs resulting from anthropogenic contamination (Table A1, Appendix A). Recent OM comprises the following maceral groups: huminite, vitrinite, liptinite, and inertinite. CMs resulting from anthropogenic contamination include hard coal, coke, char, soot, and coal- and petroleum-derived fluorescent materials such as coal-tar pitch and asphalt- and bitumen-like substances. Morphologies of various CM particles such as recent OM, coal, char, and coal-tar pitch in soil or sediment samples have been presented elsewhere

(Karapanagioti et al., 2000; Ghosh et al., 2003), thus, only photographs of representative anthropogenic CM particles in selected samples are presented here (Figure A2, Appendix A).

Recent OM, asphalt- and bitumen-like substances, and soot were found in all samples, while hard coal, char, and coke were often below the detection limit (0.2 vol % for particles greater than 1 to 2 microns) and never exceeded 1.0 % (Table A1, Appendix A). Estimation of mean mass percentages of CMs in each sample indicates that recent OM dominates all soil and sediment samples, ranging from 52.4% to 79.0% (Figure 2.2). The fractions of soot are higher in lake sediments and unsealed parking lot dust than in other samples, ranging from 17.3 to 20.9%. Asphalt- and bitumen-like substances dominate unsealed parking lot dust (50.9%), and are a major component of residential street dust (45.1%), along with recent OM (43.7%). The fraction of asphalt- and bitumen-like substances decreases progressively from unsealed parking lot and residential street dust, to streambed sediment (36.1%), to lake sediments (5.1-11.1%). This suggests that these particles are transported to the lake with runoff, diluted by other CM particles, and possibly removed/degraded over time in buried sediments.

Coal-tar pitch was found in six samples, and its percent contribution varies widely. It dominates sealed parking lot dust (57.5%), and is a small part of unsealed parking lot dust, commercial soil, surficial lake sediment, and streambed sediment (7.8%, 3.6%, 3.2%, and 1.4%). Occurrence of coal-tar pitch in unsealed parking lot dust and commercial soil likely result from offsite transport from sealed parking lots by vehicle or wind (Van Metre et al., 2009). Coal-tar pitch in streambed sediment and surficial lake

sediment likely results from runoff from parking lots. Coal-tar pitch either was not detected or was detected at a very low proportion in lake sediment at lower depths (Table A1, Appendix A). This suggests that (1) runoff of coal-tar particles has increased in recent years, (2) runoff of other particle types relative to coal tar has decreased in recent years, and/or that (3) coal-tar particles are unstable in water and are removed/degraded with time.



	RSD	SPD	UPD	RS	CS	IBS	LS 0-5	LS 10-15	LS 25-30
Recent OM	43.7	5.8	24.0	79.0	75.0	52.4	65.1	77.3	71.7
Hard Coal	0.0	0.8	0.0	0.3	0.3	0.0	0.3	0.0	0.5
Char	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0
Coke	0.0	0.3	0.0	0.3	0.0	0.3	0.3	0.0	0.3
Asphalt- and Bitumen-like Substances	45.1	29.0	50.9	15.8	14.5	36.1	11.1	5.1	6.2
Coal-Tar Pitch	0.0	57.5	7.8	0.0	3.6	1.4	3.2	0.0	0.4
Soot	11.2	6.7	17.3	4.5	6.6	9.8	20.1	17.5	20.9

Figure 2.2. Mass percentages of carbonaceous materials (CMs) in Lake Como watershed samples.

2.3.3 Distribution of OC

The TOC and OC contributed by different types of CMs vary among samples (Table 2.1). The distribution of OC among CMs in samples also is different (Figure A3,

Table 2.1. TOC and OC contributed by CMs in Lake Como watershed samples.

Sample	TOC (g OC/100g bulk sample)	OC Contributed by CMi in Sample (g OC/100g bulk sample)						
		Recent OM	Hard Coal	Coke	Char	Soot	Asphalt- and Bitumen-like Substances	Coal-Tar Pitch
RSD	2.87±0.18	1.21±0.09	0.00	0.00	0.00	0.23±0.07	1.42±0.11	0.00
SPD	4.20±0.29	0.24±0.04	0.04±0.02	0.02*	0.00	0.22±0.07	1.49±0.11	2.18±0.18
UPD	2.78±0.25	0.63±0.07	0.00	0.00	0.00	0.35±0.09	1.60±0.16	0.18±0.02
RS	2.80±0.13	2.16±0.11	0.01*	0.01*	0.00	0.10±0.02	0.52±0.04	0.00
CS	4.00±0.07	2.96±0.09	0.01*	0.00	0.00	0.20±0.07	0.69±0.07	0.13±0.02
IBS	2.22±0.02	1.12±0.04	0.00	0.01*	0.00	0.16±0.04	0.91±0.04	0.03*
LS 0-5	3.92±0.06	2.65±0.13	0.01*	0.02*	0.00	0.61±0.13	0.53±0.04	0.11±0.02
LS 10-15	4.71±0.23	3.77±0.25	0.00	0.01*	0.00	0.64±0.16	0.29±0.04	0.00
LS 25-30	5.04±0.14	3.75±0.18	0.03±0.02	0.02*	0.00	0.84±0.20	0.39±0.04	0.02*

* Standard deviation is below 0.005.

Appendix A). The TOC contents in lake sediments are 3.92, 4.71, and 5.04 g OC/100 g bulk sample for depths of 0-5 cm, 10-15cm, and 25-30cm, respectively, and the increasing trend suggests greater accumulation of OM in sediments in past years. These values are higher than that for the bed sediment in the influent stream (2.22 g OC/100 g bulk sample), indicating that lake sediment acts as a sink for CMs. Two processes likely contribute to the increase in TOC in lake sediment relative to streambed sediment. Lake sediment is very fine grained and OC correlates to percent fines in aquatic sediments (Horowitz and Elrick, 1987), suggesting less dilution of OC in lake sediment by coarser material relative to streambed sediment. Secondly, autochthonous production of organic matter in the lake contributes to OM in lake sediments. The OC contributed by different types of CMs in each sample generally mirrors results for mass percentages of CMs in each sample presented in Figure 2.2, with small relative differences in percent contributions.

2.3.4 Correlations between PAHs and CMs

To investigate the relations between CMs and PAHs, logarithm values of total PAHs ($\log(\sum_{13} \mathrm{PAH})$), high molecular weight (HMW) PAHs, and low molecular weight (LMW) PAHs in samples were plotted against OC contents of selected CMs (Figure 2.3). Extensive research has shown positive correlations between $\sum$PAH and TOC or soot carbon (SC) in soil and sediment samples (Tsapakis et al., 2003; Zhang et al., 2004), but no correlation was observed between $\log(\sum_{13} \mathrm{PAH})$ and TOC or SC here (Figure 2.3a and 2.3b). However, values of $\log(\sum_{13} \mathrm{PAH})$ are positively correlated to the sum of OC in soot, coal tar, and asphalt- and bitumen-like substances ($R^2 = 0.66$), and this correlation is

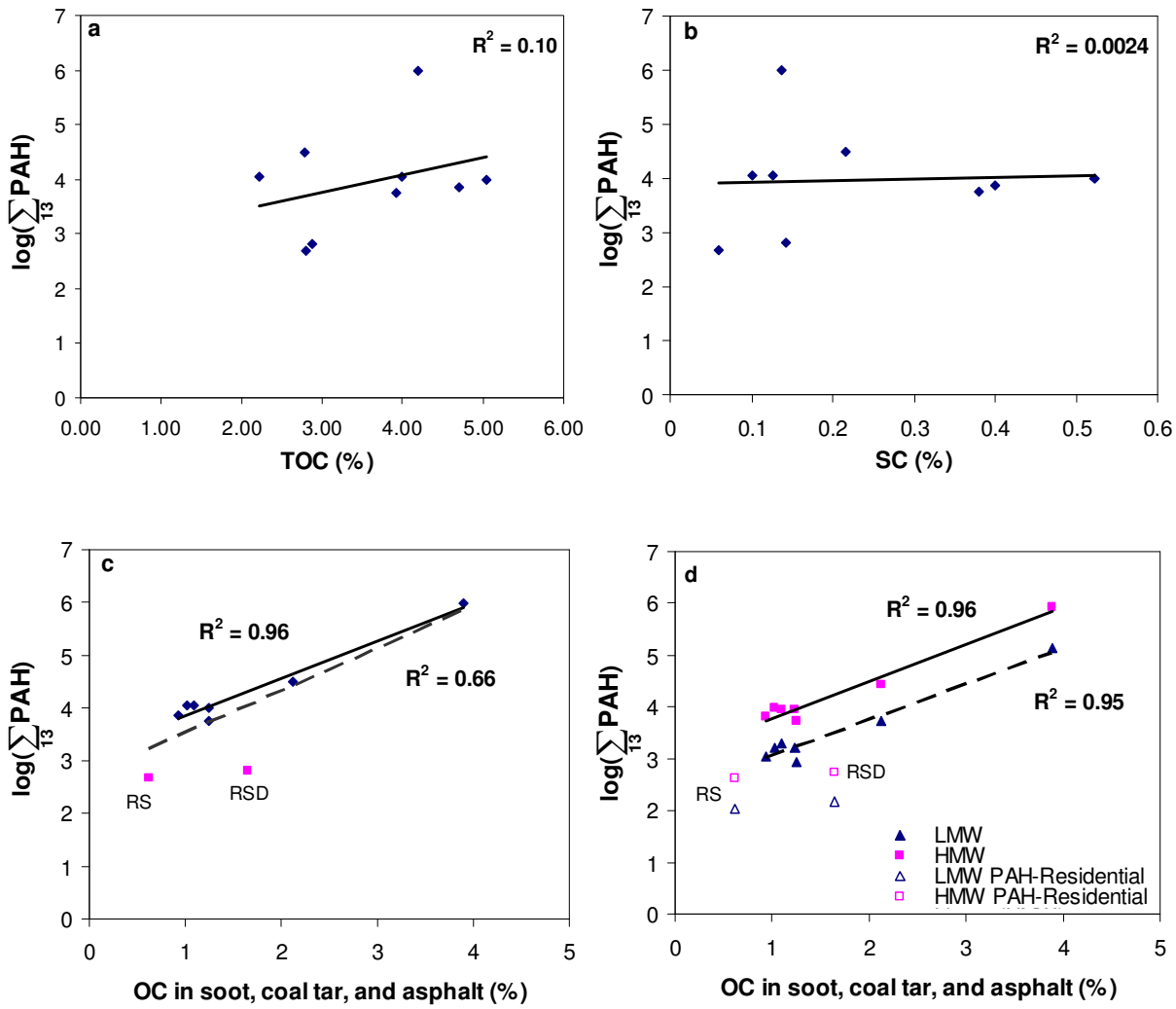


Figure 2.3. Correlations between total PAHs and organic carbon (OC) contents in different CMs in Lake Como watershed samples: (a) TOC vs. $\log(\sum_{13}\mathrm{PAH})$; (b) SC vs. $\log(\sum_{13}\mathrm{PAH})$ (SC is determined using the ratio of f_{sc} and f_{oc} in diesel soot (SRM 1650)(Bucheli and Gustafsson, 2000); (c) Sum of OC in soot, coal tar, and asphalt- and bitumen-like substances vs. $\log(\sum_{13}\mathrm{PAH})$ (solid line indicates the regression of all points; dotted line indicates the regression of all points except residential soil (RS) and residential street dust (RSD); (d) Sum of OC in soot, coal tar, and asphalt- and bitumen-like substances vs. $\log(\sum_{13}\mathrm{PAH})$ (soild line indicates the regression of HMW PAHs in all points except RSD and RS; dotted line indicates the regression of LMW PAHs in all points except RSD and RS.)

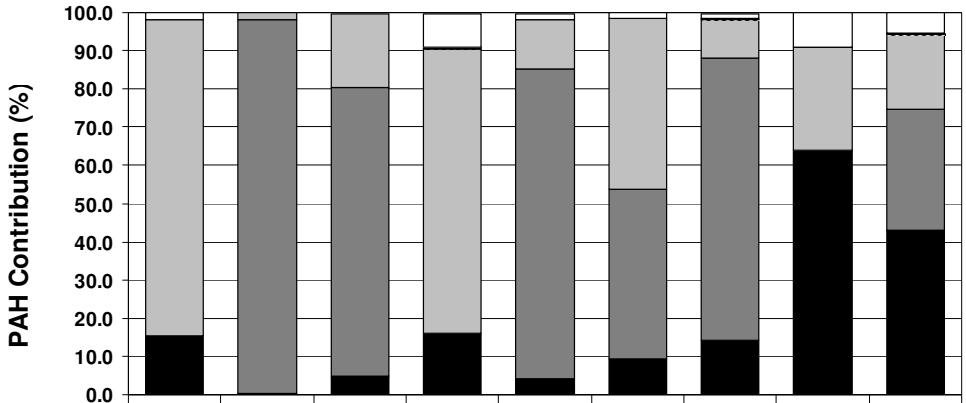
much improved (R^2 = 0.96) when residential soil and residential street dust are excluded (Figure 2.3c). The improved correlation likely results because residential sources of OC have large contributions from recent OM and much lower PAH concentrations, suggesting different PAH–OC dynamics than for commercial source materials. This modified correlation indicates that coal tar, asphalt, and soot particles are likely sources or carriers of PAHs in the watershed, and that PAH levels in the stream and lake are more affected by CMs from commercial land use areas (i.e., commercial soil, dust from sealed and unsealed parking lots) than residential areas.

Petrogenic PAHs are derived from natural OM and petroleum-based products and contain predominantly LMW PAHs (2-3-ring), whereas pyrolytic PAHs are produced during combustion (including pyrolysis) and contain predominantly HMW PAHs (4-6 ring). The 13 PAHs were divided into LMW and HMW PAHs and their logarithm values were plotted against the sum of OC in soot, coal tar, and asphalt- and bitumen-like substances, again excluding the residential soil and street dust samples. HMW PAHs and LMW PAHs both are significantly correlated with the sum of OC (R^2 = 0.96 and 0.95) (Figure 2.3d). Concentrations of HMW PAHs are higher than LMW PAHs in all samples, indicating that combustion sources (e.g., soot, coal tar, asphalt) dominate PAHs in all samples.

2.3.5 Distribution of PAHs

The distribution of PAHs among CMs was estimated using measured or literature values of PAH concentrations in CM particles and mass percentages of CMs determined from quantitative petrography and measured or literature values of CM density (see

Appendix A for details) (Figure 2.4). These estimates represent potential relative contributions because actual PAH loadings for each CM in each sample were not measured (Figure 2.4), and because literature values associated with different CMs result in estimated $\sum_{11} \text{PAH}$ that exceed measured $\sum_{11} \text{PAH}$ (data not shown). This is not surprising given that literature values typically are determined for relatively fresh CM particles, and particle weathering and transport reduce PAH concentrations over time. PAHs can also redistribute over time from more weakly to more strongly sorbing CMs.



	RSD	SPD	UPD	RS	CS	IBS	LS 0-5	LS 10-15	LS 25-30
Recent OM	1.9	0.0	0.2	9.0	1.6	1.6	1.5	9.1	5.3
Hard Coal	0.0	0.0	0.0	0.3	0.1	0.0	0.1	0.0	0.3
Char	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Coke	0.0	0.0	0.0	0.3	0.0	0.1	0.1	0.0	0.2
Asphalt- and Bitumen-like Substances	82.7	1.9	19.1	74.2	13.0	44.6	10.1	27.0	19.4
Coal-Tar Pitch	0.0	97.7	75.6	0.0	80.9	44.6	74.0	0.0	31.7
Soot	15.3	0.3	4.9	16.2	4.2	9.2	14.1	64.0	43.0

Figure 2.4. Distribution of PAHs among CMs in Lake Como watershed samples.

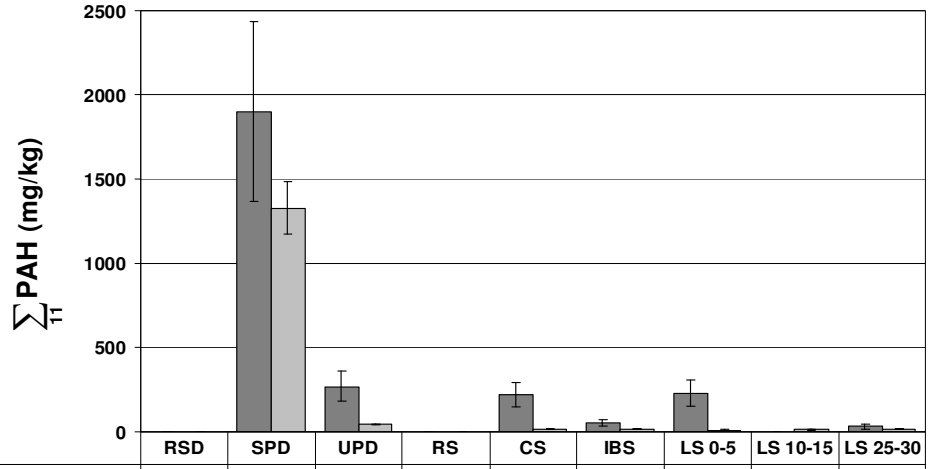
The estimated values suggest that the majority of PAHs in residential street dust and residential soil are associated with asphalt- and bitumen-like substances (83% and 74%, respectively). The majority of PAHs in sealed parking lot dust, unsealed parking lot dust, commercial soil, and top sediments are associated with coal-tar pitch (98%, 76%,

81%, and 74%, respectively). In streambed sediment, asphalt- and bitumen-like substances and coal-tar pitch play equally important roles, although the amount of asphalt- and bitumen-like substances is 25 times greater than the amount of coal-tar pitch. Soot dominates the distribution of PAHs in deeper lake sediments: 64% in sediments for the 10-15 cm depth and 43% for the 25-30 cm depth. The results suggest that coal-tar pitch, soot, and asphalt- and bitumen-like substances are important PAH sources in urban lake sediments. These results are consistent with the correlations between $\log(\sum_{13} \mathrm{PAH})$ and OC in soot, coal-tar pitch, and asphalt- and bitumen-like substances discussed in the previous section.

2.3.6 PAH Loading from Coal-Tar Pitch

The mass of PAHs associated with coal-tar pitch in different samples was estimated to more directly explore its potential contribution to total PAH loadings. Results are shown in Figure 2.5. Recall that the measured value of the $\sum_{11} \mathrm{PAH}$ concentration in coal-tar particles picked from the sealed parking lot sample was used. The estimated PAH loading contributed by coal-tar particles to 1 kg of sealed parking lot dust is 1,900 mg; this is not significantly different from the measured $\sum_{11} \mathrm{PAH}$ in this sample. Given that greater than 97% of the total PAHs in this sample are from coal tar (Figure 2.4), this agreement indicates that parameter inputs used in our estimation were adequately determined for this sample. Extending the coal-tar loading results to other samples, the potential PAH loadings from coal tar are greater than the measured $\sum_{11} \mathrm{PAH}$ in all samples where coal-tar particles were detected. These

differences are expected because PAH concentrations associated with coal-tar particles will decrease during runoff, during transport and deposition in surface water bodies, and in sediments after burial as a result of several processes, including volatilization, solubilization, degradation, and mass transfer to other CMs. Nevertheless, the results suggest that coal-tar particles are an important source of PAHs in urban lake sediments.



	RSD	SPD	UPD	RS	CS	IBS	LS 0-5	LS 10-15	LS 25-30
Potential Contribution from Coal Tar	0	1900	270	0	220	54	230	0	31
Measured Concentration	0.84	1330	44	0.72	16	15	9.5	11	15

Figure 2.5. Comparison between potential PAH loadings from coal-tar pitch and measured total PAHs in Lake Como watershed samples ($\sum_{11}$PAH as used here is the sum of 11 PAHs: phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo(a)pyrene, indeno[1,2,3-cd]pyrene, and benzo[ghi]perylene. Error bars represent the precision of estimation or measurement. For estimated potential PAH loadings from coal tar pitch, it is ±1 standard deviation. For measured total PAHs in samples, it is absolute variation).

It is reasonable to infer from these estimates and the correlations between CMs and PAHs (Figure 2.3) that coal-tar pitch, asphalt, and soot are the primary sources and carriers of PAHs in our studied watershed. Several decades of research on urban sources of PAHs mainly focused on automobile exhaust, lubricating oils, gasoline, tire particles, asphalt and bitumen, and atmospheric deposition (Wakeham et al., 1980; Takada et al.,

1990; Simcik et al., 1996; Brandt and De Groot, 2001; Pengchai et al., 2004). Only recently has use of coal-tar sealants been identified as an important urban source of PAHs (Mahler et al., 2005). Because of the high intrinsic PAH levels in coal tar and the widespread and repeated application of coal-tar sealants on impervious surfaces, the abrasion of sealant likely generates a significant amount of coal-tar particles that contribute to PAH contamination in urban settings (Van Metre et al., 2009). Lacking specific knowledge of how coal-tar particles influence the transport and fate of PAHs in urban watersheds makes it difficult to make informed management decisions. For example, if coal-tar pitch is an important source of PAHs in urban lake sediments, stormwater management strategies that rely on trapping relatively coarse sediments might be ineffective. Thus improving understanding of the relations between PAHs with CM particles in urban runoff should assist in stormwater management and policy decision.

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Chapter 3

Potential Contributions of Asphalt and Coal Tar to Black Carbon Quantification in Urban Dust, Soils, and Sediments

3.1. Introduction

Black carbon (BC) is a particulate carbonaceous material (CM) produced from the incomplete combustion of fossil fuel and biomass (Goldberg, 1985). It is ubiquitous in soil, sediment, water, and the atmosphere, and is involved in many biogeochemical and environmental processes (Kuhlbusch, 1998; Schmidt and Noack, 2000; Forbes et al., 2006). BC sequestered in soils and sediments plays an important role as a sink of carbon (C) in the global C cycle because of its stability in the environment (Gustafsson and Gschwend, 1998; Kuhlbusch, 1998; Masiello and Druffel, 1998). Because of its strong sorption properties, BC sequestered in soils and sediments also affects the transport and fate of persistent organic pollutants (POPs) in aquatic environments, such as polychlorinated biphenyls (PCBs) (Jonker and Smedes, 2000; Jonker and Koelmans, 2002) and polycyclic aromatic hydrocarbons (PAHs) (Cornelissen et al., 2005; Jonker and Koelmans, 2002).

Although petrogenic sources of BC (weathering of graphite from rocks) have been reported in marine sediments (Dickens et al., 2004), BC is usually pyrogenic in origin, and spans a continuum of materials ranging from slightly charred biomass to highly refractory soot (Elmquist et al., 2006; Hedges et al., 2000; Masiello, 2004). The BC continuum is often broadly separated into two groups, char-BC and soot-BC, which

have different physicochemical properties. Char-BC is charred organic residues (e.g., wood char) formed at lower temperatures, and retains some morphological features of the precursors (Nguyen et al., 2004). Soot-BC is the condensed vapor phase of combustion and consists of a more randomly ordered inner core and a more crystallized outer shell (Gustafsson et al., 2001). The formation mechanisms of char- and soot-BC cause them to be more recalcitrant than other biologically or geologically-generated CMs, such as humic substances, coal, and kerogen.

Current methods to quantify BC in soils and sediments include quantitative petrography (Cornelissen et al., 2004), acid dichromate oxidation (Gelinas et al., 2001; Jeong et al., 2008; Lim and Cachier, 1996; Masiello and Druffel, 1998; Masiello et al., 2002; Song et al., 2002), and chemo-thermal oxidation at 375ºC (CTO-375) (Elmquist et al., 2004; Gustafsson et al., 2001; Gustafsson and Gschwend, 1997; Gustafsson et al., 1997; Nguyen et al., 2004). The first of these methods requires particles larger than the wavelength of light, and employs fluorescent and phase contrast microscopy. The latter two of these methods rely on the chemical and thermal stability of BC. They involve removing minerals and non-BC CM components using chemical treatments and/or thermal oxidation, followed by elemental analysis. Because of the complexity of natural matrices, and the existence of potential interfering materials, BC contents in soils and sediments determined by different techniques can vary widely (Hammes et al., 2007; Schmidt et al., 2001). Some non-pyrogenic CMs, such as melanoidin, kerogen, lignite coal, and bituminous coal, have been suggested to result in overestimation of BC in soil and sediment samples because these materials are either chemically recalcitrant or

charred during heating (Brodowski et al., 2005; Gustafsson et al., 2001; Hammes et al., 2007).

In urban watersheds, asphalt and coal tar particles worn from infrastructure surfaces (pavements and roofs) can be present in soils, stream and lake sediments, and their effect on BC quantification has heretofore not been explored. Asphalt (in this study) is the dark brown to black cementitious material that remains after the distillation of crude oil and commonly used as a paving material. The words bitumen and asphaltic bitumen have been used instead of asphalt in countries other than the United States (Zakar, 1971). Coal tar is a black sticky substance that remains after coal carbonization or gasification. It is widely used as a binding material in the aluminum and graphite industries, and as a primary ingredient of sealcoats used in pavement and building applications. Asphalt and coal-tar-based sealcoats undergo weathering and break into particles as a result of vehicle traffic, exposure to sunlight and air, and freeze-thaw cycles (Freemantle, 1999; Mahler et al., 2005). Runoff can carry particles into soils, streams, and lakes. The pyrogenic origins of asphalt and coal tar suggest they may be resistant to chemical and thermal treatment used for BC quantification.

The primary objectives of this study are to explore the effects of asphalt and coal tar on the quantification of BC in a range of urban environmental samples, and to evaluate biases in the different methods used for quantifying BC. Samples evaluated were reference asphalt and coal-tar materials, as well as pavement dust, residential and commercial soil, and lake sediments from a small urban watershed. Total BC was quantified using a series of chemical treatments that includes Cr_2O_7 oxidation, and CTO-375. BC species including soot and char/charcoal, asphalt, and coal tar were quantified

using petrographic analysis. This approach allows us to test the hypothesis that both asphalt and coal tar are resistant to oxidation using Cr_2O_7 or CTO-375, and therefore contribute to BC amounts determined with these methods.

3.2 Materials and Methods

3.2.1 Sample Collection, Preparation, and C Analysis

Field samples (pavement dust, soils, and lake sediments) from Lake Como watershed, Fort Worth, Texas, asphalt and coal-tar particles picked from representative field samples, and reference asphalt binder and coal-tar sealcoat were used in this study. Details of the Lake Como sampling site and sample collection methods were described in Chapter 2. Briefly, one composite residential street dust sample was collected from three asphalt-paved residential streets using nylon push brooms and stainless steel dust pans. Two composite parking lot dust samples were collected; one was a composite of dust from three coal-tar-sealed commercial parking lots and the other was a composite of dust from three unsealed asphalt or cement commercial parking lots. Two composite surface soil samples (top 2 cm) were collected randomly at approximately 40 locations near roads, sidewalks and driveways using stainless steel scoops; one was from a residential neighborhood and the other was from a commercial area. Three sediment cores several meters apart were collected from a single site in Lake Como using a box corer. The cores were vertically extended and sliced at 5-cm intervals, and subsamples from the same depths (depth from the top: 0-5 cm, 10-15 cm, and 25-30 cm) were combined from the three cores to create three large-volume samples. Each composite sample was homogenized after passing through a 1-mm sieve.

Particles of asphalt and coal tar were physically separated from unsealed parking lot dust and sealed parking lot dust, respectively, after treatment with hydrochloric and hydrofluoric acid (HCl/HF) to remove carbonate and silicate minerals and enrich in C. The target particles were identified in bulk samples with a Leitz DMRX-MPVSP photometer microscope using reflected white light and UV+violet-light illumination (fluorescence mode). The particles were then picked from the bulk samples using tweezers. The reference asphalt binder was obtained from Frontier Refining, Inc., in Cheyenne, WY. The reference coal tar was obtained by evaporating the liquid component of a coal-tar-based emulsion driveway sealcoat, obtained from Henry Company, El Segundo, CA.

The C contents of all bulk samples were determined with a CE 440 CHN analyzer (Exeter Analytical, Inc., North Chelmsford, MA) in the Microanalysis Laboratory at the University of Illinois at Urbana-Champaign (UIUC), after the removal of inorganic C with 5% H_2SO_3 followed by oven drying, and is referred to as total organic C (TOC). The TOC includes both non-BC organic carbon (OC) and BC.

3.2.2 Density Separation

Representative sub-samples of Lake Como watershed field samples were separated into light (LFr) and heavy (HFr) fractions with a solution of 1.60 g/cm^3 sodium polytungstate. Both fractions were oven dried at 60ºC, pulverized, and passed through a 100-mesh sieve to enhance reaction kinetics of subsequent chemical and thermal treatments.

3.2.3 C_2O_7 Oxidation

Both HFr and LFr fractions were subject to a series of chemical treatment steps to obtain fractions enriched in one or more particulate CMs. Procedures were the same as described in Jeong et al. (Jeong et al., 2008; Jeong and Werth, 2005). Briefly, samples were treated sequentially with HCl, HF/HCl, trifluoroacetic acid (TFA)/HCl, sodium hydroxide (NaOH), and acid dichromate ($K_2Cr_2O_7/H_2SO_4$) to remove carbonates, silicate minerals (Durand, 1980), easily hydrolyzable organic matter (Gelinas et al., 2001), fulvic and humic acids (Swift, 1996), and more recalcitrant humin and kerogen (Lim and Cachier, 1996; Masiello et al., 2002), respectively. Mass fractions of different CM enrichments were obtained by measuring changes of sample mass after each treatment step, and the final residues (i.e., after $K_2Cr_2O_7/H_2SO_4$) are referred to as BC fractions. More than three replicate HFr fractions were sequentially treated through $K_2Cr_2O_7/H_2SO_4$, hereafter referred to as Cr_2O_7 treatment. Only one sample of each LFr fraction was treated in this way due to sample mass limitations. The C and hydrogen (H) contents of LFr and HFr fractions after the removal of inorganic C, and their BC enrichment fractions, were determined using a CHN analyzer. The final C in BC enrichment fractions is referred to as BC determined by Cr_2O_7 oxidation. The BC contents in both fractions are expressed as gram BC per kilogram of bulk samples (g/kg) in the results.

The same sequential chemical treatment was also applied to the reference asphalt and coal tar samples. To enhance the reaction rates, fine particles of coal tar, or coal tar and asphalt coated on inert supporting materials, were used. Support materials inert to all chemicals used during treatment were not identified. As a result, pyrite (WARD'S Natural Science, Rochester, NY) was used as the support material for treatment with HCl

and HF/HCl because it is resistant to these two acids but not dichromate, and glass was used as the support material for treatment with TFA/HCl, NaOH, and $K_2Cr_2O_7/H_2SO_4$, because it is resistant to strong oxidants but not HF. Dried coal tar was cut into < 1 mm pieces and asphalt was coated on fine pyrite particles (< 1 mm) before use in HCl and HF/HCl treatment. A control with pyrite particles was also performed. Asphalt and coal tar were coated on glass slides (2 cm by 2 cm) in thin layers (< 1 mm) for subsequent chemical treatment steps. Changes in sample mass after each treatment step were recorded. The final remaining mass percentage was determined by the combination of remaining mass percentages after each step of chemical treatment. The C and H contents of original samples after the removal of inorganic C and the residues after the final Cr_2O_7 oxidation were measured by CHN analysis. Chemical treatment through Cr_2O_7 was not applied to asphalt and coal-tar particles separated from the Lake Como unsealed and sealed parking lot samples, respectively, due to the limited mass of these samples.

3.2.4 Thermal Treatment (CTO-375)

BC contents in bulk samples and LFr and HFr fractions were determined in triplicate by a modified CTO-375 method (Gustafsson and Gschwend, 1997). About 20-50 mg of well-pulverized samples (< 150 μm) were combusted in a Thermolyne F62700 muffle furnace (Barnstead International, Dubuque, IA) in excess air at 375 °C for 24 h, followed by carbonate removal with 1M HCl, and the C and H contents of the remaining mass were determined by CHN analysis. The measured C contents after CTO-375 and HCl treatment are the BC contents. BC contents in reference asphalt and coal tar materials, and in separated asphalt and coal-tar particles from the Lake Como samples, were also estimated with CTO-375.

3.2.5 Organic Petrography

Petrographic methods and results were reported in Chapter 2, and are presented in this chapter for comparison. Quantitative organic petrographic analysis was performed after the removal of carbonate and silicate minerals with HCl/HF. Sample preparation involved embedding CM-enriched samples on the surface of epoxy resin, allowing the resin to cure and harden, and then polishing the sample surface. Embedded samples were observed with a Leitz DMRX-MPVSP photometer microscope using reflected white light and UV+violet-light illumination (fluorescence mode). CM particles were identified and classified according to maceral groups and their subgroups defined by Taylor et al. (1998). Volume fractions of macerals in each sample were determined by point counting of at least 500 macerals using a multi-point cross-hair ocular. The overall accuracy has been determined to be approximately ±2% (Taylor et al., 1998).

The contributions of different CMs to the TOC of each sample were estimated with volume fractions of CMs determined by organic petrography, densities and OC contents of CMs determined from the literature or in our laboratory, and TOC of bulk samples. The corresponding equations for this calculation and sources of density and OC contents are shown in Appendices A and B (Table A1, A2, and B1).

The BC contents of CMs identified with petrography were determined by multiplying OC contributions by BC to OC ratios (BC/OC) obtained from the literature or measured in our laboratory. For soot, a literature value of BC/OC (0.63) was obtained from the average BC contents after CTO-375 of several reference materials, including diesel soot SRM-2975, diesel soot SRM-1650, and n-hexane soot (Elmquist et al., 2006). For asphalt and coal tar, BC/OC ratios were measured for reference materials using both

Cr_2O_7 oxidation and CTO-375. Values from Cr_2O_7 oxidation were used when comparing BC from this method with BC from petrography, and values from CTO-375 were used when comparing BC from this method to BC from petrography. Char was not present in sufficient quantities to justify calculating BC quantities, and other CMs do not directly contribute to BC contents.

3.3 Results and Discussion

3.3.1 BC Determined by Cr_2O_7 Oxidation

The TOC contents of bulk samples, mass percentages of LFr and HFr fractions, and the distribution of OC and BC between LFr and HFr fractions are shown in Table 3.1. Recall that OC includes both non-BC and BC fractions of C after treatment to remove inorganic C. The majority of mass is associated with HFr fractions in all samples (97.1-99.7%), so are the OC and BC. The OC contents range from 14.8 g/kg to 49.6 g/kg in HFr fractions, and from 0.8 g/kg to 8.6 g/kg in LFr fractions. The dominance of HFr-associated OC over LFr-associated OC is greater in the sediments (~98%) than in the soils and dust (63-90%). The discrepancies (ranging from 0.1 to 25%) between measured TOCs of bulk samples and the sum of OC in LFr and HFr samples is attributed to the loss of water soluble OC during density separation.

Table 3.1. Measured TOC in bulk samples, the mass percentages of LFr and HFr fractions, the distribution of OC and BC between LFr and HFr fractions, and the ratios of H/C in BC determined by Cr_2O_7 oxidation.

Sample ID		RSD	SPD	UPD	RS	CS	LS 0-5	LS 10-15	LS 25-30
TOC (g/kg) [a]		28.7±1.8	42.0±2.9	27.8±2.5	28.0±1.3	40.0±0.7	39.2±0.6	47.1±2.3	50.4±1.4
Mass (%)	**LFr**	2.22±0.10[b]	2.09±0.12	1.91±0.08	0.88±0.08	2.25±0.13	0.36±0.02	0.32±0.02	0.30±0.02
	HFr	97.07±0.46	97.68±0.12	97.47±0.36	98.82±0.30	97.71±0.18	99.64±0.03	99.68±0.03	99.71±0.03
OC (g/kg)	**LFr**	8.57	8.31	6.57	2.26	7.00	0.95	0.76	0.78
	HFr	14.83	35.56	15.10	20.76	31.27	35.40	41.16	49.55
	Sum	23.4	43.87	21.67	23.02	38.27	36.35	41.92	50.33
Contribution to OC (%)	**LFr**	36.63	18.94	30.31	9.84	18.28	2.60	1.81	1.55
	HFr	63.37	81.06	69.69	90.16	81.72	97.40	98.19	98.45
BC (g/kg)	**LFr**	1.38	2.97	0.75	0.26	0.44	0.14	0.17	0.19
	HFr	4.87	13.82	4.18	3.49	2.59	9.99	11.11	11.51
	Sum	6.25	16.79	4.93	3.75	3.03	10.13	11.28	11.70
Contribution to BC (%)	**LFr**	22.08	17.68	15.27	6.88	14.41	1.42	1.50	1.61
	HFr	77.92	82.32	84.73	93.12	85.59	98.58	98.50	98.39
H/C in BC	**LFr**	0.11	0.06	0.09	0.11	0.11	0.10	0.10	0.10
	HFr	0.12	0.07	0.12	0.11	0.10	0.11	0.12	0.12

a. Original data was presented in Chapter 2
b. Represents averages and standard deviations of replicates ≥3

Similar to OC, the majority of BC is associated with HFr fractions in all samples, and the dominance of HFr-associated BC over LFr-associated BC is greater in the sediments (> 98%) than in the soils and dust (78-93%). Sealed parking lot dust has the largest amount of total BC (16.8 g/kg), followed by sediment samples (11.7, 11.3, and 10.1 g/kg for depths of 25-30cm, 10-15cm, 0-5 cm, respectively), residential street dust (6.3 g/kg), unsealed parking lot dust (4.9 g/kg), residential soil (3.8 g/kg), and commercial soil (3.0 g/kg). H/C ratios of BC in LFr and HFr fractions separated by Cr_2O_7 oxidation are between 0.06 and 0.1 (Table 3.1), within the range of reported values determined by Cr_2O_7 oxidation for the BC continuum, especially for char-BC and soot-BC (0-0.6 by Hammes et al. (2007) and 0-0.8 by Kuo et al. (2008)).

Mass loss of reference asphalt and coal tar materials after each step of chemical treatment is presented in Figure B1 (Appendix B). Approximately 90% of the original asphalt mass remains after Cr_2O_7 oxidation; ~3% is lost after HCl/HF demineralization, ~6% after TFA and NaOH extraction, and ~1% after Cr_2O_7 oxidation. Approximately 46% of the original coal tar mass remains after Cr_2O_7 oxidation; ~15% is lost after HCl/HF demineralization, ~37% after TFA and NaOH extraction, and ~2% after Cr_2O_7 oxidation. CHN analysis indicates that BC in Cr_2O_7-oxidized asphalt residue (referred to as asphalt-BC) is 727 g/kg of asphalt, and BC in Cr_2O_7-oxidized coal-tar residue (referred to as coal-tar-BC) is 245 g/kg of coal tar. H/C ratios of asphalt and coal tar residues are 0.1 and 0.05, within the aforementioned range for BC continuum (Hammes et al., 2007; Kuo et al., 2008) (Table B2 in Appendix B).

3.3.2 BC Determined by CTO-375

The BC contents in LFr and HFr fractions determined by CTO-375 are presented in Table 3.2. The amounts of BC detected by CTO-375 are consistently lower than those detected by Cr_2O_7 oxidation in the same samples; however, some trends are similar. The majority of BC is associated with HFr fractions in all samples (> 98% in the sediments, and 69-95% in the soils and dust). Sealed parking lot dust has the largest amount of BC in bulk samples (3.0 g/kg), followed by sediment samples (2.4, 2.1, and and 2.1 g/kg for depths of 25-30cm, 10-15cm, 0-5 cm, respectively), soils (1.5 g/kg for commercial soil and 1.1 g/kg for residential soil), and dust (1.0 g/kg for unsealed parking lot dust and 0.9 for residential street dust). The differences between the sum of BC in LFr and HFr fractions and BC determined in bulk samples (5 to 39% difference) is due to experimental errors and loss of BC during density separation. The H/C ratios of BC in bulk samples determined by CTO-375 are between 0.1 and 0.4 (Table 3.2), also within the range of reported values determined by CTO-375 for the BC continuum, especially for char-BC and soot-BC (0-0.6 by Hammes et al. (2007)).

BC determined by CTO-375 in the commercial coal tar product is 71.8 g/kg coal tar, similar to that in separated coal tar particles (69.2 g/kg coal tar) (Table B2).When combusted at 375 ºC with air for 24 h, commercial asphalt product had nearly no residue left; neither did separated asphalt particles, indicating that asphalt is not thermally recalcitrant. This result agrees with the previous report that pyrogenous asphalt undergoes thermal decomposition (depolymerization) when heated to a temperature above 300 ºC (Abraham 1960). The H/C ratio of coal-tar residues is 0.04 for the commercial product and 0.02 for the separated particles (Table B2).

Table 3.2. BC contents in bulk samples, the distribution of BC between LFr and HFr fractions, and the ratios of H/C in BC determined by CTO-375 method.

Sample ID		RSD	SPD	UPD	RS	CS	LS 0-5	LS 10-15	LS 25-30
BC (g/kg)	LFr	0.31	0.45	0.28	0.056	0.16	0.034	0.026	0.024
	HFr	1.03	1.75	0.61	1.16	1.00	1.80	2.23	1.77
	Sum	1.34	2.20	0.89	1.22	1.16	1.83	2.26	1.79
	Bulk	0.90	2.97	1.00	1.10	1.50	2.12	2.15	2.40
Contribution to BC (%)	LFr	23.02	20.44	31.01	4.64	13.77	1.82	1.16	1.32
	HFr	76.98	79.56	68.99	95.36	86.23	98.18	98.84	98.68
H/C in BC	Bulk	0.22	0.10	0.15	0.26	0.18	0.35	0.35	0.41

3.3.3 Char, Soot, Asphalt, and Coal Tar Determined by Organic Petrography

Two categories of CMs were identified by organic petrography: recent organic matter (OM) and anthropogenic CMs. Recent OM includes the following maceral groups: huminite, vitrinite, liptinite, and inertinite. CMs resulting from anthropogenic contamination include hard coal, coke, char, soot, and coal- and petroleum-derived fluorescent materials such as coal tar and asphalt which were referred to as coal-tar pitch and asphalt-like and bitumen-like substances in Chapter 2. The TOC of bulk samples estimated by summing OC contributed by all types of CMs identified with petrography (Table B1 in Appendix B) was compared with TOC measured by CHN analysis (Table 3.1); the results are presented in the Appendix B (Figure B2). The difference between the petrographic-TOC and CHN-TOC is between 25 % and 50%, indicating the magnitude of error in TOC for the range of samples evaluated using petrographic analysis.

Based on the measured TOC and the percentages of OC contributed by char, soot, asphalt, and coal tar, the OC contents of these CMs are presented in Figure 3.1. Char is often below the detection limit of organic petrography (0.2 vol % for particles greater than 1 to 2 microns) (Chapter 2). Its contribution to OC is negligible even though it was detected in some samples. Soot-OC and asphalt-OC were found in all samples. Soot-OC is higher in sediments (6.1-8.4 g/kg), but lower in soils and dust (1.0-3.5 g/kg). Asphalt-OC is higher in dust (14.2-16.0 g/kg), but lower in soils and sediments (2.9-6.9 g/kg). Coal-tar-OC dominates sealed parking lot dust (21.8 g/kg) and also exists in unsealed parking lot dust, commercial soil, and lake sediments for the depth of 0-5 and 25-30 cm (1.8, 1.3, 1.1, and 0.2 g/kg).

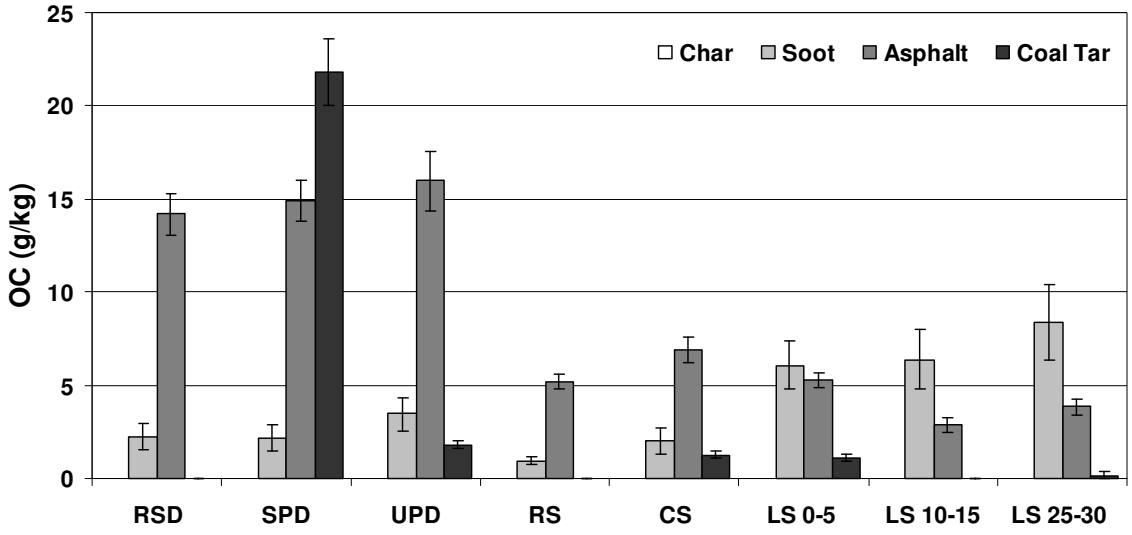

Figure 3.1. OC contributed by char, soot, asphalt, and coal tar in Lake Como watershed samples determined by organic petrography (samples include residential street dust (RSD), sealed parking lot dust (SPD), unsealed parking lot dust (UPD), residential soil (RS), commercial soil (CS), lake sediment from 0-5 cm depth (LS 0-5), lake sediment from 10-15 cm depth (LS 15-20), and lake sediment from 25-30 cm depth (LS 25-30) (Chapter 2).

3.3.4 Comparison of BC Quantified by Cr_2O_7 Oxidation, CTO-375, and Organic Petrography

BC contents quantified by Cr_2O_7 oxidation, CTO-375, and organic petrography are compared in Figure 3.2. The sum of BC in LFr and HFr fractions determined by Cr_2O_7 oxidation, BC in bulk samples determined by CTO-375, and soot-BC determined by organic petrography are compared (the amount of char-BC is negligible). Soot-BC determined by organic petrography and BC determined by CTO-375 are within a factor of 2 or statistically identical in several cases, but the amount of BC in samples quantified by Cr_2O_7 oxidation is 2-12 times greater than soot-BC quantified by organic petrography, and 2-7 times greater than BC quantified by CTO-375.

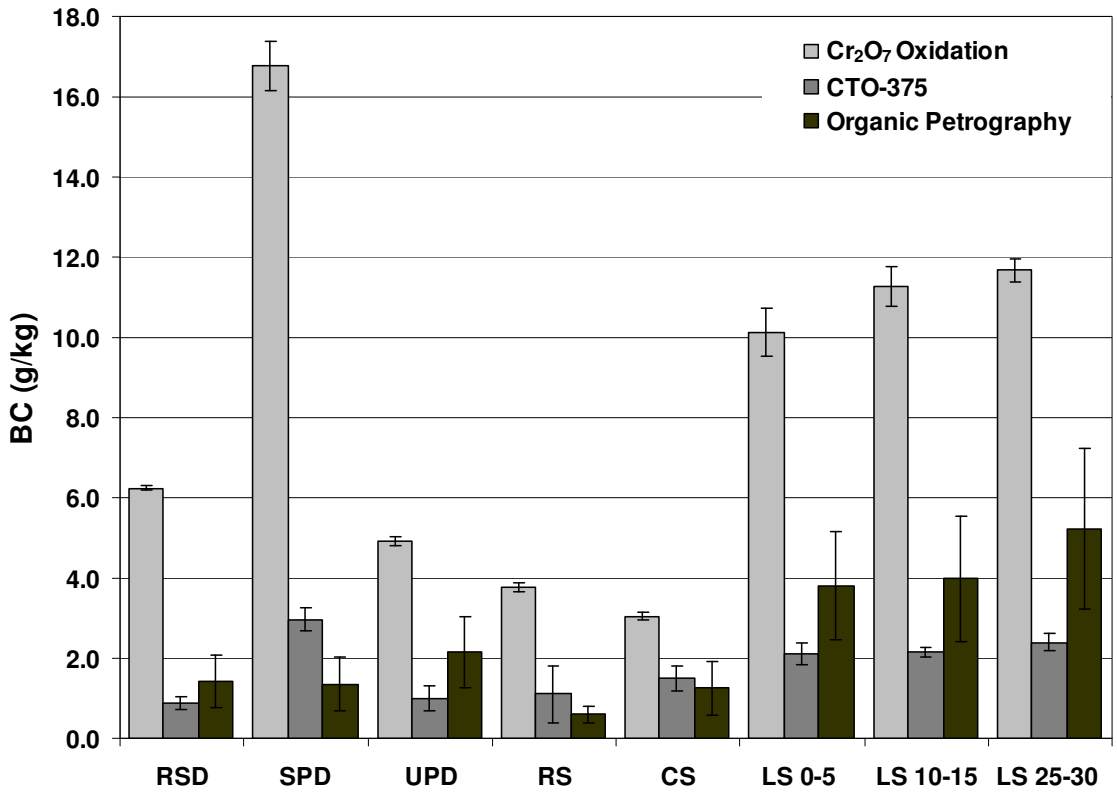

Figure 3.2. The comparison of BC in samples quantified by Cr_2O_7 oxidation, CTO-375, and. Soot-BC by organic petrography.

According to organic petrography, soot-BC contents are higher in the three lake sediment samples (3.8-5.2 g/kg) than in soil and dust samples (0.6-2.2 g/kg); however, sealed parking lot dust has the most abundant BC detected by Cr_2O_7 oxidation and CTO-375 methods, followed by sediments. The BC in sealed parking lot dust is 16.8 g/kg with Cr_2O_7 oxidation and 3.0 g/kg with CTO-375. The BC contents in sediments are 10.1-10.7 g/kg with Cr_2O_7 oxidation and 2.1-2.4 g/kg with CTO -375. Although these three quantification methods showed different patterns of BC distribution among different

types of samples (sediments, soils, and dust), they revealed a common trend that BC contents in sediments increase with depth of sediments, suggesting the accumulation of relatively more BC in sediments in past years, and the stability of BC in aquatic environment.

3.3.5 Contribution of Asphalt and Coal Tar to BC Determined by Cr_2O_7 Oxidation

The chemical treatment results of the reference asphalt and coal tar samples suggest that these materials likely contribute to high BC contents in samples determined with Cr_2O_7 oxidation. Hence, we included the contributions of BC by asphalt and coal tar with the contribution of soot in the petrographic results, and compared these values to the total BC determined by Cr_2O_7 oxidation in Figure 3.3. The BC contributed by asphalt and coal tar were calculated from the ratios of BC/OC in reference asphalt (0.86) and coal tar (0.39) materials (via Cr_2O_7 oxidation (Table B2)) and the OC contents contributed by asphalt and coal tar in each sample by petrography (Figure 3.1). The distribution patterns of total BC in pavement dust, soils, and sediments determined by these two methods are similar with greater amount of total BC in sealed parking lot dust than in other samples. Compared to the 2 – 12 times of difference between BC contents estimated by these two methods without considering the contribution of coal tar and asphalt (Figure 3.2), the difference after accounting for the contribution of coal tar and asphalt is within a factor of 2.5. Although OC contributed by coal tar in the sealed parking lot dust is higher than that contributed by asphalt, BC contributed by coal tar is lower than that contributed by asphalt in the same sample as a result of the higher BC/OC ratio of asphalt.

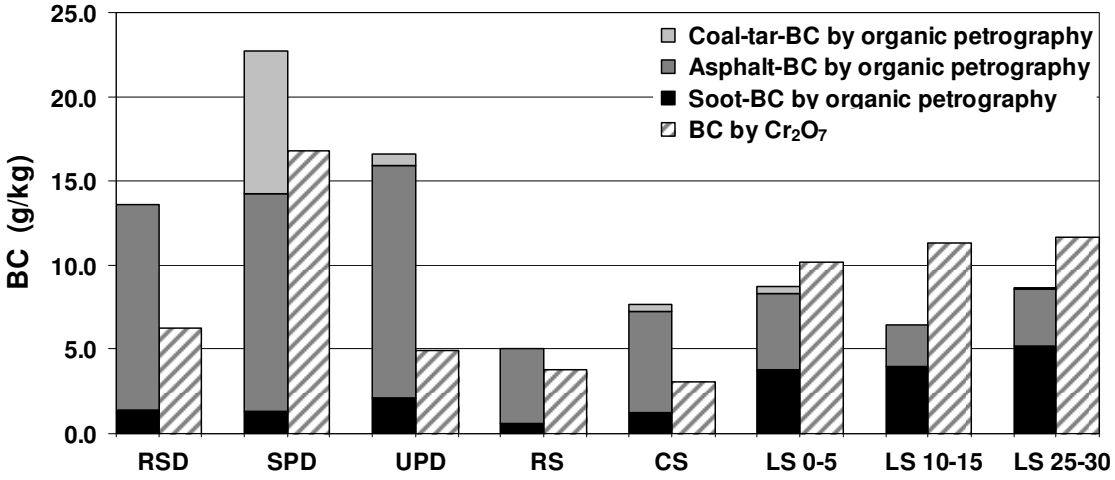

Figure 3.3. The comparison of BC quantified by Cr_2O_7 oxidation to the sum of soot-BC, asphalt-BC, and coal-tar-BC quantified by organic petrography.

Both asphalt and coal tar are mixtures of many organic compounds, and their chemical compositions and reactivity to chemicals depend on source materials (i.e. crude oil and coal) and production processes. Asphalt contains saturated and unsaturated aliphatic and aromatic compounds with up to 150 C atoms. Studies have showed that asphalt is highly resistant to chemical agents (including acids and bases) at ambient temperatures (Zakar, 1971). Coal tar are mixtures of hundreds of compounds composed of about two-thirds aromatic hydrocarbons and one-third of heterocyclic aromatic compounds (Chambrion et al., 1995). The estimated water solubility of coal tar is 16 mg/L (Peters and Luthy, 1993). Compared to coal tar, the oily composition of asphalt makes it less permeable to water (Zakar, 1971), reducing the penetration depth of aqueous phase chemicals; therefore, asphalt is more resistant to wet chemical oxidative treatment than coal tar, resulting in the higher measured BC/OC ratio. The stronger chemical recalcitrance of asphalt versus coal tar also partly explains the higher asphalt

contents in sediments determined by petrography, because chemical recalcitrance is more important for the stability of BC than thermal or physical recalcitrance (Liang et al., 2008).

The greatest difference between total BC determined by petrography and by Cr_2O_7 oxidation was found in unsealed parking lot dust and residential street dust, which have relatively high contents of asphalt (Figure 3.3). This can be attributed to the overestimation of asphalt-BC in field samples when using BC/OC ratios from reference asphalt materials determined by Cr_2O_7 oxidation. Asphalt in field samples undergoes weathering in sunlight and air. Photooxidation of the lower molecular-weight oil fractions generates more water-soluble asphalt, and makes it more easily attacked by chemical agents (Oliver and Gibson, 1972; Zarkar, 1971); hence, chemical reactions for unweathered reference asphalt material may not be as complete as for weathered asphalt particles in environmental samples.

3.3.6 Contribution of Coal Tar to BC Determined by CTO-375

The CTO-375 results of the reference coal tar and asphalt samples suggest that coal tar likely contributes to BC contents in samples determined with CTO-375, whereas asphalt does not. Hence, we compared the contributions of BC by coal tar and soot in the petrographic results with the total BC determined by CTO-375 in Figure 3.4. The BC contents contributed by coal tar were calculated from the ratio of BC/OC in reference coal tar samples (0.11) (Table B2) and OC in coal tar determined by petrography (Figure 3.1).

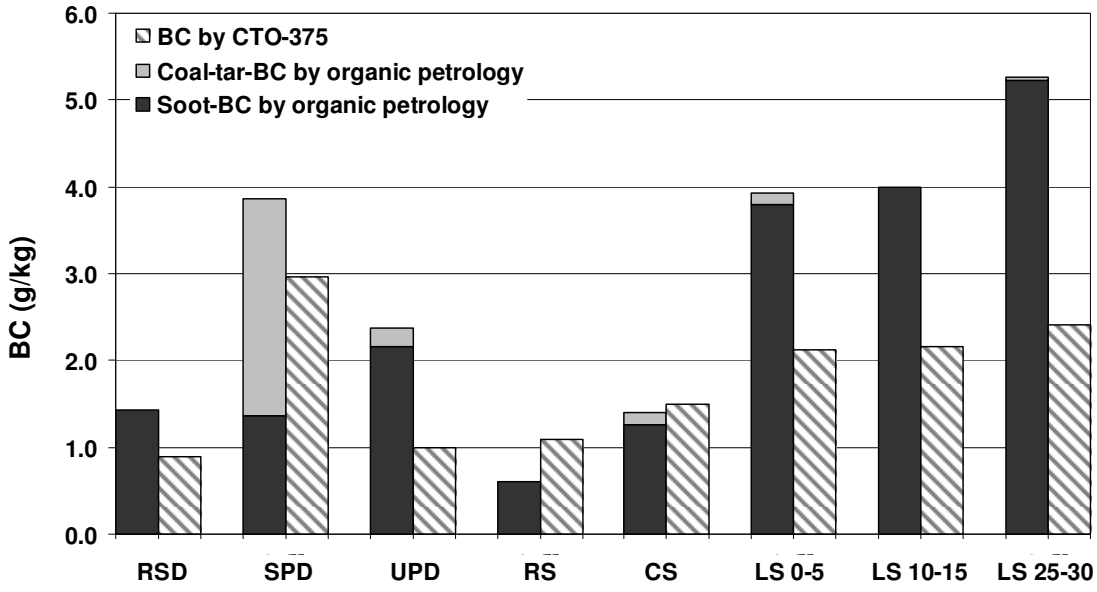

Figure 3.4. The comparison of BC quantified by CTO-375 method to the sum of soot-BC and coal-tar-BC quantified by organic petrography.

The distribution pattern of BC in pavement dust, soils, and sediments estimated by these two methods are similar: BC is higher in sealed parking lot dust and sediments, lower in other samples. The BC content in sealed parking dust estimated by petrography is about 46% of that determined by CTO-375 without considering the contribution of coal tar (Figure 3.2); however, by counting the contribution of coal tar to BC content, the amount of BC in sealed parking lot dust estimated by petrography is closer (within 30%) to that determined by CTO-375 (Figure 3.4). Including coal-tar-BC also results in slightly better agreement between petrographic and CTO-375 measurements of commercial soil-BC. For other samples, agreement is either slightly worse or unaffected.

The sum of soot-BC and coal-tar-BC estimated by petrography is greater than the amount of BC quantified by CTO-375, except for the residential soil and commercial soil

samples. The artifact of CTO-375 that creates BC through inadvertently charring might be responsible for the higher BC contents in two soil samples because relatively more grass debris were observed in these two samples (Nguyen et al., 2004; Masiello, 2004).

The CTO-375 method has been widely applied to quantify the most condensed forms of BC that are highly resistant to thermal treatment (Elmquist et al., 2006; Hammes et al., 2007). Generated during the coking process at 1100 ºC, the thermal recalcitrance of coal tar is expected. Abraham (1961) indicated that certain coal tar carries variable amounts of so-called "free C" when overheated in their process of manufacture, and the "free C" may consist in part of amorphous C, similar to lampblack (oil-soot). Khalil et al. (2006) also reported that a fraction of CTO-375-measured-BC in manufactured gas plant impacted sediments was affected by coal-tar pitch.

3.3.7. Environmental Significance

Asphalt and coal tar are commonly used in infrastructure construction in the urban environment. About 70 billion lb of asphalt is used annually in the U.S. and most often in the construction of roads, parking lots, walkways, and other paved surfaces (Freemantle, 1999). Of the 2.27 million miles of paved road in the United States, 94% are surfaced with asphalt (http://www.encyclopedia.com). Although national use is not reported, the sealcoat industry estimates that in the State of Texas, 225 million L of refined coal-tar-based sealcoat are applied annually; the New York Academy of Sciences reported estimated annual use of coal-tar-based sealcoat in the New York harbor watershed of approximately 5.3 million L (Van Metre et al., 2009). The amount of weathered asphalt and coal tar particles in runoff cannot be neglected, nor can their roles as sources of anthropogenic CMs in urban soils, and sediments of streams, and lakes.

Because of their pyrogeneous origins and chemical and thermal recalcitrance, asphalt and coal tar likely contribute to the pool of BC, although they haven't been considered in the BC continuum. Methods based on chemical and thermal oxidation will possibly overestimate soot-BC and char-BC in urban environmental samples that contain asphalt and coal tar, and result in errors balancing the global BC budget. This overestimation can also lead to a misinterpretation of the role of BC in controlling the transport and fate of organic contaminants in the environment because the affinity of organic contaminants to asphalt and coal tar is different from that to soot. Therefore, caution is advised when measuring BC contents in urban environmental matrices using either chemical or thermal methods. We recommend that for more accurate quantification, organic petrography can be coupled to either chemical or thermal BC quantification methods. However, this approach may fail to count particles smaller than 1.0 μm due to its detection limit (0.2 vol % for particles greater than 1 to 2 μm), and it requires further study using different environmental matrices and calibration against different consensus-BC reference materials.

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Chapter 4

Phenanthrene Sorption by Carbonaceous Materials in Urban Dust, Soils, and Sediments Containing Asphalt and Coal Tar

4.1 Introduction

Sorption to carbonaceous materials (CMs) is an important process controlling the transport and fate of hydrophobic organic compounds (HOCs) in the environment. Over the last several decades, extensive research has been done to expand our understanding of sorption interactions between HOCs and CMs. Sorption not only depends on the amount of CMs present in a soil or sediment, but also the nature of CMs (Grathwohl, 1990; Jonker and Koelmans, 2001; Karapanagioti et al., 2000; Kleineidam et al., 1999; Kleineidam et al., 2002).

Numerous investigators have shown that various CMs have distinct sorption properties and capacities due to their different origin and geological history. Sorption to more condensed form of CMs like kerogen (Grathwohl, 1990) and soot (Ghosh et al., 2000) is more favorable than sorption to more labile recent OM. Kleineidam et al. (1999) found that kerogen in sedimentary rock sorbs more phenanthrene than relatively recent organic matter (OM) in soils, and Jonker and Koelmans (2001, 2002) found that soot sorbs 10-1000 times more polycyclic aromatic hydrocarbons (PAHs) per unit weight of sorbent than amorphous sedimentary OM. One form of a "dual-mode" model was developed and modified to describe the sorption of HOCs to sediments and soils (Accardi-Dey and Gschwend, 2002; Gustafsson et al., 1997; Xia and Ball, 1999). According to this model, CMs in the soils and sediments consist of two domains: 1) soft amorphous CMs showing linear and noncompetitive absorption (Huang et al., 1997;

Pignatello and Xing, 1996), and 2) hard condensed CMs that show nonlinear, extensive and competitive adsorption (Huang et al., 1997; Xia and Ball, 1999). The total HOC sorption can then be expressed as a superposition of partitioning and adsorption. Sequestration and slow desorption of HOCs are presumed to be dominated by retention within condensed CMs (CCMs) (Abu and Smith, 2005).

Humin, kerogen, and black carbon (BC) (including char/charcoal and soot) are usually considered as CCMs according to their origins and experiment-based definitions (Pan et al., 2006; Ran et al., 2007a, 2007b). Our results in Chapter 2 showed that asphalt and coal tar are ubiquitous in urban dust, soils, and sediments, and pyrogenic asphalt and coal tar are resistant to Cr_2O_7 oxidation and may contribute to BC measurements in samples from urban areas (Chapter 3); therefore, asphalt and coal tar may contribute to the sorption capacities of the CCMs and influence their sorption properties. Recently, the influence of coal-tar pitch on PAH sorption in sediments has been studied (Bayard et al., 2000; Benhabib et al., 2006; Breedveld et al., 2007; Khalil et al., 2006). Khalil et al. (2006) developed a pitch-partitioning inclusive model to describe PAH partitioning behavior in sediments that contain significant quantities of pitch residue, and indicated that the partitioning behavior may be dominated by the sorption characteristics of pitch and not by natural OM or BC.

The objective of this study is to investigate the correlation between CM properties and their corresponding sorption affinity to PAHs, and to evaluate the influence of asphalt and coal tar on PAH sorption to CMs in urban dust, soils, and sediments. A better understanding of how CM properties influence sorption abilities will make it possible to predict PAH sorption to CM particles in complex environmental matrices, to determine

the primary mechanisms that control the redistribution and persistence of PAHs in urban watersheds, and to assess the associated environmental risks of contaminated sediments.

4.2 Materials and Methods

4.2.1 Sample Collection

Samples were collected from Lake Como watershed, Fort Worth, Texas, including one street dust sample, two parking lot dust samples, two surface soil samples, and three lake sediment samples. The street dust sample was a composite of dust from three asphalt-paved residential streets. One parking lot dust sample was a composite of dust from three coal-tar-sealed commercial parking lots and the other was a composite of dust from three unsealed asphalt or cement commercial parking lots. Two surface soil samples (top 2 cm) were collected randomly at approximately 40 locations near roads, sidewalks and driveways; one was from a residential neighborhood and the other was from a commercial area. Three sediment cores several meters apart were collected from a single site in Lake Como using a box corer. The cores were vertically extended and sliced at 5-cm intervals, and subsamples from the same depths (depth from the top: 0-5 cm, 10-15 cm, and 25-30 cm) were combined from the three cores to create three large-volume samples. Each composite sample was homogenized after passing through a 1-mm sieve. Details of the Lake Como sampling site and sample collection methods were described in Chapter 2.

4.2.2 Density Separation

Representative sub-samples of Lake Como watershed field samples were separated into light (LFr) and heavy (HFr) fractions with a solution of 1.60 g/cm^3 sodium polytungstate. Both fractions were oven dried at 60ºC, pulverized, and passed through a 100-mesh sieve to enhance reaction kinetics of subsequent chemical and thermal treatments.

4.2.3 CCM Separation

The fractions enriched in CCMs were obtained by treating HFr fractions sequentially with HCl, HF/HCl, trifluoroacetic acid (TFA)/HCl, and sodium hydroxide (NaOH) to remove carbonates, silicate minerals (Durand, 1980), easily hydrolyzable OM (Gelinas et al., 2001), and fulvic and humic acids (Swift, 1996), respectively. The remaining residues were referred to as HFr-CCM fractions in this report. Procedures were the same as described in Jeong et al. (Jeong et al., 2008; Jeong and Werth, 2005).

4.2.4 Sample Characterization

The specific surface area (SSA) of bulk samples and HFr and LFr fractions were measured with the multipoint Brunauer-Emmet-Teller (BET) method using an Accelerated Surface Area and Porosimetry system (ASAP 2010).

The C and hydrogen (H) contents of bulk samples, HFr and LFr fractions, and the HFr-CCM fractions were determined using a CE 440 CHN analyzer (Exeter Analytical, Inc., North Chelmsford, MA) in the Microanalysis Laboratory at the University of Illinois at Urbana-Champaign (UIUC), after the removal of inorganic C followed by oven drying. The oxygen (O) analysis was measured using a Leco RO-478 oxygen analyzer (Leco

Corp., St. Joseph, MI) at Huffman Laboratories, Inc. (Golden, CO) following ASTM D5622.

Surface functional groups were analyzed with a diffuse reflectance Fourier transform infrared (DR-FTIR) spectrometer (Nexus 670 FT-IR, Thermo Nicolet Co.) equipped with a deuterated triglycine sulfate (DTGS) detector following Wander and Traina (1996). Powdered bulk samples and HFr-CCM fractions were mixed with powdered KBr until homogeneous and then analyzed with a constant flow of dried air in order to minimize infrared absorption by water vapor. DR-FTIR spectra were obtained using 500 scans collected at 4 cm^{-1} resolution from 4000 to 400 cm^{-1} and analyzed with OMNIC software (Thermo Nicolet Co., Fitchburg, WI).

4.2.5 Sorption Experiment

Sorption isotherms were measured using established batch equilibrium methods (e.g. Chiou and Kile, 1998; Xia and Ball, 1999; Xing et al., 1996) with ^{14}C- phenanthrene (Sigma-Aldrich, St. Louis, MO) as the sorbate to distinguish spiked sorbate from background contaminants. Sorbents include bulk samples, LFr and HFr fractions, and HFr-CCM fractions. ^{14}C-phenanthrene was used as received, and the purities and specific activities are 99+% and 8.2 mCi/mmol. Sorption experiments were conducted in 30-mL glass centrifuge tubes with PTFE-lined solid phenolic screw caps. The mass of a sorbent added to each tube was adjusted to achieve 20-70% uptake of sorbate. After the sorbent was saturated with background solution containing 0.005 M $CaCl_2$ and 0.02% NaN_3 (by weight) overnight, a stock solution of sorbate in methanol (1-25 μL) was injected into the tubes. The spiked solutions were always at or below 0.1% of the total volume in the tubes to minimize cosolvent effects (Gossett, 1987). Tubes were capped immediately after

stock solution injection and then tumbled end-over-end at 1 rpm in a dark room at 25°C. Preliminary experiments were performed to determine the period of time needed to achieve apparent sorption equilibrium. After establishment of sorption equilibrium, sorbents and aqueous phases were separated by centrifugation at 6500 rpm (rcf =6116 g) for 30 min, and 2.5 mL of supernatant was taken for scintillation counting (LS3801, Beckman Instruments, Fullerton, CA) to determine the remaining ^{14}C- phenanthrene in aqueous phase. The amount of sorbate in the sorbed phase was calculated by the difference between the amount initially added and that remaining in the solution.

The sorption data were fit with both the Freudnlich isotherm model (Eq 1) and the linear partitioning model (Eq 2):

$$logC_S = logK_F + N\ logC_W \qquad \text{(Eq 1)}$$

$$C_S = K_D C_W \qquad \text{(Eq 2)}$$

where C_S is the solid-phase concentration (μg/kg) and C_W is the aqueous concentration (μg/L); K_F is the Freundlich solid-water distribution coefficient [(μg/kg)/(μg/L)^N]; K_D is the linear solid-water partition coefficient (L/kg); and N is the Freundlich exponent.

The sorption contributions of CM fractions to bulk samples were determined by assuming that, at a fixed aqueous concentration, the mass sorbed to each fraction i is the same when this fraction is alone, or part of the bulk sample. Mathematically, we define the sorption contribution of fraction i at a given concentration C as:

$$Sorption\ \ Contribution\ \ of\ \ Fraction\ \ i = \frac{C_{S,i}}{C_{S,bulk}} \times 100\% \qquad \text{(Eq 3)}$$

where $C_{S,i} = K_{F_i} C^{N_i} \times m_i$

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

4.3 Results and Discussions

4.3.1 Properties of CMs

As illustrated in Chapter 3, the OC contents in LFr fractions are higher than in HFr fractions (Table 4.1), but the majority of OC is associated with HFr (52 – 98%) due to the dominant mass in HFr fractions (Figure 4.1). The OC contents in HFr-CCM fractions range from 51.2% to 72.5% and account for 25 – 68% of the OC in bulk samples, with the highest value in sealed parking lot dust. The H/C atomic ratios range from 0.44 to 0.76 in bulk samples, 0.13 to 0.83 in HFr fractions, 0.10 to 0.17 in LFr fractions, and 0.07 to 0.11 in HFr-CCM fractions. The O/C ratios of HFr-CCM fractions range from 0.10 to 0.47, lower than the average O/C ratios (0.53) for typical humic substances extracted from soils and sediments (Wang and Xing, 2005), suggesting a higher degree of maturation than humic substances; however, the O/C ratios of HFr-CCM fractions are higher than those of BC in soil samples determined with combustion at 375ºC by Ran et al. (2007b) (0.078-0.13), indicating that the degree of maturation of HFr-CCM fractions is lower than BC.

Table 4.1. Physicochemical properties of bulk samples, LFr and HFr fractions, and HFr-CCM fractions (LS 0-5, LS 10-15, LS 25-30, RS, CS, RSD, SPD, and UPD represent lake sediments from 0-5 cm depth, lake sediments from 10-15 cm depth, lake sediments from 25-30 cm depth, residential soil, commercial soil, residential street dust, sealed parking lot dust, and unsealed parking lot dust, respectively).

Sample ID	Fraction	OC (%)	H (%)	O (%)	H/C	O/C	SSA (m^2/g)
RSD	Bulk	2.87	1.39	nd*	0.49	nd	0.67
	LFr	38.58	5.73	nd	0.15	nd	0.59
	HFr	1.53	1.26	nd	0.83	nd	1.20
	HFr-CCM	63.22	6.81	10.68	0.11	0.17	nd
SPD	Bulk	4.20	2.33	nd	0.55	nd	0.20
	LFr	39.71	4.09	nd	0.10	nd	0.35
	HFr	3.64	0.47	nd	0.13	nd	0.75
	HFr-CCM	72.45	4.81	7.54	0.07	0.10	nd
UPD	Bulk	2.78	1.31	nd	0.47	nd	0.49
	LFr	34.30	5.15	nd	0.15	nd	0.51
	HFr	1.55	0.97	nd	0.63	nd	1.02
	HFr-CCM	65.64	6.85	9.73	0.10	0.15	nd
RS	Bulk	2.80	1.22	nd	0.44	nd	3.09
	LFr	26.14	4.27	nd	0.16	nd	1.23
	HFr	2.10	0.31	nd	0.15	nd	2.77
	HFr-CCM	54.46	5.73	17.93	0.11	0.33	nd
CS	Bulk	4.00	2.44	nd	0.61	nd	5.24
	LFr	31.14	4.26	nd	0.14	nd	1.37
	HFr	3.20	0.63	nd	0.20	nd	3.41
	HFr-CCM	51.22	4.73	24.19	0.09	0.47	nd
LS 0-5	Bulk	3.92	2.33	nd	0.59	nd	9.17
	LFr	26.20	4.37	nd	0.17	nd	2.33
	HFr	3.55	2.14	nd	0.60	nd	7.16
	HFr-	59.67	6.17	16.82	0.10	0.28	nd
LS 10-15	Bulk	4.71	2.35	nd	0.50	nd	9.31
	LFr	23.90	3.71	nd	0.16	nd	2.78
	HFr	4.13	2.02	nd	0.49	nd	6.81
	HFr-CCM	62.88	6.68	16.85	0.11	0.27	nd
LS 25-30	Bulk	5.04	3.83	nd	0.76	nd	7.76
	LFr	27.00	4.19	nd	0.16	nd	2.80
	HFr	4.99	2.44	nd	0.49	nd	6.68
	HFr-CCM	62.91	6.76	16.02	0.11	0.25	nd

* nd: not determined.

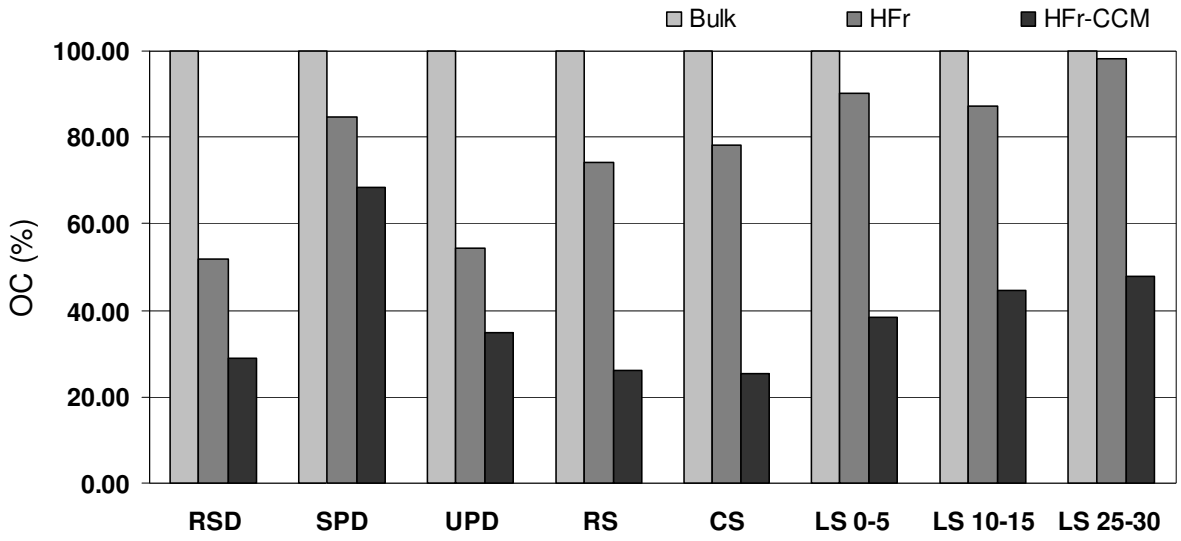

Figure 4.1. The percentages of OC contributed by HFr-CCM and HFr fractions to bulk samples from Lake Como watershed.

SSA of bulk samples, LFr and HFr fractions, and HFr-CCM fractions all follow the same trend: lake sediment > soil > dust, but no trend was observed for different fractions of the same sample (Table 4.1). The greatest SSA in bulk sediment samples is likely due to the presence of relatively large amounts of clay minerals. Bulk dust samples (e.g., residential street, sealed parking lot, and unsealed parking lot dust) have the lowest SSA. This makes sense because asphalt and coal tar pitch have low porosity, and petrographic analysis results (Chapter 2) show that these materials are the dominant CMs in dust samples from residential streets and sealed and unsealed parking lots.

DR-FTIR spectra of bulk samples and HFr-CCMs are shown in Figures 4.2 and 4.3. The spectra of all bulk samples are quite similar in terms of peak positions and relative intensities. All bulk samples have peaks derived from alcohol and phenol O-H stretching (3640-3610 cm-1), methyl C-H stretching (2920 cm-1), methylene C-H

stretching (2850 cm-1), carboxylic acid O-H stretching (~2500 cm-1), C=O stretching (~1800 cm-1), conjugated aromatic systems (1590~1610 cm-1), aliphatic C-H bending (~1450 cm-1), C-O stretching (1040-1300 cm-1), and aromatic out of plane bending with different degrees of substitution (900-700 cm-1) (Jeong and Werth, 2005; Ran et al., 2007b) (Figure 4.2).

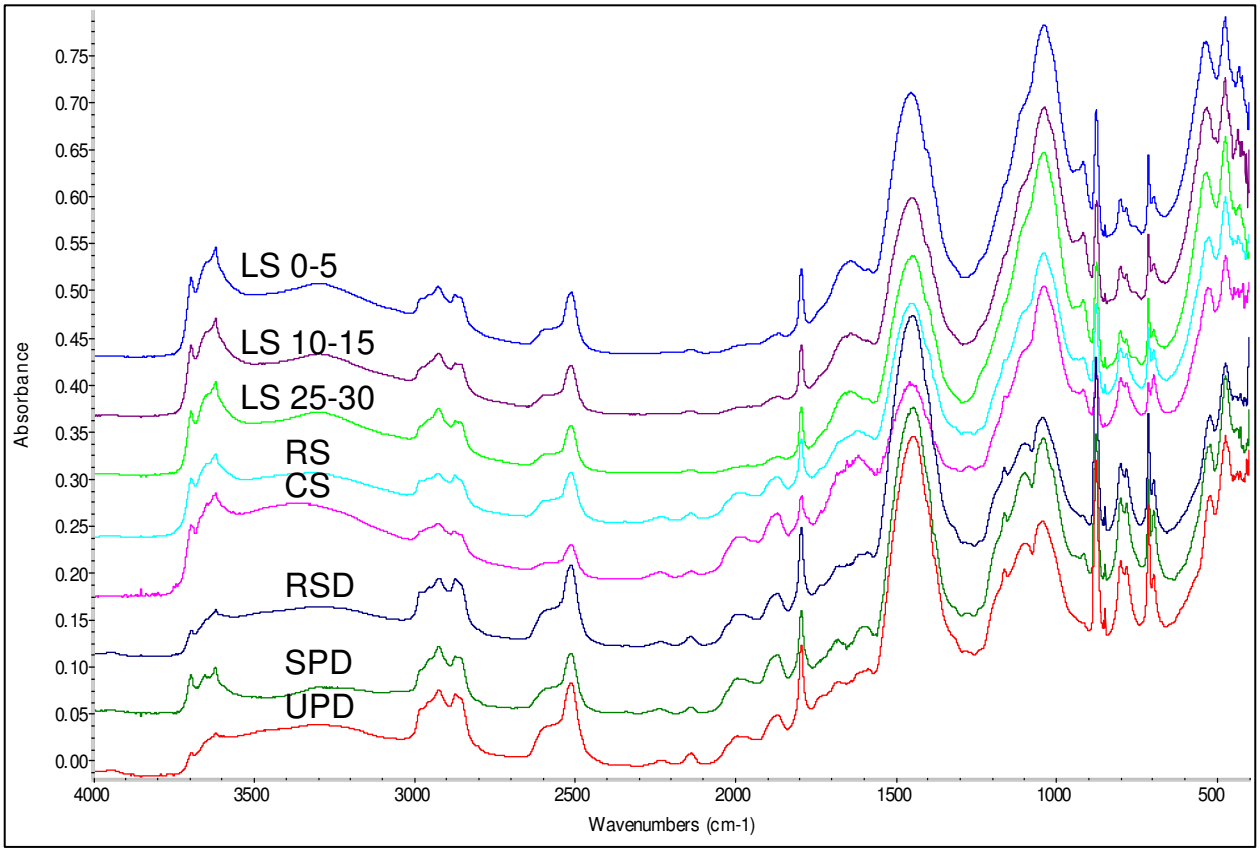

Figure 4.2. DR-FTIR spectra of bulk samples from Lake Como watershed.

DR-FTIR spectra of HFr-CCM fractions (Figure 4.3) are markedly different from those of the bulk samples (Figure 4.2). The spectra of HFr-CCM fractions for soils and sediments are generally similar, and those for the three dust samples are similar. For

sealed parking lot samples, a significant difference can be observed regarding the location of aromatic C-H stretching peak (3100-3000 cm-1), indicating the abundance of aromatic compounds in coal-tar pitch. Consistent with Ran et al. (2007b), after chemical treatment with HF/HCl, TFA, and NaOH, peaks for the aliphatic (2920 and 2850 cm-1) and conjugated aromatic groups (1590~1610 cm-1) are stronger than other groups. The aromatic carbonyl/carboxyl C=O stretching (1704 cm-1) indicates the condensed CMs have some aromatic acids and aldehydes. Although this peak is weaker than nearby conjugated aromatic systems (1590~1610 cm-1) in soil and sediment samples, the difference is smaller in dust samples, suggesting that dust samples have relatively more aromatic acids and aldehydes. The aromatic out of plane bending (900-700 cm-1) is obviously stronger in dust samples, similar to the signature peaks observed in coal tar pitch and asphalt in a previous study (Alcaniz-Monge et al., 2001). However, the relative intensities of these peaks among three dust samples are not the same. The peak at 800 cm-1 is more intense in the sealed parking lot dust than in residential street dust and unsealed parking lot dust. This may indicate the difference of the relative abundance of coal tar and asphalt in these samples.

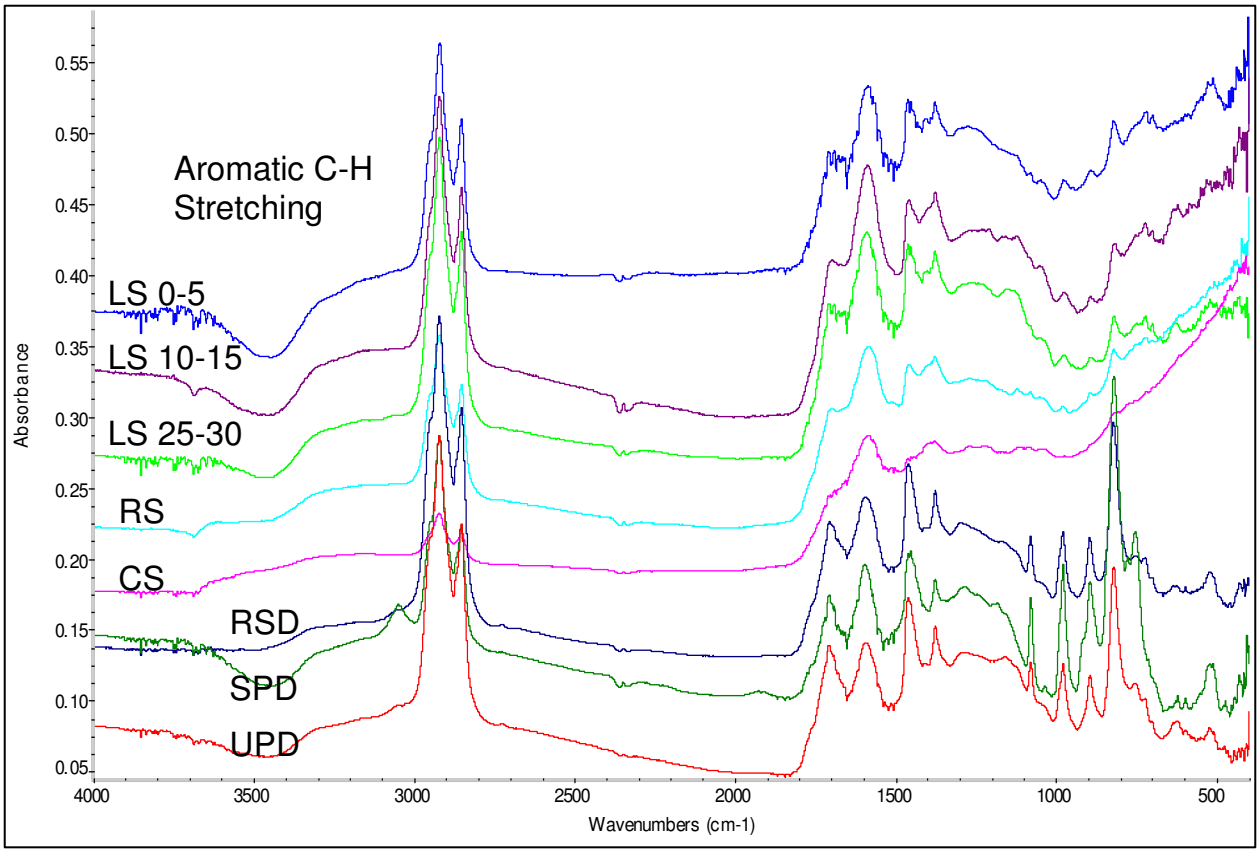

Figure 4.3. DR-FTIR spectra of HFr-CCM fractions for samples from Lake Como watershed (LS 0-5, LS 10-15, LS 25-30, RS, CS, RSD, SPD, and UPD represent lake sediment at depth of 0-5 cm, lake sediment at depth of 10-15 cm, lake sediment at depth of 25-30 cm, residential soil, commercial soil, residential street dust, sealed parking lot dust, and unsealed parking lot dust, respectively).

4.3.2 Sorption Isotherms

Freundlich and linear isotherm parameters and OC normalized sorption coefficients of bulk samples, LFr and HFr fractions, and HFr-CCM fractions from the Lake Como watershed are presented in Table 4.2. All sorption isotherms are nearly linear with N values between 0.90 and 1.00. This indicates partitioning is the dominant sorption mechanism. Freundlich constants (K_F) of LFr fractions are greater than those of HFr fractions and bulk samples due to the high OC contents in LFr fractions. The Freundlich sorption coefficients (K_F) of HFr-CCMs are about 16-45 times of those of HFr fractions,

Table 4.2. Sorption isotherm parameters of bulk samples, LFr and HFr fractions, and HFr-CCM fractions of Lake Como watershed samples.

Sample ID		$logK_F$ $(\mu g/kg)/(\mu g/L)^N$	N	R_F^2	$logK_D$ (L/kg)	R_D^2	log Koc $(L/kg\ C)$
RSD	Bulk	3.13	0.93	0.995	2.99	0.995	4.54
	LFr	3.89	0.99	0.985	4.03	0.984	4.45
	HFr	3.11	0.93	0.996	2.94	0.999	4.76
	HFr-CCM	4.79	0.99	0.992	4.70	0.990	4.90
SPD	Bulk	3.57	0.94	0.995	3.48	0.999	4.86
	LFr	4.20	0.94	0.989	4.10	0.999	4.50
	HFr	3.47	0.94	0.992	3.40	0.992	4.83
	HFr-CCM	4.67	1.00	0.998	4.70	0.999	4.84
UPD	Bulk	2.97	1.00	0.996	2.96	0.999	4.51
	LFr	4.06	0.95	0.983	4.06	0.995	4.53
	HFr	3.05	0.97	0.994	3.00	0.999	4.81
	HFr-CCM	4.76	0.99	0.996	4.80	0.995	4.99
RS	Bulk	2.79	0.95	0.980	2.70	0.999	4.25
	LFr	3.86	0.93	0.990	3.65	0.995	4.23
	HFr	2.91	0.90	0.977	2.75	0.999	4.43
	HFr-CCM	4.70	0.96	0.997	4.61	0.998	4.87
CS	Bulk	2.96	0.94	0.969	3.04	0.993	4.44
	LFr	3.83	0.96	0.981	3.92	0.992	4.42
	HFr	3.00	0.93	0.972	3.02	0.994	4.52
	HFr-CCM	4.56	0.98	0.997	4.54	0.999	4.83
LS 0-5	Bulk	3.30	0.91	0.998	3.03	0.997	4.43
	LFr	4.26	0.91	0.996	4.08	0.977	4.66
	HFr	3.24	0.93	0.999	3.03	0.996	4.48
	HFr-CCM	4.88	0.94	0.997	4.68	0.994	4.90
LS 10-15	Bulk	3.38	0.97	0.999	3.31	0.989	4.63
	LFr	4.28	0.91	0.995	4.12	0.999	4.74
	HFr	3.34	0.95	0.999	3.17	0.997	4.55
	HFr-CCM	4.79	0.99	0.998	4.73	0.995	4.93
LS 25-30	Bulk	3.43	0.96	0.998	3.35	0.997	4.65
	LFr	4.23	0.92	0.996	3.99	0.975	4.56
	HFr	3.36	0.98	0.997	3.32	0.999	4.62
	HFr-CCM	4.76	1.00	0.996	4.67	0.996	4.88

and up to 81 times greater than those of bulk samples, largely due to the enriched OC contents of these samples. The K_{oc} values of HFr-CCM are about 1.4-2.8 times greater than those of HFr fractions, and approximately equal to those for the sealed parking lot dust sample. This implies that the CCMs occupy a larger fraction of the HFr in sealed parking lot dust than in other samples, consistent with results in Figure 4.1, which shows the highest OC mass in sealed parking lot dust after treatment through NaOH extraction. For soil and dust samples, OC normalized sorption coefficients (K_{oc}) 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 (Chapter 2).

4.3.3 Contribution of CM Fractions to Phenanthrene Sorption

The sorption contributions of HFr-CCM and HFr fractions to bulk samples at the equilibrium concentration of 10 μg/L are shown in Figure 4.4. The equilibrium concentration of 10 μg/L was chosen based on the PAH source study by Mahler et al. (2005). They reported that the concentrations of dissolved PAHs in runoff from coal tar sealed parking lots ranged from 2.3-16 μg/L. The sorption contributions of untreated HFr fractions to the bulk samples are greater than 77% due to their relatively large mass contents and OC contents. Sorption contributions over 100% suggest that CMs with higher sorptivity may have been exposed by physical shaking during density separation. The sorption contributions of the HFr-CCM frations to the bulk samples are between

57% and 97%, and six of eight samples are above 80%. Hence, sorption of phenanthrene to the bulk samples is controlled by sorption to the CCMs in the HFr fractions.

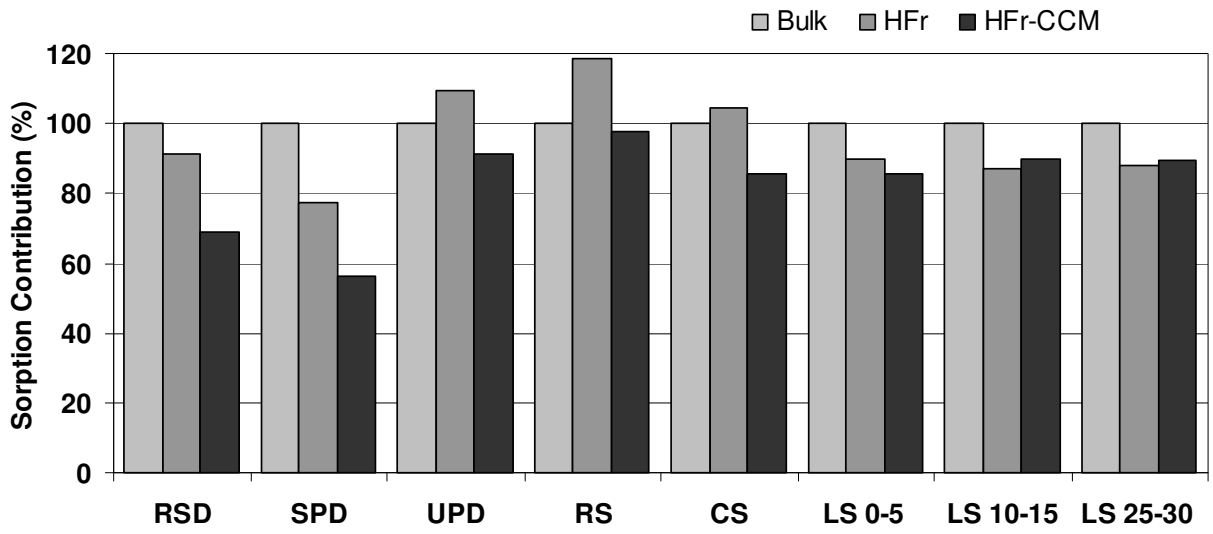

Figure 4.4. Sorption contribution by HFr and HFr-CCM fractions to Lake Como watershed samples at an equilibrium concentration of *Ce* = 10 ug/L.

4.3.4 Influence of Asphalt and Coal Tar on Sorption

Parameters of CM properties such as H/C and O/C values of bulk samples, LFr and HFr fractions, and HFr-CCM fractions were compared to the sorption coefficients ($logK_F$ and $logK_{OC}$) and no statistically relevant correlations were observed (not shown). This implies that sorption properties of our samples are not controlled by the degree of CM maturation, which is estimated with H/C and O/C ratios (Ran et al., 2007b).

SSA values of bulk samples, LFr, and HFr fractions, and HFr-CCM fractions were also compared to the sorption coefficients and no statistically relevant correlations were observed either (not shown). This suggests that surface adsorption is not the

dominant sorption mechanism in our samples, consistent with the linear sorption isotherms of all samples and fractions. The partitioning-dominated sorption mechanism likely is attributed to the contribution of asphalt and coal tar to overall sorption. The asphalt-water and coal-tar-water distribution coefficients for phenanthrene are $10^{5.7}$ and $10^{5.3}$ L/kg, respectively (Brandt and De Groot, 2001; Endo and Schmidt, 2006), about one order of magnitude higher than amorphous OM-water distribution coefficient ($10^{4.3}$ L/kg) (Schwarzenbach et al., 2003), but 2 and 5 times lower than soot-water distribution coefficients, e.g., a value of $10^{5.93}$ L/kg was measured for traffic soot (Jonker and Koelmans, 2002). The overall sorption of phenanthrene can be dominated by partitioning to amorphous OM, asphalt, and coal tar due to their high contents in our samples.

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Appendix A.

Supporting Information for Chapter 2

Data Analysis

The input variables in our analysis include volume fractions of macerals in each sample (Table A1), density and OC contents (Table A2), and PAH concentrations of macerals or CMs (Table A3). Values were obtained from laboratory measurements or the literature. The uncertainty analysis was performed with Crystal Ball 2000 (Oracle Corp.) by assigning a uniform or normal distribution to each variable as defined in Table A4. The volume fractions of macerals in samples determined by organic petrography follow the normal distribution (*1*). The normal distribution was also assigned to the PAH concentrations in macerals by fitting the measured data in literature. The normality of the distribution was determined using the Anderson-Darling test and the Shapiro-Wilk test with Systat 12 (Systat Software, Inc.). The distribution of PAH concentrations in soot particles was changed to normal using a log-log transformation. Because there is very little information about the distributions of the density and OC contents of macerals, a uniform distribution was used (*2*, *3*).

Monte Carlo simulation was used to obtain the probability associated with the convolution of the input variables. Five hundred trials were sufficient to reach stable results. The resulting distributions were subjected to robust regression analysis of least trimmed squares with Systat 12. Means, standard deviations, and confidence levels of output parameters were obtained after eliminating the outliers.

Output parameters calculated from input variables include mass percentage and mass content of each CMs, OC contributed by CMs in samples, relative PAH contribution from CMs, and potential PAH loading on coal tar. Equations used to calculate these parameters are listed in Table A5. The remaining table (A6) and figures (A1-A4) are referred to in the text of Chapter 2.

Table A1. Maceral groups and their subgroups quantified with petrographic analysis.

QUANTITATIVE MICROSCOPICAL ANALYSIS

Location: Lake Como, Lake Fosdic (Texas) | **Lithology:** lake sediments, soils, street dusts, parking dusts | **Composition** (Vol. %, 500 points counted on two polished mounts)

Preparation: polished mount of organic concentrate (after acid treatment, no crushing) | **Sample :**

	Maceral group	Maceral subgroup / Maceral	Reflected light (oil immersion)	Fluorescence (uv-light + violet-light excitation; oil immersion)	LS 0 - 5	LS 10 - 15	LS 25 - 30	IBS infl. b. s.	LFS Fosdic	CS com. soil	RS resid. s.	RSD street d.	UPD unseal.p.	SPD sealed p.
Recent organic matter (soil, peat, lake sediment...) and Organic matter in ancient sediments	Huminite	Telohuminite	fragments (10-700 µm) of ungelified or partly gelified tissues (stems, roots) reddish-brown and middle grey	dark-brown to orange-brown	3.8	2.4	5.3	29.7	29.0	54.4	33.9	23.6	13.4	4.3
		Detrohuminite	fine humic detritus (<10 µm) that may be cemented by amorphous humic matter	dark-brown to non-fluorescing	50.4	54.5	56.3	10.7	29.0	8.7	31.0	2.6	4.3	0.2
		Gelohuminite	amorphous humic gel (gelinite) and coll excretions (corpohuminite)	dark-brown to non-fluorescing	1.8	0.8	0.8	3.5	3.7	5.3	5.5	4.8	3.1	1.0
	Vitrinite	Telovitrinite	/											
		Detrovitrinite	isolated fragmentary particles of gelified tissues, homogeneous, middle grey to light grey (wide range of reflectance), equidimentional, 2 to 10 µm; most of them are monomaceral coal particles (vitrite)	non-fluorescing	0.6	0.6	1.2	0.4	0.4	0.2	x			
		Gelovitrinite	/											
	Liptinite	Sporinite	orange-brown to dark grey microspores (spores, pollen)	moderately intense to intense, yellow-brown, yellow	1.6	3.0	2.6	0.6	2.3	1.2	0.3			
		Cutinite	orange-brown to dark grey fragments of cuticles	moderately intense to intense, yellow-brown, yellow	0.2	0.2	x	1.8	2.5	1.7	x	4.9	1.2	
		Fluorinite	small intra-cellular granules in fragments of leaf tissues (lipid secretions)	moderately intense to intense, yellow-green, yellow	x				x					
		Suberinite	fragments of tissues (25 to 300 µm), orange-brown; bark-or cork-derived tissues	intense green and yellow-green	0.4	0.6	1.0	2.3	0.8	0.7	0.8	2.8		0.2
		Resinite	intra-/extra-cellular resin bodies, terpene resinites	intense yellow, green		0.2	0.2	2.9	3.7	0.7		4.5	2.1	0.2
		Chlorophyllinite	occurs sporadically as small particles (1-5 µm)	intense blood-red					x					
		Telalginite	/											
		Lamalginite	/											
		Liptodetrinite	small fragments of liptinites less than 10 µm in size; occurs associated with detrohuminite	moderately intense to intense, yellowish-brown to yellow	8.7	17.9	7.4	0.4	6.2	0.2	6.3		0.3	
		Bituminite: AOM												
		- orange-brown	/											
		- gray to gray-brown	/											
		- orange-brown matrix	/											
		Migrabitumen: non-fluorescing	/											
		Oil inclusions	/											
		Oil expulsions	/											
	Inertinite	Fusinite	high reflecting, white tissues (degradofusinite), 10 to 300 µm		x		0.2	x	0.2	0.7	x	x		
		Semifusinite	low reflecting, light-grey tissues: oxysemifusinite (dehydratation/oxidation), degradosemifusinite (biodegradation), 10 to 200 µm					x		x				x
		Funginite	middle grey to light grey sclerotia, single or multi-celled fungal spores, hyphae and other fungal remains		x	x	x	0.2	0.2	1.0	1.3	0.6	x	
		Secretinite	/											
		Macrinite	/											
		Microinite	/											
		Inertodetrinite	isolated fragmentary particles of semifusinite and fusinite: homogeneous, light grey to white, equidimentional, 2/4 to 10 µm		0.8	0.2	0.6	0.2	0.4	1.0	0.3			
	Natural coke		/											
	Natural char		/											
Anthropogenic contamination	Hard coal	Sub-bituminous coal			0.2		0.4			x				
		High-volatile bit. coal	low coal particles are strongly weathered and show oxidation rims		x		x		x	0.2	x			
		Medium-volatile bit. coal	/											
		Low-volatile bit. coal	/											
		Anthracite	contains pyrite, some particles are weathered					x			0.2			0.6
	Coke (coal carbonization)		subrounded to angular carbon particles showing a wide range of microstructures (porosity, pore sizes and shapes, cell-wall thicknesses) and microtextures identified by anisotropy, shape and size of domains		0.2	x	0.2	0.2	0.2	x	0.2	x	x	0.2
	Char (mostly from coal combustion)		spheroidal carbon particles with vesicles, more or less porous and anisotropic, mostly high reflecting: thin-walled cenospheres (tenuispheres), thick-walled cenospheres (crassispheres)		x	0.2	x	x	x	x	x			x
	Soot (traffic, oil combustion)		subangular carbon particles with grainy texture, mostly isotropic, more or less porous, yellowish-gray to white or blue-gray, heterogeneous reflectance; some with cracks	blue-gray soot : dark brown; greenish films of hydrocarbons are often generated during the fluorescence excitation; gray, white soot : non-fluorescing	15.8	13.8	16.5	7.4	9.0	5.0	3.4	8.5	13.1	5.0
	Coal- and Petroleum-derived fluorescent materials (tar, oils, lubricants...)		dark gray, reddish-brown, dark brown, sticky, subangular asphalt-like particles, presence of scratches (softness of the material), some with peripherical differentiation (darker), pores, granular surface, cracks	moderately intense reddish-brown, dark brown	5.2	1.4	1.3	9.5	4.3	1.8	10.8	32.9	45.3	26.4
			dark brown or black bitumen-like substances occuring as sticky irregular bodies and droplets; some are multivacuolate (gas bubbles?) or show flow structure or network texture (in fluorescence); often yellow-green fluorescing oil drops and oil films partly covering the bitumen-like substances	moderately intense to intense brown-yellow, orange-brown; high yellow fluorescence of the embedding resin in contact with the bitumen (resin acts as a chemical extractor)	7.1	4.2	5.6	28.8	8.1	13.7	6.0	14.8	9.5	4.9
			coal tar pitch: more or less fine granular, gray, gray-brown, some with scratches, contains often thin anisotropic coke particles and cenospheres	non-fluorescing or expulsion of green fluorescing hydrocarbons under UV irradiation; high yellow-orange fluorescence of the embedding resin in contact with the pitch particles (resin acts as a chemical extractor)	3.2	x	0.4	1.4	x	3.5	x		7.7	57.0

Note that concerning the huminite group and vitrinite group, the table shows only the maceral subgroups. AOM: Amorphous Organic Matter. x : present but not expressed as percentage due to scarcity
Other encountered materials: plastics (samples IBS, RSD, UPD, SPD), paint particles (UPD), metals (samples IBS, LFS, CS, RSD, UPD, SPD)

Table A2. Densities and OC contents of maceral groups reported in literature or measured in our laboratory.

Maceral Group	Density (g/cm^3)	OC Content (wt %)
Huminite[a]	1.12 (4)	60-77 (5)
Vitrinite	1.28-1.70 (6)	70.5-96 (1, 7)
Liptinite	1.10-1.22 (6)	83 - 89 (8)
Inertinite	1.30-1.45 (4)	71.0–94.0 (9)
Hard Coal	Bituminous coal:1.15-1.7 (4); Anthracite coal:1.32-1.80 (4)	85.2-96.4 (10)
Coke	1.6-1.8 (11)	87-89 (1)
Char	0.1-1.0 (12)	66-87 (13)
Soot	1.22-1.82 (10)	32.2-77.0 (10, 14)
Asphalt- and bitumen-like substances[a, b]	1.07	84.1-84.7
Coal-tar pitch[a, b]	1.16	62.4-63.1

a. Closely spaced values above and below the point value (i.e., within 0.0001%) were used as the lower and upper limits of a uniform distribution to meet the functional requirement of Crystal Ball
b. Data were measured in our laboratory with commercial asphalt and coal-tar sealant which are similar to the product used in sampling sites.

Table A3. The sum of 11 PAHs in CMs reported in literature or measured in our laboratory (phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo(a)pyrene, indeno[1,2,3-cd]pyrene, and benzo[ghi]perylene).

CM Particles	Total PAHs[a] (mg/kg)	Standard Deviation
Recent OM[a]	68	33
Coal[b]	620	400
Coke[b]	510	270
Char/charcoal[c]	44	NA[e]
Soot[d]	85	5.3
Asphalt[a]	2,850	160
Coal-tar pitch[a]	75,000	21,700

a. Recent OM, asphalt, and coal-tar pitch were separated from samples and PAHs were measured in our laboratory.
b. Coal and coke particles were separated from coke oven site soil(*15*).
c. Char/charcoal particles were from combustion of bark (*10*).
d. Soot samples were collected from vehicle exhaust pipes, including gasoline and diesel soot (*16*), and the mean and standard deviation of log-log-transformed data were used.
e. NA: not available

Table A4. Assigned probability distribution of input variables used in Crystal Ball.

Assumption Cells	Probability Distribution
Volume fraction (%)	Normal distribution[a]
Density of macerals (g/cm^3)	Uniform distribution
Organic carbon (OC) content of macerals (g/100g)	Uniform distribution
PAHs in macerals (mg/kg)	Normal distribution[b]

a. Mean was determined by petrographic analysis (Table A1), and the standard deviation was obtained by interpolating the correlation between mean and standard deviation of maceral counts of duplicate samples in literature (*17*), $Standard\ \ Deviation = 0.30 \times Mean^{0.51}$.
b. Mean and standard deviation of normal distribution were obtained through our measurement or literature data (Table A3) except soot and char/charcoal. The log-log-transformed values of PAHs in soot were assigned to follow the normal distribution. The Uniform distribution was assigned to PAHs in char/charcoal because of the limit of data.

Table A5. Forecasting cells (output parameters) with equations defined in Crystal Ball.

Forecasting cells	**Equations**
Mass percentage of CM_i (%)	$Mass\ Percentage\ of\ CM_i = \frac{Volume\ Percentage\ of\ CM_i \times Density\ of\ CM_i}{\sum_i (Volume\ Percentage\ of\ CM_i \times Density\ of\ CM_i)} \times 100\%$
Mass content of CMi (g CMi / 100g bulk sample)	$Mass\ Content\ of\ CM_i\ in\ Sample = Mass\ Percentage\ of\ CM_i \times Total\ CM\ in\ Sample$
OC from CM_i in each sample (g OC / 100 g bulk sample)	$OC\ Contributed\ by\ CM_i = \frac{Mass\ Percentage\ of\ CM_i \times OC\ Content\ of\ CM_i}{\sum_i (Mass\ Percentage\ of\ CM_i \times OC\ Content\ of\ CM_i)} \times TOC\ of\ Bulk\ Sample$
Percent of PAHs distributed in CM_i in each sample (%)	$PAHs\ in\ CM_i(\%) = \frac{Mass\ Percentage\ of\ CM_i \times PAHs\ in\ CM_i}{\sum_i (Mass\ Percentage\ of\ CM_i \times PAHs\ in\ CM_i)} \times 100\%$
Potential PAH loadings from coal tar pitch in each sample (mg PAHs / kg bulk sample)	$Potential\ PAHs\ from\ Pitch = PAHs\ in\ Pitch\ Particles \times Mass\ Content\ of\ Pitch\ in\ Sample$

Table A6. Correlation coefficients between total PAHs and OC contents in different CMs ($\log(\sum_{13} \mathrm{PAH}) = ax + b$).

x		**a**	**b**	**R^2**
OC in coal tar, asphalt, and soot (%)	With RS and RSD	0.80	2.74	0.66
	Without RS and RSD	0.71	3.14	0.96
OC in coal tar, asphalt, and soot (%)	HMW PAHs	0.71	3.08	0.96
	LMW PAHs	0.69	2.37	0.95

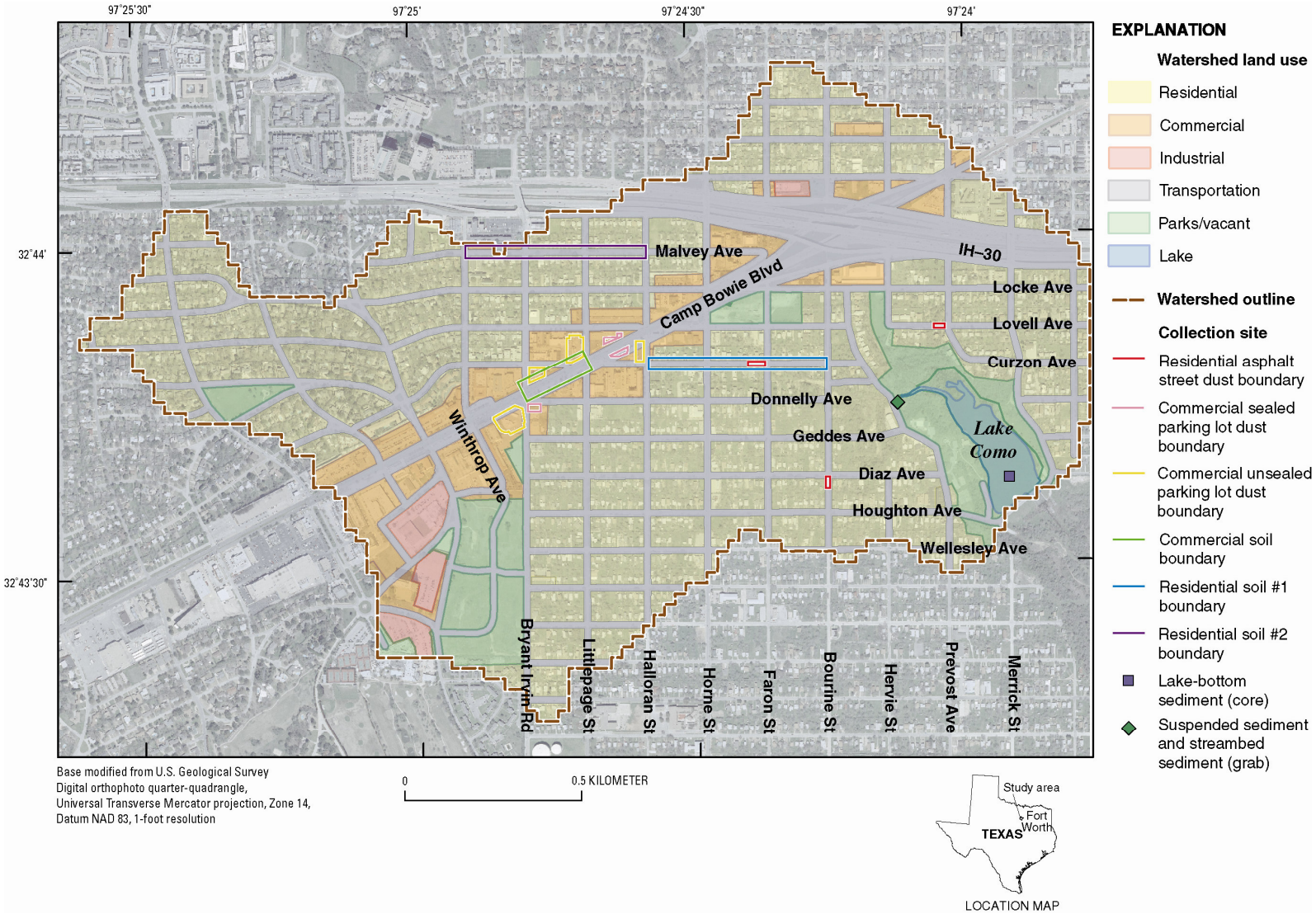


Figure A1. Sites where samples were collected in Lake Como watershed, Fort Worth, Texas (*18*).

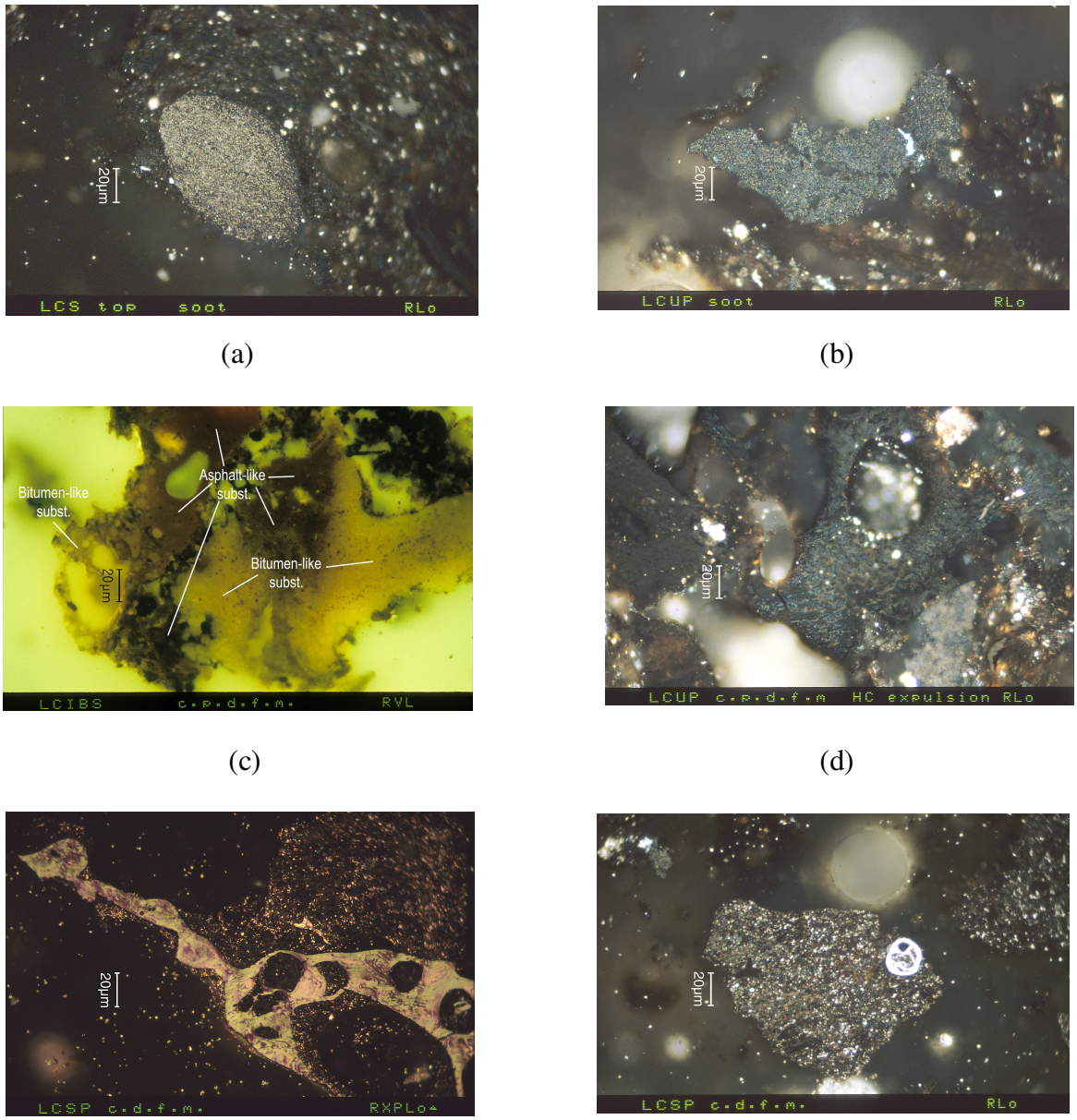
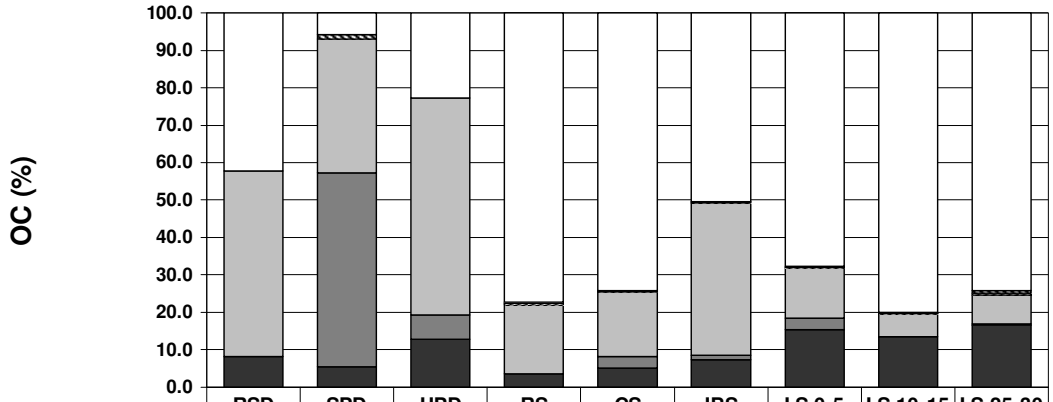


Figure A2. Photomicrographs illustrating the different CMs present in the selected Lake Como watershed samples: (a) rounded soot particle from top sediment of 0-5 cm; (b) porous blue grey soot from unsealed parking lot dust; (c) asphalt-like substances and bitumen-like substances from streambed sediment. Note the flow srtucture with bubbles and the bright yellow exsudates; (d) asphalt with large vesicles from unsealed parking lot dust; (e) coal tar pitch (right above corner) containing a coke particle showing large pores from sealed parking lot dust; (f)coal tar pitch embedding a cenosphere (multi-celled body) from sealed parking lot dust (Note than (a), (b), (d), and (f) used white reflected light and oil immersion; (c) used fluorescence mode and oil immersion; (e) used obliquely crossed polars, lambda plate, oil immersion) .



	RSD	SPD	UPD	RS	CS	IBS	LS 0-5	LS 10-15	LS 25-30
Recent OM	42.4	5.8	22.8	77.3	74.1	50.3	67.5	80.2	74.4
Hard Coal	0.0	1.0	0.0	0.3	0.4	0.0	0.3	0.0	0.6
Char	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Coke	0.0	0.4	0.0	0.4	0.0	0.4	0.4	0.1	0.4
Asphalt- and Bitumen-like Substances	49.6	35.6	58.0	18.6	17.4	40.9	13.4	6.1	7.6
Coal-Tar Pitch	0.0	52.1	6.6	0.0	3.2	1.2	2.8	0.0	0.4
Soot	8.0	5.2	12.6	3.4	5.0	7.3	15.5	13.6	16.6

Figure A3. Distribution of OC among CMs in Lake Como watershed samples.

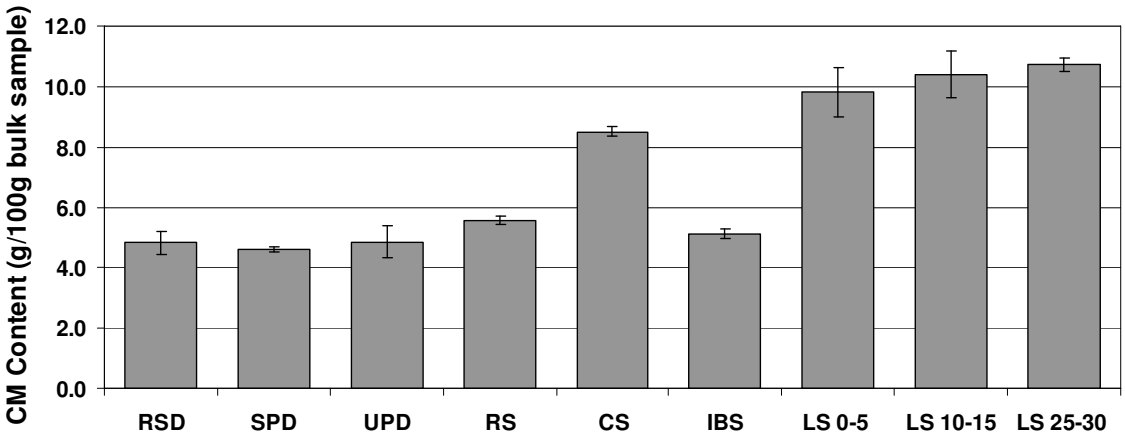


Figure A4. Total CM contents in Lake Como watershed samples (error bars represent ±1 standard deviation).

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Appendix B.

Supporting Information for Chapter 3

The equations to estimate the TOC determined by organic petrography are listed in Table B1, and the TOC estimated by petrography is compared to that measured by elemental analysis in Figure B2. The mass loss of asphalt and coal tar after each step of chemical treatment used in Cr_2O_7 oxidation is presented in Figure B1. Table B2 shows the chemical characteristics of reference asphalt and coal tar materials and the BC contents determined in these reference materials by Cr_2O_7 Oxidation and CTO-375. Tables (B1 and B2) and figures (B1 and B2) are referred to in the text of Chapter 3.

Table B1. Equations to estimate the TOC determined by organic petrography.

Forecasting cells	**Equations**	
Mass percentage of CM_i (%)	$Mass\ Percentage\ of\ CM_i = \frac{Volume\ Percentage\ of\ CM_i \times Density\ of\ CM_i}{\sum_i (Volume\ Percentage\ of\ CM_i \times Density\ of\ CM_i)} \times 100\%$	(1)
Mass content of CMi (g CMi / kg bulk sample)	$Mass\ Content\ of\ CM_i\ in\ Sample = Mass\ Percentage\ of\ CM_i \times Total\ CM\ in\ Sample$	(2)
OC from CM_i in each sample (g OC / kg bulk sample)	$OC\ Contributed\ by\ CM_i = Mass\ Content\ of\ CM_i \times OC\ Content\ of\ CM_i$	(3)
TOC (g OC / kg bulk sample)	$TOC = \sum_i OC\ Contributed\ by\ CM_i$	(4)

Table B2. Chemical characteristics of reference asphalt and coal tar materials and their BC contents determined by Cr_2O_7 Oxidation and CTO-375.

	OC(g/kg)	H/C	BC by Cr_2O_7			BC by CTO-375		
			BC (g/kg)	H/C	BC/OC	BC(g/kg)	H/C	BC/OC
Commercial Asphalt	844.3±4.2	0.13	727.2±0.2	0.12	0.86	ND*	ND	ND
Commercial Coal Tar	627.6±4.8	0.06	244.7±1.7	0.05	0.39	71.8±1.5	0.04	0.11
Picked Asphalt Particles	834.3±31.2	0.08	ND	ND	ND	ND	ND	ND
Picked Coal Tar Particles	572.2±5.8	0.06	ND	ND	ND	69.2*	0.02	0.12

* ND: not detected

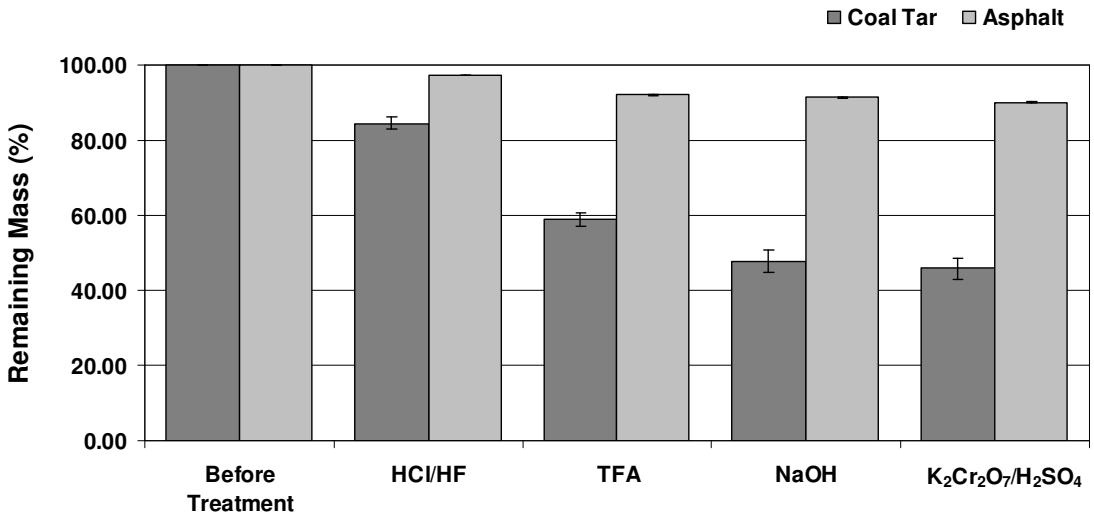

Figure B1. The mass loss of asphalt and coal tar after each step of chemical treatment used in Cr_2O_7 oxidation.

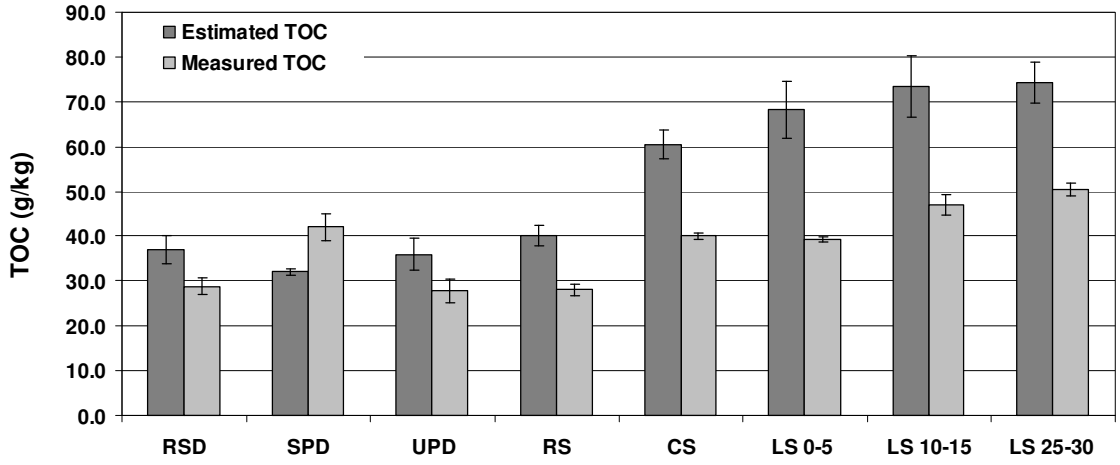

Figure B2. Comparison of petrography-estimated TOC to measured TOC in Lake Como watershed samples of residential street dust (RSD), sealed parking lot dust (SPD), unsealed parking lot dust (UPD), residential soil (RS), commercial soil (CS), lake sediment from 0-5 cm depth (LS 0-5), lake sediment from 10-15 cm depth (LS 15-20), and lake sediment from 25-30 cm depth (LS 25-30).

Appendix C.

PAH Distribution and Sorption to Density-separated Fractions of Urban Dust, Soils, and Sediments in Fosdic Lake Watershed, Fort Worth, Texas

C.1 Sample Collection

Samples of urban dust, soil, and lake sediment were collected from the Fosdic Lake watershed in Fort Worth, Texas, at the same time when Lake Como watershed samples were collected. Fosdic Lake watershed samples include residential street dust (F-RSD), sealed parking lot dust (F-SPD), unsealed parking lot dust (F-UPD), soil from residential area (F-RS), soil from commercial area (F-CS), and three Fosdic Lake sediments (depths from the top: 0-5 cm, 15-20 cm, and 25-30 cm) (F-LS1, F-LS2, and F-LS3). Sample collection and preparation methods were the same as described in Chapter 2 for Lake Como watershed samples. Details of the sampling sites (Figure C1) and methods are presented in Wilson et al. (*1*).

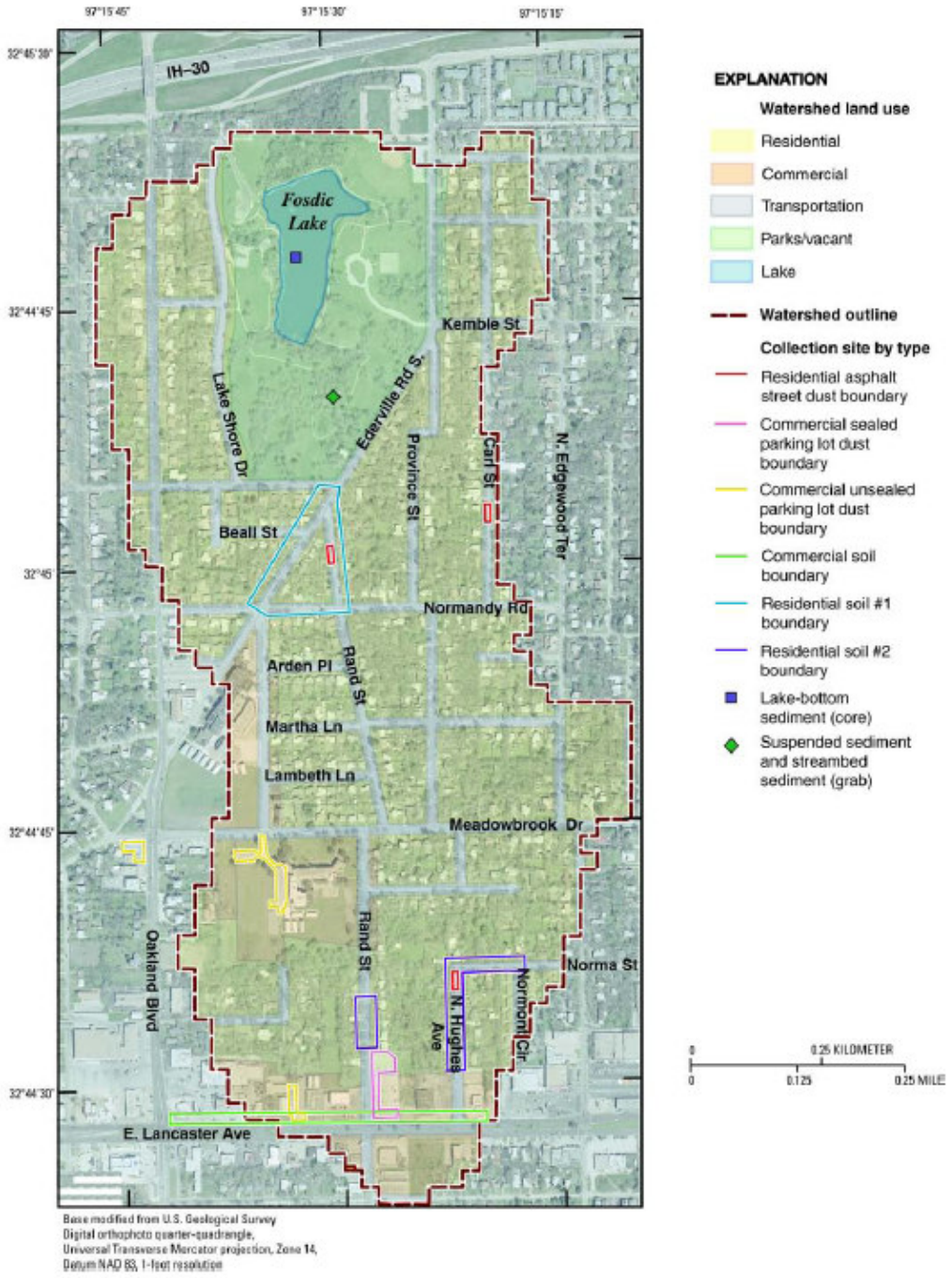

Figure C1. Sites where samples were collected in Fosdic Lake watershed, Fort Worth, Texas (*1*).

C.2 Density Separation

Representative sub-samples of Fosdic Lake watershed samples were separated into light (LFr) and heavy (HFr) fractions with a solution of 1.60 g/cm^3 sodium polytungstate as described in Chapter 3. Same as Lake Como watershed samples, the majority of mass is associated with HFr fractions, ranging from 92.1% to 99.6% (Figure C2).

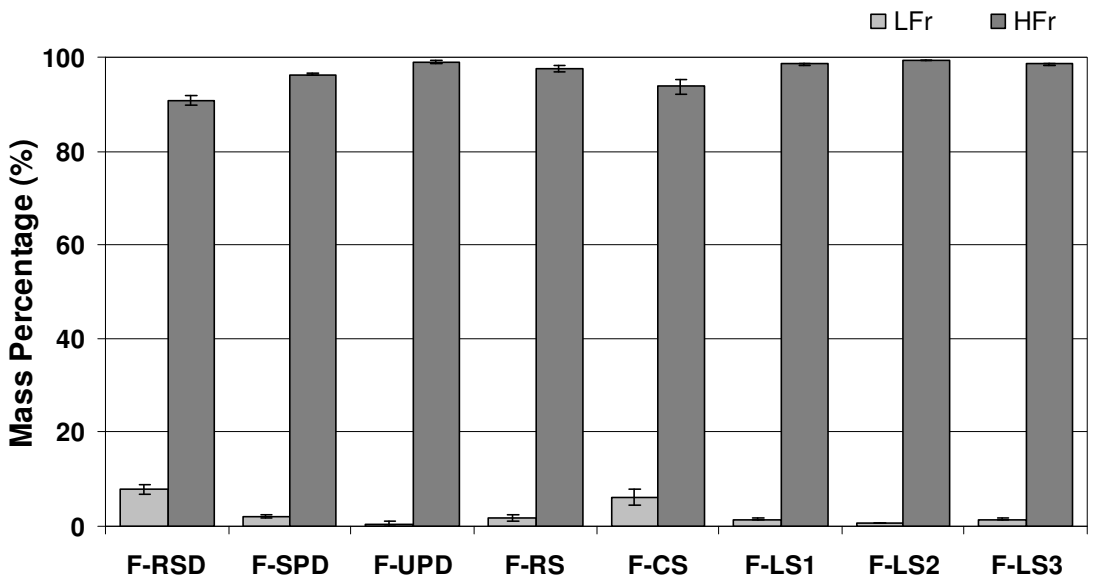

Figure C2. Mass percentages of LFr and HFr fractions of Fosdic Lake watershed samples.

C.3 Carbon Analysis

Organic carbon (OC) contents of bulk samples and LFr and HFr fractions were determined with a CE 440 CHN analyzer (Exeter Analytical, Inc.) in the Microanalysis Laboratory at UIUC after the removal of inorganic carbon. Although OC contents in LFr fractions are 4 to 22 times higher than those in HFr fractions (Table C1), the majority of

OC is associated with HFr fractions in all samples except in the sample F-RSD (Figure C3).

Table C1. OC contents in bulk samples and LFr and HFr fractions of Fosdic Lake watershed samples.

OC (%)	F-RSD	F-SPD	F-UPD	F-RS	F-CS	F-LS1	F-LS2	F-LS3
Bulk	3.36	4.04	1.56	3.92	4.68	8.29	7.15	7.02
LFr	30.09	44.34	33.76	27.96	24.86	35.87	30.11	32.32
HFr	1.35	3.84	1.64	2.21	3.73	7.87	6.86	7.82

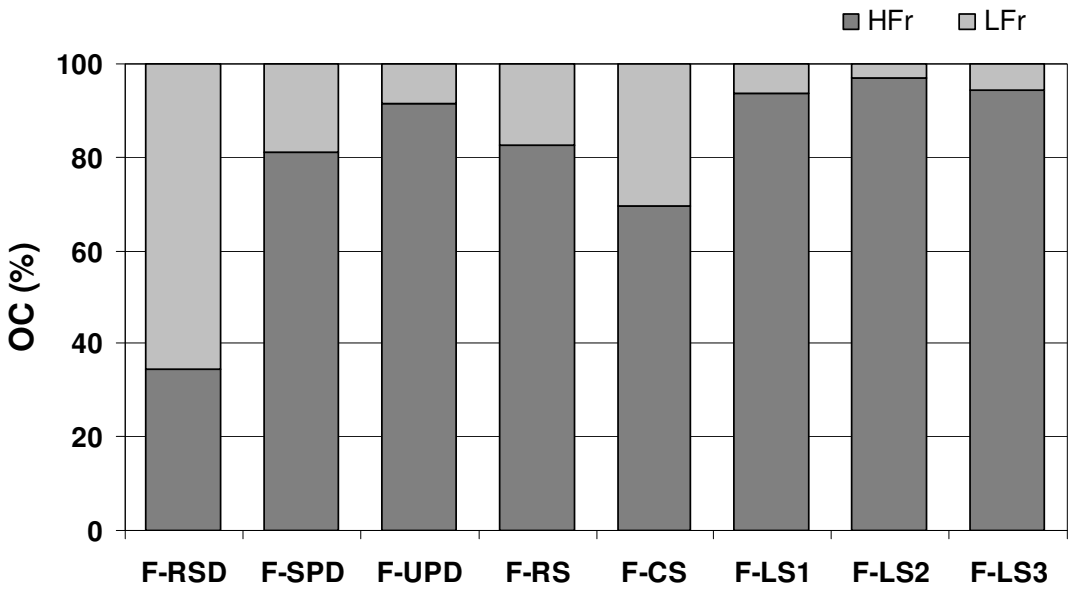

Figure C3. The distribution of OC between LFr and HFr fractions of Fosdic Lake watershed samples.

C.4 PAH Analysis

Eighteen parent PAHs, nine specific alkyl-PAHs, and the homologous series of alkyl-PAHs in bulk samples were determined at the USGS laboratory as described in Chapter 2. The sum of 13 consensus-based sediment-quality-guideline (SQG) PAHs in bulk samples are reported to compare with the probable effect concentration (PEC) and the threshold effect concentration (TEC) (*2*) (Figure C4).

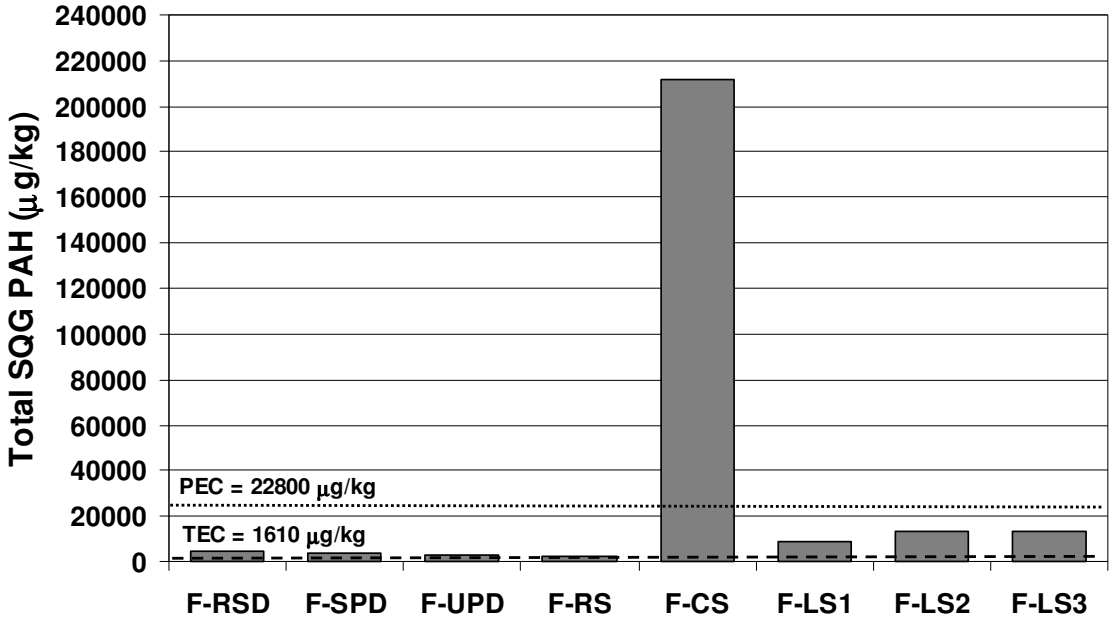

Figure C4. Total SQG PAHs in Fosdic Lake watershed samples.

Density-separated LFr and HFr fractions were extracted with acetone and dichromathane by accelerated solvent extraction (ASE) at UIUC (EPA method 3545). The extract was cleaned with silica gel (EPA method 3630c), and 16 EPA priority PAHs were analyzed with GC/MS following EPA method 8270c. The sum of 16 EPA PAHs was reported as total PAHs for LFr and HFr fractions. Except for the sample F-CS, the total of 16 PAHs are 4-27 times higher in LFr fractions than in HFr fractions due to the

higher OC contents in LFr fractions (Figure C5). However, most PAHs are associated with HFr fractions (>65%) in all samples (Figure C6). This can be attributed to the dominant mass (>92%) and dominant OC content (>70%) in HFr fractions for most samples (Figure C2 and C3). Our results are different from what was observed in two estuarial sediments from NY/NJ Harbor by Rockne et al. (*3*). In their study, 54% and 85% of PAHs were associated with low density fractions that represent 15% and 3.6% of total sediment mass, and 22% and 34% of total OC mass. This suggests that not only the amount of CMs but also the type, properties, and sorption capacity of CMs determine the distribution of PAHs. It is expected that CMs in urban watershed samples and estuarial harbor sediments are different in compositions and properties because they come from different source materials and age under different environmental conditions. The source-determined PAH compositions play an import role as well. These may also be the reasons that more than 75% of PAHs are associated with HFr of residential street dust which represents less than 35% of total OC in the sample (Figure C3 and C6).

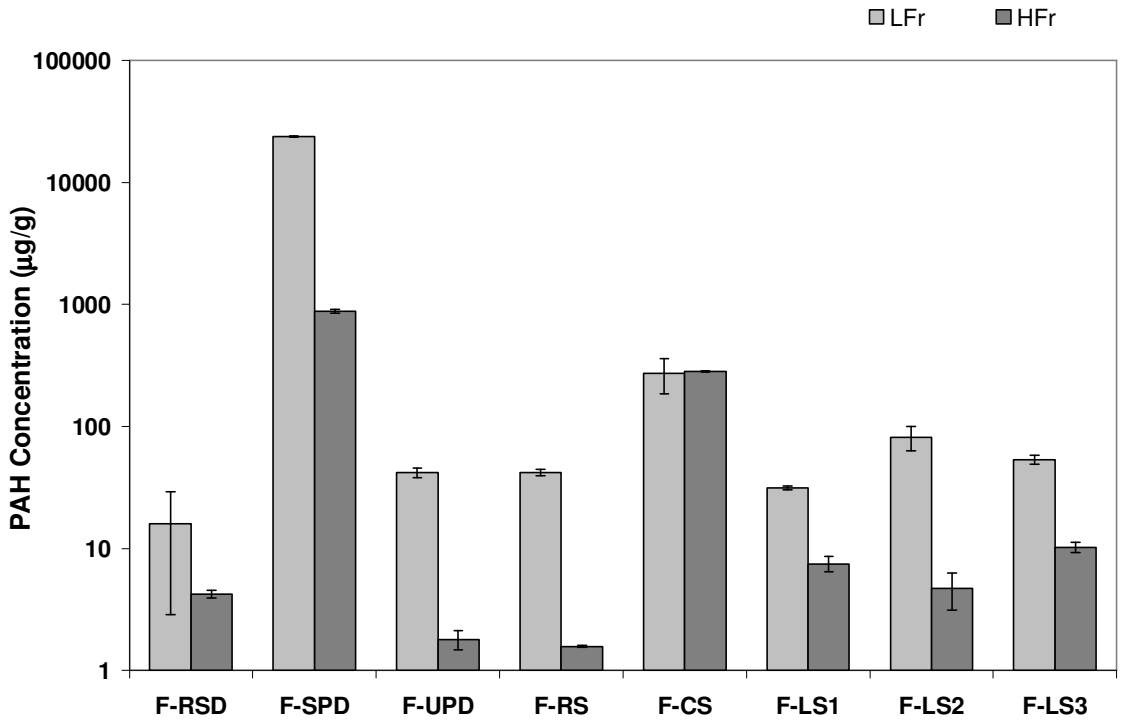

Figure C5. Concentrations of 16 EPA PAHs in LFr and HFr fractions of Fosdic Lake watershed samples.

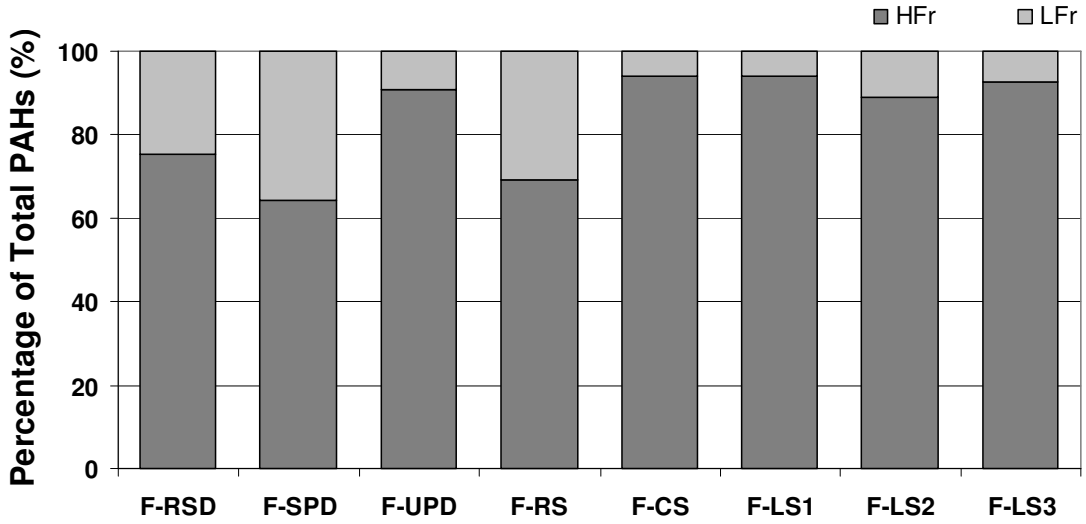

Figure C6. Distribution of 16 EPA PAHs in LFr and HFr fraction of Fosdic Lake watershed samples.

C.5 Phenanthrene Sorption Measurement

Sorption isotherms were measured using established batch equilibrium methods with ^{14}C-phenanthrene as the sorbate and LFr and HFr fractions as sorbents. Experiment details were given in Chapter 4. The sorption data were fit with both the Freudnlich isotherm model (Eq 1) and the linear partitioning model (Eq 2):

$$logC_S = logK_F + N\ logC_W \qquad \text{(Eq 1)}$$

$$C_S = K_D C_W \qquad \text{(Eq 2)}$$

where C_S is the solid-phase concentration (μg/kg) and C_W is the aqueous concentration (μg/L); K_F is the Freundlich solid-water distribution coefficient [(μg/kg)/(μg/L)^N]; K_D is the linear solid-water partition coefficient (L/kg); and N is the Freundlich exponent.

The OC normalized partitioning coefficient (K_{OC}) was calculated with Eq 3:

$$K_{OC} = \frac{K_D}{f_{OC}} \qquad \text{(Eq 3)}$$

The relative contributions of HFr and LFr fractions to phenanthrene sorption were calculated using:

$$Relative\ \ Sorption\ \ Contribution\ \ of\ \ Fraction\ \ i = \frac{C_{S,i}}{\Sigma C_{S,i}} \times 100\% \qquad \text{(Eq 4)}$$

Similar to samples from Lake Como watershed, sorption isotherms for samples from Fosdic Lake watershed are all nearly linear (N >0.90, Table C2). The $logK_{oc}$ values of HFr fractions are higher than those of LFr fractions, with the greatest difference in the sample F-RSD. It is reasonable to assume that more condensed CMs which have stronger sorption capacity are associated with HFr than with LFr in our samples even though further verification is still needed. In contrast, Rockne et al. (*3*) reported that $logK_{oc}$

Table C2. Sorption isotherm parameters of LFr and HFr fractions of Fosdic Lake watershed samples.

Sample ID	Fraction	$logK_F$ $(\mu g/kg)/(\mu g/L)^N$	N	$logK_D$ (L/kg)	log Koc (L/kg C)
F-RSD	LFr	3.91	0.95	3.76	4.28
	HFr	3.24	0.91	2.99	4.86
F-SPD	LFr	4.18	0.99	4.10	4.46
	HFr	3.47	0.94	3.24	4.65
F-UPD	LFr	4.09	0.99	3.99	4.46
	HFr	3.35	0.90	3.03	4.81
F-RS	LFr	3.95	0.95	3.91	4.46
	HFr	3.17	0.92	2.99	4.65
F-CS	LFr	3.93	0.95	3.79	4.40
	HFr	3.32	0.93	3.14	4.57
F-LS1	LFr	3.88	0.99	3.83	4.28
	HFr	3.34	0.97	3.34	4.44
F-LS2	LFr	3.90	0.98	3.92	4.44
	HFr	3.47	0.99	3.45	4.61
F-LS3	LFr	3.84	0.99	3.92	4.41
	HFr	3.42	0.95	3.33	4.44

values of low density fractions were approximately 10 times higher than those of high density fractions in their estuarial sediment samples. Although the results of our study are different from those of Rockne et al.(*3*), the conclusion is the same that the majority of native PAHs are associated with the fraction of CMs that have higher sorption capacity. In our results, this fraction is the HFr fraction (Figure C7). HFr fractions dominate sorption with contributions of more than 67%. This suggests that redistribution of PAHs between LFr and HFr is not likely, and HFr fractions concentrate, transport, and retain

the majority of total PAHs in urban watersheds. The sorption contributions of HFr fractions are generally higher in sediments than in soil and dust samples. A similar trend was also observed in the distribution of native PAHs between the two fractions (Figure C6). This suggests that relatively more PAHs are concentrated in HFr as well as CMs when they are carried by particles, transported from land surface to the lake, and buried in sediments.

The facts that the majority of the total PAHs are preferentially associated with heavy particles in pavement dust, soils, and sediments, and they tend to concentrate more in heavy particles during transport have potential implications for sediment management.

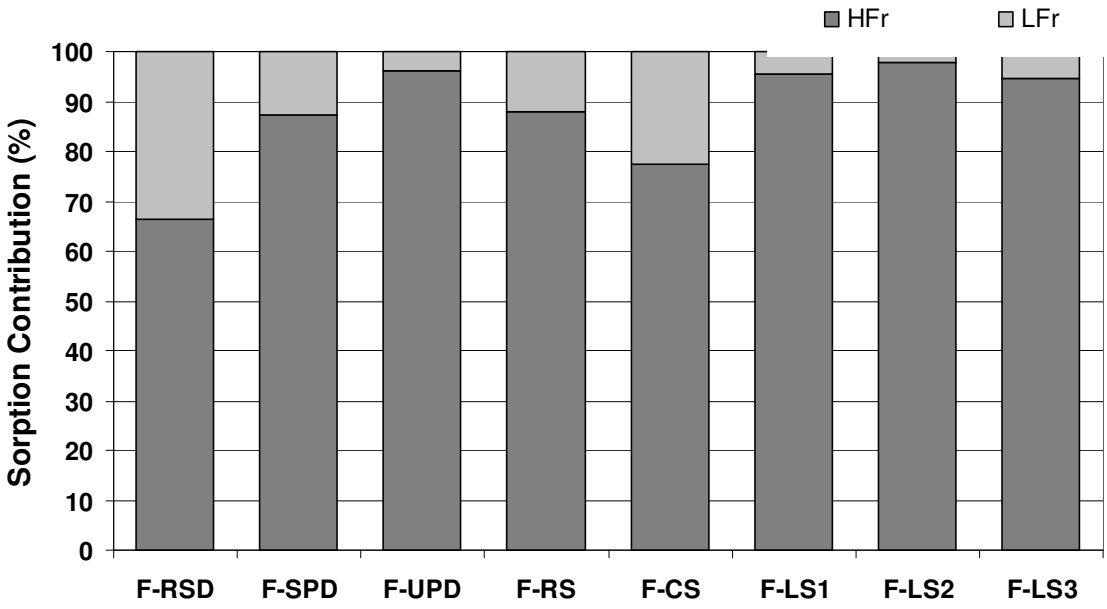

Figure C7. Relative sorption contribution of LFr and HFr fractions of Fosdic Lake watershed samples at an equilibrium concentration of Ce = 10 ug/L.

References

(1) Wilson, J.T., P.C. Van Metre, C.J. Werth, Y. Yang, 2006, Particle-associated contaminants in street dust, parking lot dust, soil, lake- bottom sediment, and suspended and streambed sediment, Lake Como and Fosdic Lake watersheds, Fort Worth, Texas, 2004 U.S. Geological Survey Data Series 211. Denver, CO, U.S. Geological Survey http://pubs.usgs.gov/ds/2006/211/ (accessed May 2009), 24pp.

(2) MacDonald, D.D., C.G. Ingersoll, T.A. Berger, 2000, Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems, Archives of Environmental Contamination and Toxicology, 39, 20-31.

(3) Rockne, K.J., L.M. Shor, L.Y. Young, G.L. Taghon, D.S. Kosson, 2002, Distributed sequestration and release of PAHs in weathered sediment: The role of sediment structure and organic carbon properties, Environmental Science & Technology, 36, 2636-2644.

Evaluating Alternatives for Watershed-Scale Design of BMPs

Basic Information

Title:	Evaluating Alternatives for Watershed-Scale Design of BMPs
Project Number:	2006IL134G
Start Date:	8/16/2006
End Date:	8/15/2008
Funding Source:	104G
Congressional District:	12th District, IL
Research Category:	Engineering
Focus Category:	Management and Planning, Hydrology, Models
Descriptors:	
Principal Investigators:	John William Nicklow

Publication

1. Kaini, P., K. Artita, J. Nicklow, 2007, Evaluating optimal detention pond locations at a watershed scale, in Proceedings of the 2007 World Environmental and Water Resources Congress, American Society of Civil Engineers, Reston, VA, CD-ROM.
2. Artita, K.S., P. Kaini, and J.W. Nicklow, 2008, Generating alternative watershed-scale BMP designs with evolutionary algorithms, in Proceedings of the 2008 World Environmental and Water Resources Congress, American Society of Civil Engineers, Reston, VA, CD-ROM (in press).
3. Kaini, P., K.S. Artita, and J.W. Nicklow, 2008, Designing BMPs at a watershed-scale using SWAT and a genetic algorithm, in Proceedings of the 2008 World Environmental and Water Resources Congress, American Society of Civil Engineers, Reston, VA, CD-ROM (in press).
4. Artita, K.S., M.W. Sears, P. Kaini, and J.W. Nicklow, (in preparation), An information theoretic approach to sensitivity analysis of distributed watershed models, Journal of Hydrology.
5. Artita, K.S., P. Kaini, and J.W. Nicklow, (in preparation), Examining the possibilities: Generating alternative watershed-scale BMP designs with evolutionary algorithms, Journal of Water Resources Planning and Management.

National Institutes of Water Resources/
Illinois Water Resources Center
Annual Report

1. **Project Number:** 2006IL134G

2. **Project Title and PIs:** Evaluating Alternatives for Watershed-Scale Design of BMPs; Dr. John W. Nicklow, P.E., P.H., D.WRE, Professor, Department of Civil and Environmental Engineering, Southern Illinois University at Carbondale (SIUC)

3. **Research Category:** Best Management Practices, Decision Support Modeling

4. **Problem and Research Objectives:** Best management practices (BMPs) are widely-used structural or non-structural methods intended to manage and/or improve the quantity and quality of stormwater runoff. BMPs are commonly individually designed and site-specific. Studies (e.g., Ferguson, 1991), however, suggest that such fragmented layouts may actually worsen stormwater impacts at the scale of a watershed, thus negating the intended purpose of runoff controls. Detention systems and other structural BMPs are instead most cost-effective when designed and implemented in regionally-strategic combinations to meet related stormwater treatment goals. Implementation of a watershed-scale BMP design is often challenged by conflicting objectives (e.g., environmental, ecological, economic criteria) as well as unquantifiable (and therefore, unmodeled) objectives. Identifying a least cost BMP design and several alternative, near-optimal combinations allows decision-makers to assess tradeoffs between designs and will likely result in a more effective reduction of stormwater impacts at lower stakeholder cost.

   The objective of this research was the development of a new, publicly-available decision-support framework and software model that bridges the gap between individual BMP design and the implementation of watershed-scale runoff controls. The corresponding computational model is capable of determining the least-cost combination of BMP design (including types, sizes, and locations of BMPs), along with a set of near-optimal alternatives for the control of stormwater impacts. This decision-making framework was developed and tested on Silver Creek watershed, a portion of the Lower Kaskaskia watershed in southern Illinois. To promote the realization of benefits of watershed-scale design in professional practice, the methodology and application results have been disseminated to federal and state agency personnel, concerned local stakeholders, and the wider water resources community through regional meetings and workshops, an outreach bulletin, nationally-organized conferences, and peer-reviewed journal articles.

5. **Methodology:** A decision support model has been created by linking evolutionary optimization algorithms (EAs) with the U.S. Department of Agriculture's Soil and Water Assessment Tool (SWAT). The initial model underwent testing, evaluation, and refinement to improve predictive capacity and computational performance. The resulting modeling framework is capable of determining watershed-scale BMP designs that:

Minimize → total cost of BMPs

Subject to →
i. governing physical laws of watershed hydrology and water quality,
ii. BMP size constraints (e.g., maximum detention pond area)
iii. maximum peak flow and sediment load rates (i.e., water quantity and quality constraints),
iv. BMP placement constraints (i.e., no BMPs can be placed in subbasins with wetlands or forests as its dominant land use type).

Within the new model, SWAT is used to solve constraints that govern watershed hydrology such that the complex interactions between water quantity and quality are fully captured. SWAT also simulates several standard structural BMPs, including detention ponds, infiltration ponds, parallel terraces, grade stabilization structures, grassed waterways, and filter strips. Meanwhile, the EA identifies optimal BMP designs and solves the overall optimization problem. Two types of EAs, a genetic algorithm (GA) and a species conserving genetic algorithm (SCGA), are used for solution to this problem. The GA solves the problem by finding a single near-optimal solution; the SCGA produces multiple alternative designs that vary minimally in cost from that of the optimum, but are maximally different with respect to design parameters (i.e., BMP type, size, and/or location) and unmodeled objectives (e.g., stakeholder preferences).

To meet outreach objectives, PIs have discussed work with stakeholders in and near the test watershed, and they held a formal a workshop on July 31, 2008. Attendees included federal and state employees, city planners, and others. The workshop included presentation and demonstration of the new model and solicitation of feedback. A subsequent roundtable discussion revealed several possible future improvements, and a number of attendees were interested in applying the model to their respective local watersheds. Future collaboration with these individuals is highly likely.

6. Principal Findings to Date and Significance:

- Collection and review of pertinent scientific literature demonstrates increasing emphasis on the use of EAs in watershed-scale design of BMPs and on the need for watershed-scale designs;
- In addition to detention ponds, other structural BMPs, including infiltration ponds, grassed waterways, parallel terraces, and filter strips, have been included into the model, thus incorporating more realistic options for BMP designs;
- The integrated model (SWAT – GA – SCGA) is capable of yielding one least-cost BMP design for a watershed, followed by a number of near-optimal alternatives that can be evaluated with respect to unquantified objectives;
- Presentation of preliminary results at recent meetings, including a University-wide research meeting, local community outreach meeting, and the World Environmental and Water Resources Congress, has facilitated practical utility and cross-fertilization of concepts and interdisciplinary collaborations;
- Distribution of an educational outreach brochure that included general information about watershed-scale design of BMPs and application-specific results (i.e., proof of concept) raised interested in the topic;

7. Graduate Students Supported with Funding

Name	*Department*	*College*	*Institution*	*Degree Sought*	*Date Degree was or will be awarded*
Kim Artita	Civil Engr.	Engineering	SIUC	Ph.D.	Dec 2009
Prakash Kaini	Civil Engr.	Engineering	SIUC	Ph.D	Dec 2009
Eric Zgonina	Civil Engr.	Engineering	SIUC	M.S.	May 2009
David Macak	Elect. Engr	Engineering	SIUC	M.S.	Dec 2009
Dennis Owen	Civil Engr.	Engineering	SIUC	M.S.	Dec 2008

8. Publications and Presentations

Artita, K.S., P. Kaini, and J.W. Nicklow, 2008, Generating alternative watershed-scale BMP designs with evolutionary algorithms, in *Proceedings of the 2008 World Environmental and Water Resources Congress*, American Society of Civil Engineers, Reston, VA, CD-ROM.

Kaini, P., K.S. Artita, and J.W. Nicklow, 2008, Designing BMPs at a watershed-scale using SWAT and a genetic algorithm, in *Proceedings of the 2008 World Environmental and Water Resources Congress*, American Society of Civil Engineers, Reston, VA, CD-ROM.

Kaini, P., K.S. Artita, and J.W. Nicklow, 2007, Evaluating optimal detention pond locations at a watershed scale, in *Proceedings of the 2007 World Water and Environmental Resources* Congress, American Society of Civil Engineers, Reston, VA, CD-ROM.

Artita, K.S., M.W. Sears, P. Kaini, and J.W. Nicklow, (*in preparation*), An information theoretic approach to sensitivity analysis of distributed watershed models, *Journal of Hydrology*.

Artita, K.S., P. Kaini, and J.W. Nicklow, (*in preparation*), Examining the possibilities: Generating alternative watershed-scale BMP designs with evolutionary algorithms, *Journal of Water Resources Planning and Management.*

9. Notable Achievements:

The strategic interface between an optimization algorithm and a comprehensive watershed simulation model represents a new methodology to guide cost-effective, watershed-scale BMP design. This project demonstrates that the method and associated model are viable and, based on outreach efforts, are appealing to those involved in watershed planning. The resulting model provides watershed management institutions a useful tool for watershed planning and development by providing an optimal design, as well as multiple, near-optimal design alternatives to accommodate unmodeled objectives.

10. Related and Seed Projects:

Lant, C., Nicklow, J., Schoof, J., and Bekele, E. (2008). “Modeling interactions among 21st century climate, land use, and water quantity and quality to representative watersheds.” USEPA. (in review).

Project Proposal: Kraft, S., Lant, C., Nicklow, J., and Beaulieu, J. (2007). “Multifunctionality of agricultural landscapes using modeling and surveying.” USDA (proposal revision requested).

Balancing Irrigation and Instream Water Requirements under Drought Conditions: A Study of the Kanakee River Watershed

Basic Information

Title:	Balancing Irrigation and Instream Water Requirements under Drought Conditions: A Study of the Kanakee River Watershed
Project Number:	2007IL160B
Start Date:	3/1/2007
End Date:	8/31/2009
Funding Source:	104B
Congressional District:	15
Research Category:	Climate and Hydrologic Processes
Focus Category:	Drought, Irrigation, Groundwater
Descriptors:	
Principal Investigators:	Ximing Cai, Yu-Feng Lin, Albert Joseph Valocchi

Publication

1. Oviedo-Salcedo, D., X. Cai, A. Valocchi, Y-F Lin, 2008, Balancing Irrigation and Instream Water Requirements under Drought Conditions: A Study of Kankakee River Watershed in Illinois Water Conference Proceedings, Champaign, IL.

2008-2009 Annual Report

Balancing Irrigation and Instream Water Requirements under Drought Conditions: A Study of the Kankakee River Watershed

Submitted to
Illinois Water Resources Center

By

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Albert Valocchi (Co-PI), Professor, (217) 333 3176, valocchi@uiuc.edu
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April 15, 2009

Problem and Research Objectives

This project is to explore the tradeoff between irrigation and instream flow requirement in the Kankakee River watershed in eastern Kankakee and northern Iroquois Counties. Considering the potential increase of irrigation and other water requirements, the marginal status of riverine ecosystems, and aggravated drought conditions, conflicts between irrigation and in-stream uses may intensify in the future with the risk of reduced groundwater storage, stream depletion and resulting degradation of riverine ecosystems in the watershed. This project addresses the following objectives:

1. **Explore the spatial variability of stream-aquifer interactions at a regional scale; and establish and calibrate a numerical model of the Kankakee watershed based on the understanding of the spatial variability of hydrogeology and human interference through pumping**

2. **Understand how model uncertainty affects the tradeoffs between irrigated agriculture and instream low flow requirements**

3. **Determine the implications of the uncertainty upon groundwater pumping management policies**

During the first year of the project (2007-2008), we focused on data collection and processing and prototype model development. During the past year (2008-2009), we completed the database for the modeling work and implemented the numerical model for the study area. We started to address objective 1 and 2 directly by conceptual analysis through some hypothetical settings. We also conducted reliability-based uncertainty analysis on stream-aquifer systems. The details of the progress are reported in the following.

Principal Findings and Significance

GIS based data model development

A GIS database has been created to support the modeling work for the Kankakee watershed. The GIS database includes both the data repository and some pre-processing programs that are used to construct the numerical model. These programs are useful in the entire modeling process. First, it allows improving the conceptual model by incorporating available high quality data, closing the gap between the model and reality. Second, after adequate data processing and manipulation, the data model will be easily migrated into the preprocessing stage of the numerical model. So far a great effort has been devoted to the creation of the pre-processing program.

In order to make the numerical model represent the inherent complexities of the natural system properly, diverse types of information are required to construct the model. The data items include: hydrogeology, hydro-climatology (precipitation, streamflow, etc.), and water use such as irrigation pumping or irrigated acreage to estimate the crop water requirement. The

hydrogeology datasets include details of the spatial arrangement of the formations in addition to their physical properties (e.g. transmissivity, porosity etc). This spatial setting of the geologic strata in conjunction with the vertical and horizontal stream alignment, define the spatial variability of the stream-aquifer system at regional scale. Thus a better resolution of the interaction is achieved compared to the representation in Gross et al. 1981. The hydro-climatology dataset allows to compute the irrigation when the pumpage is not readily available and to identify the drought periods. If pumpage datasets are not available, estimation of irrigation is performed using precipitation and evapotranspiration data. Table 1 summarizes the collected datasets. The sources are provided, as well as the dataset type and a brief description on how each one is going to be used in the modeling process.

Table 1. Datasets on the GIS data model and auxiliary datasets

Dataset	**Source**	**Type**	**Use of the data for modeling**
DEM (NED 1/3 arc second)	http://seamless.usgs.gov/index.php	raster	Streambed elevation
Bedrock elevation	Center for Groundwater Science ISWS	point	Geology formations
Streams	http://nhd.usgs.gov/ via ISWS	polyline	Streams alignment
Annual pumpage	ISWS and Indiana DNR	table	Pumping schedule
Pumping well	Center for Groundwater Science ISWS	point	Well locations
Stream discharge and dtage	http://waterdata.usgs.gov/nwis/sw	table	Stream routing
Hydraulic Conductivity	Center for Groundwater Science ISWS	polygon	Transmissivity
Recharge	Center for Groundwater Science ISWS	polygon	Model input
Storage / Porosity	Center for Groundwater Science ISWS	polygon	Physical properties

Auxiliary datasets			
Dataset	**Source**	**Type**	**Use of the data for modeling**
Illinois State Border	Center for Groundwater Science ISWS	polyline	Geographic reference
County Lines	Center for Groundwater Science ISWS	polyline	Geographic reference
Township and Range	Center for Groundwater Science ISWS	polyline	Geographic reference
Watersheds	Center for Groundwater Science ISWS	polyline	Geographic reference

Figure 1 shows a portion of the study area. The caption depicts a composition of different features that recreate the physiographic characteristics and some auxiliary references. At the central part of Figure 1 is Kankakee County and the confluence of the Iroquois and Kankakee Rivers. The Digital Elevation Model –DEM- serves as a background in this depiction. DEM in conjunction with the National Hydrologic Database (NHD) is used to derive the stream and watershed boundary. The watershed boundary is further used to tentatively define no-flow boundary conditions, which will reduce the number of grids involved in the numerical model and then increase the convergence speed of the numerical model.

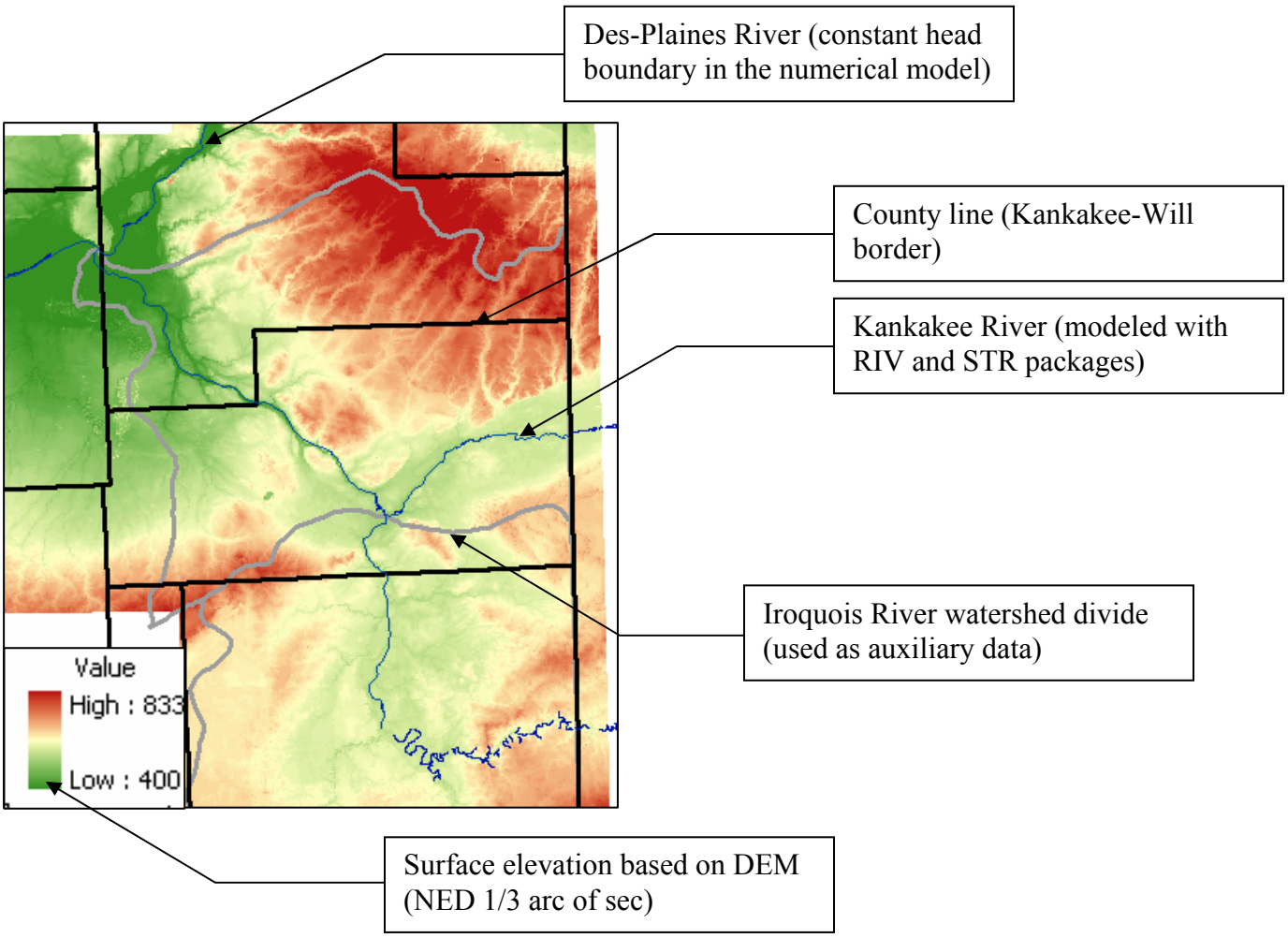

Figure 1. A GIS-based composition of a portion of the study area

Numerical model development

The prototype model described in the report of 2007-2008 has been used as a tool to test the impact of spatial variability of the stream-aquifer systems and the pumpage on different

formations. Following that work, a more complex model has been created. Procedures including pre-processing, model simulation running and post-processing have been carried out for the numerical model development. The data processed in the GIS database is translated into a graphical user interface (GUI), namely Ground Water Vistas (GWV), an interface program of the numerical model (MODFLOW). Some refinements are performed by GWV. For instance, the initial grid size is 2500 by 2500 (ft), but the river width in reality is about 150-200 (ft). Then, the grid size used for MODFLOW was reduced to 625 by 625 (ft). This change made with GWV was then updated in the database.

Boundary condition definition is an important task in modeling. The groundwater modeling literature refers frequently to the necessity of having a constant head boundary condition to help stabilize the numerical response of the model. In the Kankakee watershed, the Des-Plaines River joins the Kankakee River in the vicinity of the study area, and these rivers further join the Illinois River. A portion of the Des-Plaines and the Illinois River, located North-West of the study area has been designated as a constant head boundary. That is, the river lines are defined as "constant head boundary."

The stream has been depicted by using the NHD dataset and modeled using the RIV (river) package. First a steady state model is constructed, which constitutes the basis for the subsequent transient model. The transient model is constructed with the STR (stream) package, which allows flow routing to address the impact of pumping on low-flows. The model uses multiple layers to represent the geologic formations and the structure of the stream-aquifer system.

Pumping wells are included in the numerical model. Data on the wells, including the locations and pumping rates are collected from different sources such as the Illinois State Water Survey, the U.S. Geological Survey.

Figure 2 shows the piezometric head distribution for the third layer, which attempts to replicate the drought period of 1987-1988. The contour lines represent the piezometric head distribution under steady state conditions. It clearly shows the cone of depression due to the pumpage nearby the Iroquois and Kankakee Rivers confluence. The small circles represent the location of pumping wells extracting water from the Silurian-Devonian Dolomite aquifer. Since only the annual pumping data is available, the estimated pumping by time period (month) involves significant uncertainty. The locations of the wells and the spatial distribution of pumping also need further verification. This leaves the analysis of uncertainty with pumping a great challenge for numerical modeling.

The performance of the numerical model can be checked by mass balance verification as shown in Figure 3. Mass balance checking shows a clear hydraulic connection between the Silurian-Devonian Dolomite aquifer (where pumping occurred) and the stream. Under the steady state condition, it shows that stream supplies the irrigation water, which verifies the observation of river depletion during the drought period. Figure 3 represents the mass balance for the entire model.

The model converges under the steady state condition and it is ready to be calibrated by using observed data during 1987-1989 (Cravens at al. 1990) using PEST, a nonlinear regression program that handle the uncertainty of model parameters.

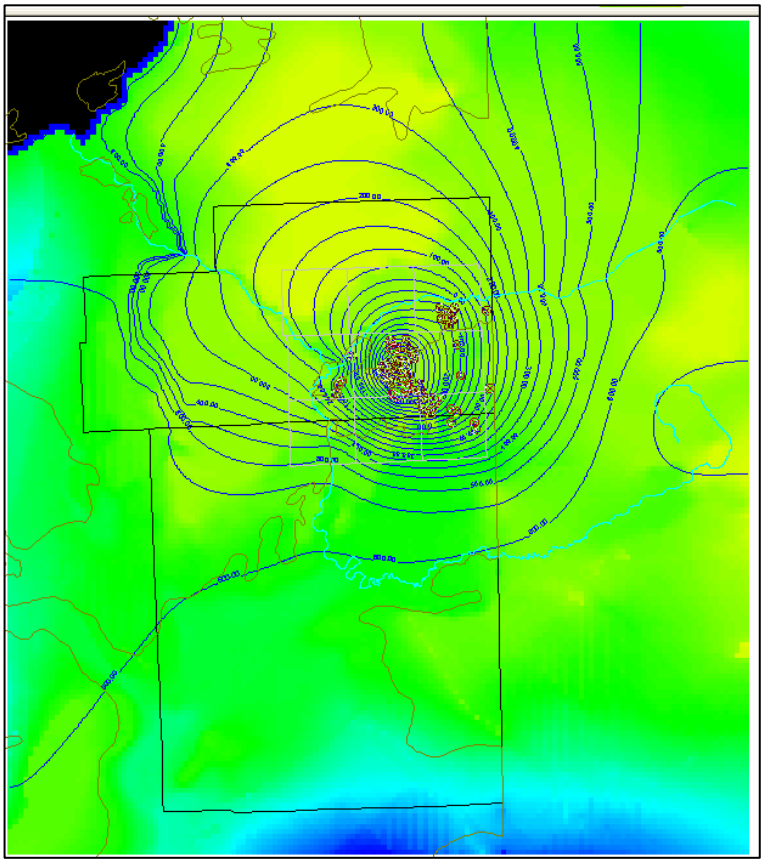

Figure 2. Head distribution in the third layer (Silurian-Devonian Dolomite aquifer), steady state condition

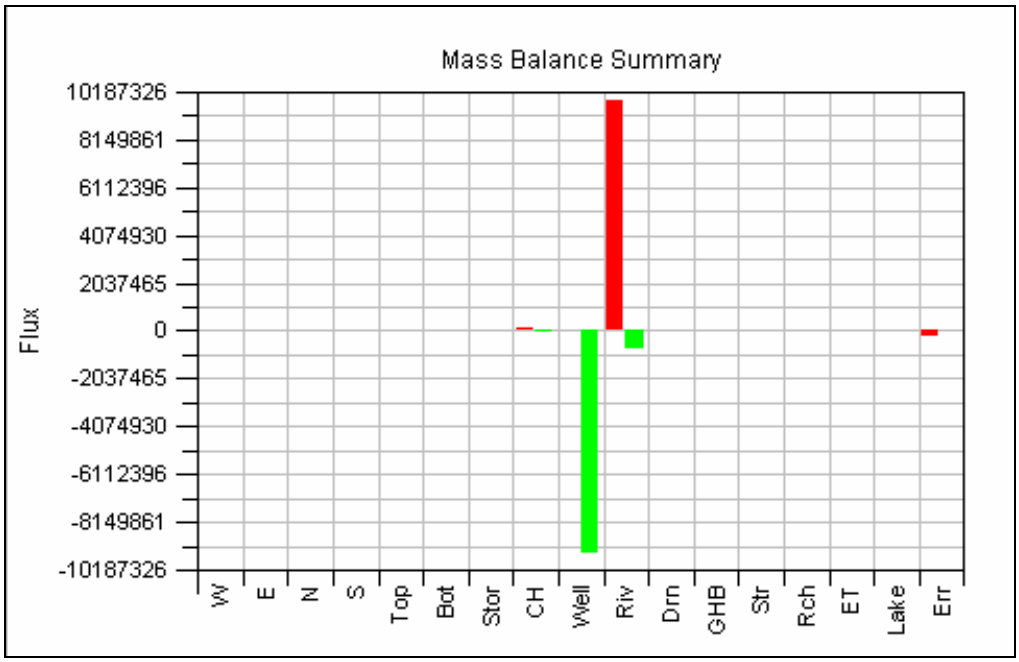

Figure 3. Mass balance under steady state conditions

Reliability-based uncertainty analysis on stream-aquifer systems

We plan to use the model described above to derive policy implications on irrigation water use in the study area. Due to the various uncertainties involved in the model, deterministic results will not yield meaningful management policies. The robust component of the policy implication will be most useful for decision making support. We have developed a framework to convert the model parameter uncertainties into the uncertainty of the model outcomes such as water table elevation and base flow. Based on extensive literature review on uncertainty quantification and approximation, we have started to develop a reliability based optimization framework to optimize irrigation scheduling under model uncertainties, as well as climate uncertainties. We also conduct some regression analysis with hypothetical problems in order to understand how uncertainty in irrigation pumping may bias parameter estimates and state prediction.

Notable achievements

In summary, the notable achievements during the past year are listed as below:

1. Completed the database for the modeling work
2. Converted the prototype model developed in the first year (2007-2008) into a numerical model and found promising results with the numerical model
3. Developed a framework for uncertainty analysis and obtained preliminary results

Based on data analysis and preliminary modeling results, we have better understanding about how irrigation pumping affects the interactions between surface water and groundwater in the study area. The major source for irrigation in the area is the Silurian Dolomite. When water is pumped intensively from this layer, the flow in the streams connected to the aquifer layer will

be affected. Moreover if the intermediate glacial drift deposits are not always present, the sand and gravel aquifer and the shallow rock aquifer could be hydraulically connected under particular circumstances. Such connection may lead to water depletion in the upper aquifer and may even affect the surface water due to the intensive pumpage in the lower aquifer. This could be the case when a drought period overlaps with the irrigation season, i.e., a natural stress on top of a human induced alteration of the natural supply system.

Preliminary results from this project have made a direct, significant contribution to two funded projects, as listed below:

- Coupling Hydrologic, Economic, and Social Network Models to Improve Understanding of Surface Water-Groundwater Interactions for Protection of Instream Flows, 8/2007-7/2011, NSF-EAR-0709735, $998,997, Nicholas Brozović (PI), John Braden, Ximing Cai, Stephen Gasteyer, and Albert Valocchi (Co-PIs), University of Illinois at Urbana-Champaign.

- Planning for Drought Preparedness in the Watershed Context: A Risk-Based Decision Analysis, NSF-CMMI-0825654, $389,348, 10/2008-9/2011, Ximing Cai (PI), Junho Song and Albert Valocchi (Co-PIs).

Students Supported with Funding

Diego Oviedo-Salcedo, PhD student, Department of Civil and Environmental Engineering, University of Illinois at Urbana-Champaign

Publications and presentations

Oviedo-Salcedo, D., X. Cai, A. Valocchi, Y-F Lin**,** Balancing Irrigation and Instream Water Requirements under Drought Conditions: A Study of Kankakee River Watershed, presented on the Illinois Water Conference, Champaign, IL 2008.

Oviedo-Salcedo, D., X. Cai, A. Valocchi, Y-F Lin**,** Uncertainty Assessment in Pumping Rates as Human Interference and its Effects on River-Aquifer Interaction in a Watershed Context, to be presented at the World Environmental and Water Resources Congress, Kansas City, MO 2009.

References

Cravens, S.J., S.D. Wilson, and R.C. Barry, 1990. Regional Assessment of the Ground-water Resources in Eastern Kankakee and Northern Iroquois Counties. *ISWS* RI-111, Champaign, Illinois.

Gross, D.L., and R.C.Berg. 1981. Geology of the Kankakee River System in Kankakee County, Illinois. Illinois Geological Survey Environmental Geology Notes 92, Champaign, IL, 80 p.

Methylmercury Bioavailability and Dynamics in the Streams of Piasa Creek Watershed: New Methods of Sampling and Analysis

Basic Information

Title:	Methylmercury Bioavailability and Dynamics in the Streams of Piasa Creek Watershed: New Methods of Sampling and Analysis
Project Number:	2007IL161B
Start Date:	3/1/2007
End Date:	8/31/2009
Funding Source:	104B
Congressional District:	15th
Research Category:	Water Quality
Focus Category:	Toxic Substances, Methods, Geochemical Processes
Descriptors:	
Principal Investigators:	Robert J. Hudson

Publication

Project Title: Methylmercury Bioavailability and Dynamics in the Streams of Piasa Creek Watershed: New Methods of Sampling and Analysis

Principal Investigator:

Robert Hudson

W-503 Turner Hall, 1102 S. Goodwin Ave., Urbana, IL 61801

rjhudson@uiuc.edu

Research Problem:

Relatively little is known about Hg contamination in Illinois surface waters. In particular, very few measurements of dissolved methylmercury (MeHg) — the most potent neurotoxin of all the Hg species and the only form of Hg that biomagnifies in aquatic food webs — in rivers and streams draining agricultural watersheds have been reported. Thus, little basis exists for linking the impacts of atmospheric deposition of Hg to MeHg in aquatic food webs, particularly in the main class of aquatic ecosystems in Illinois: riverine or lotic ecosystems.

Methodology:

The field work and lab analysis phase of our study involved obtaining measurements of filterable (or dissolved) total Hg (FTHg) and MeHg (FMeHg) levels in a small, mixed land use watershed in southwestern Illinois. We are now in the data analysis/modeling phase of the project. The study was designed to serve the following purposes:

1) Expand our knowledge of the hydrogeochemical factors influencing FTHg and FMeHg levels in Illinois' rivers and streams by measuring dissolved Hg_T and MeHg monthly at 12 sites across the Piasa Creek watershed along with *p*H, dissolved organic carbon (DOC), UV absorbance, and a suite of anions (NO_3^-, Cl^-, and SO_4^{2-}).
2) Test a newly-developed approach for sampling bioavailable MeHg – DGT probes – that could help reduce the cost of monitoring MeHg levels in surface water systems.
3) Measure MeHg in biota: crayfish, stonefly nymphs, shiners, and darters were sampled at the same 12 sites as surface water samples in June 2007. Crayfish and stonefly nymphs are less mobile than the free-swimming darters and shiners and therefore should represent location-specific indicators of MeHg bioavailability in the Piasa Creek food web.

Principal Findings and Significance.

1) Filterable MeHg and THg in streamwater were measured every month (13 events) over the period from June 2007 through June 2008 at twelve sites in the Piasa Creek watershed (Fig. 1). A total of 153 samples were analyzed for FTHg and 162 for FMeHg.
2) There is significant variation in average MeHg across the watershed (Fig. 2) that we will seek to explain using spatial data analysis and modeling. MeHg is highest in headwaters catchments with low forested area.

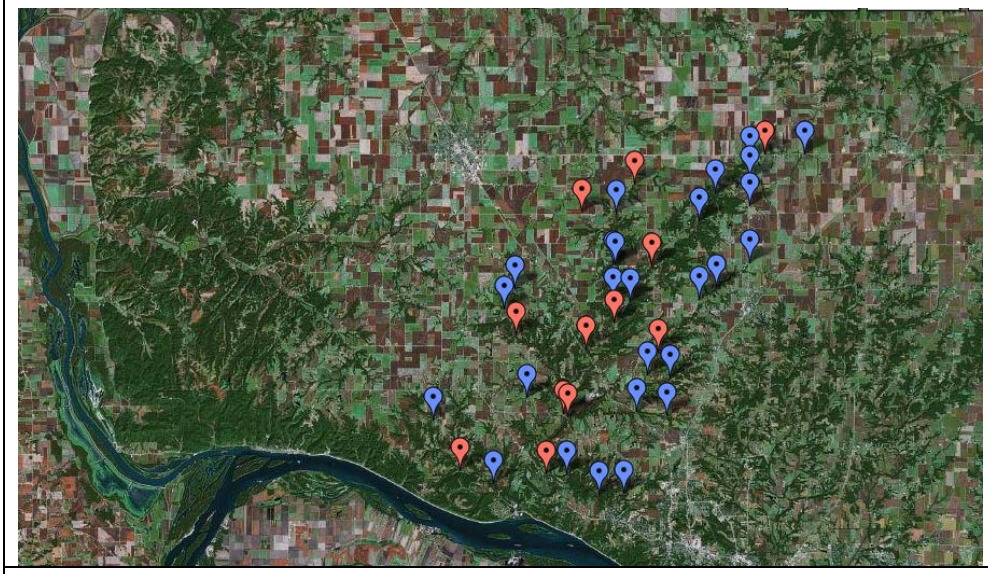

Figure 1. Sampling locations in Piasa Creek near Alton, IL. Orange symbols indicate monthly sampling locations. Blue symbols indicate locations for detailed survey of organic matter in streamwater. Image courtesy of Google Maps.

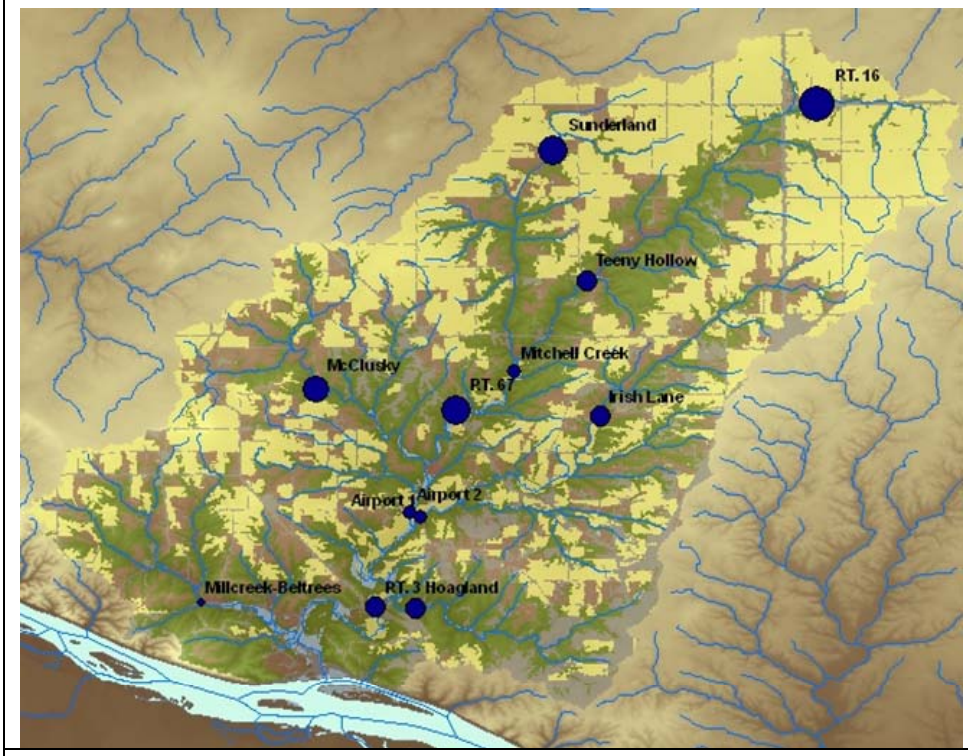

Figure 2. Spatial variability in mean MeHg in Piasa Creek. Land use is indicated by color of shading: Agriculture = Yellow, Forest = Green. Image by Chris Ivanovich.

3) As is frequently observed elsewhere, we found that total Hg and MeHg are best correlated with dissolved organic matter, measured as DOC in Piasa Creek (Fig. 3A,B). Interestingly, MeHg is correlated even more strongly with UV absorbance, a measure of hydrophobic organic matter, than with DOC (Fig. 3C).

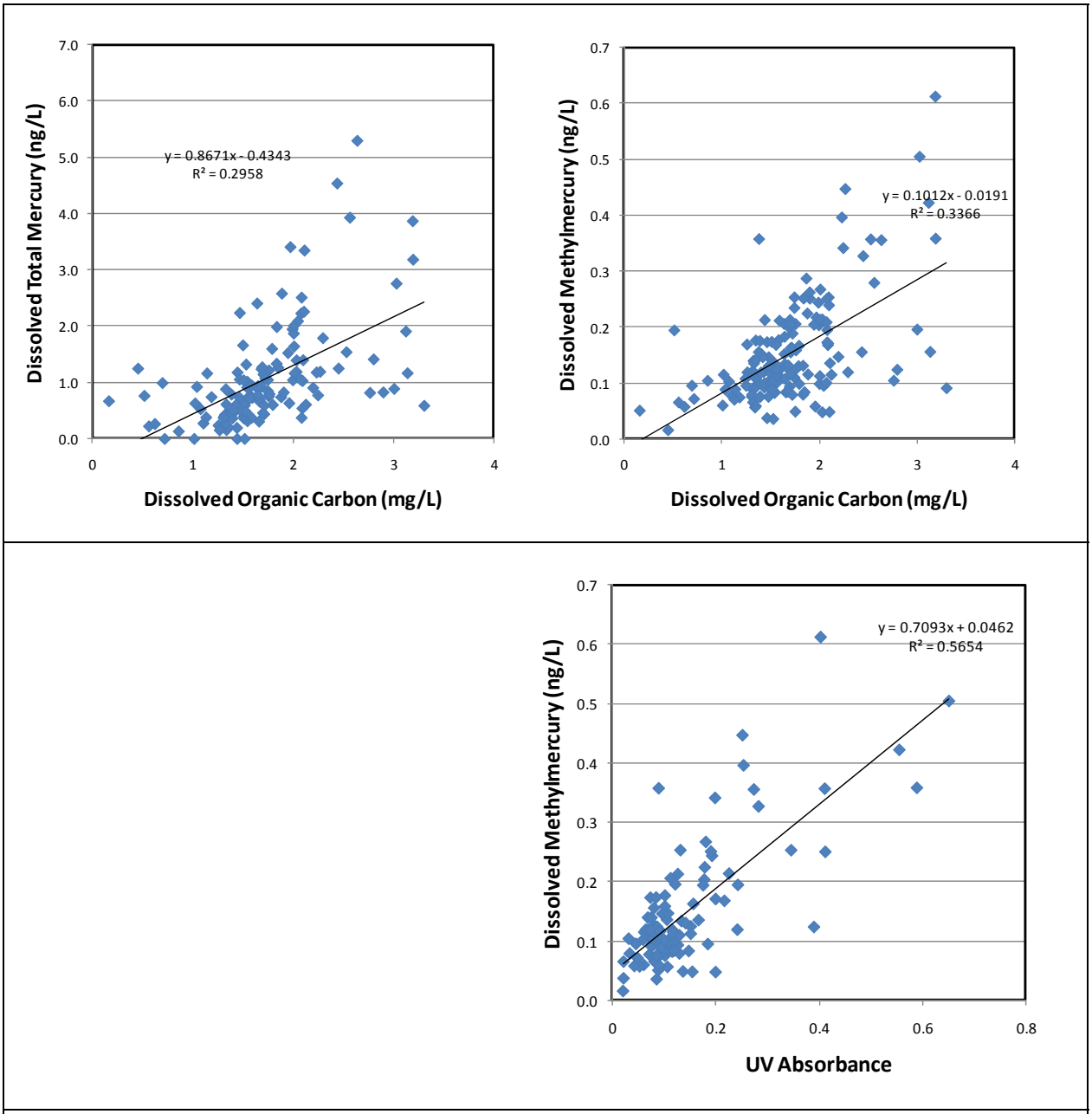

Figure 3. Bivariate plots of filtered Total Hg and MeHg in Piasa Creek samples from 2007-08 with dissolved organic matter and UV absorbance at 254 nm. A: Top right; B: Top right; C Bottom right.

4) MeHg and inorganic Hg were measured in 110 organisms collected during the summer of 2007. As these organisms are relatively low trophic level organisms, none exceeded EPA's Hg criterion of 0.3 ppm. However, when the biota MeHg data generated here are combined with the USGS National Descriptive Model of Mercury in Fish, it predicts that other resident

species (white bass and black crappie) of the Piasa Creek watershed will contain levels of MeHg that exceed the 0.3 ppm human consumption guideline designated by the USEPA at relatively small lengths of 6-8 inches. Such a prediction needs to be substantiated by measuring the MeHg content of these other resident fish species, because they are popular among human that consume fish for sustenance.

5) The DGT-type passive sampling devices were deployed during June 2007 at the twelve regular sampling locations. However, data were obtained from only 10 sites as humans disturbed the probes deployed at two sites. Some probes appeared to have not functioned properly, apparently because the high water velocities in the stream caused leakage of water past the diffusive gel layer. Modifications to the design of the physical properties of the probes are needed before re-testing. Nevertheless, a weak relationship of DGT-MeHg to MeHg in biota was observed (Fig. 4B).

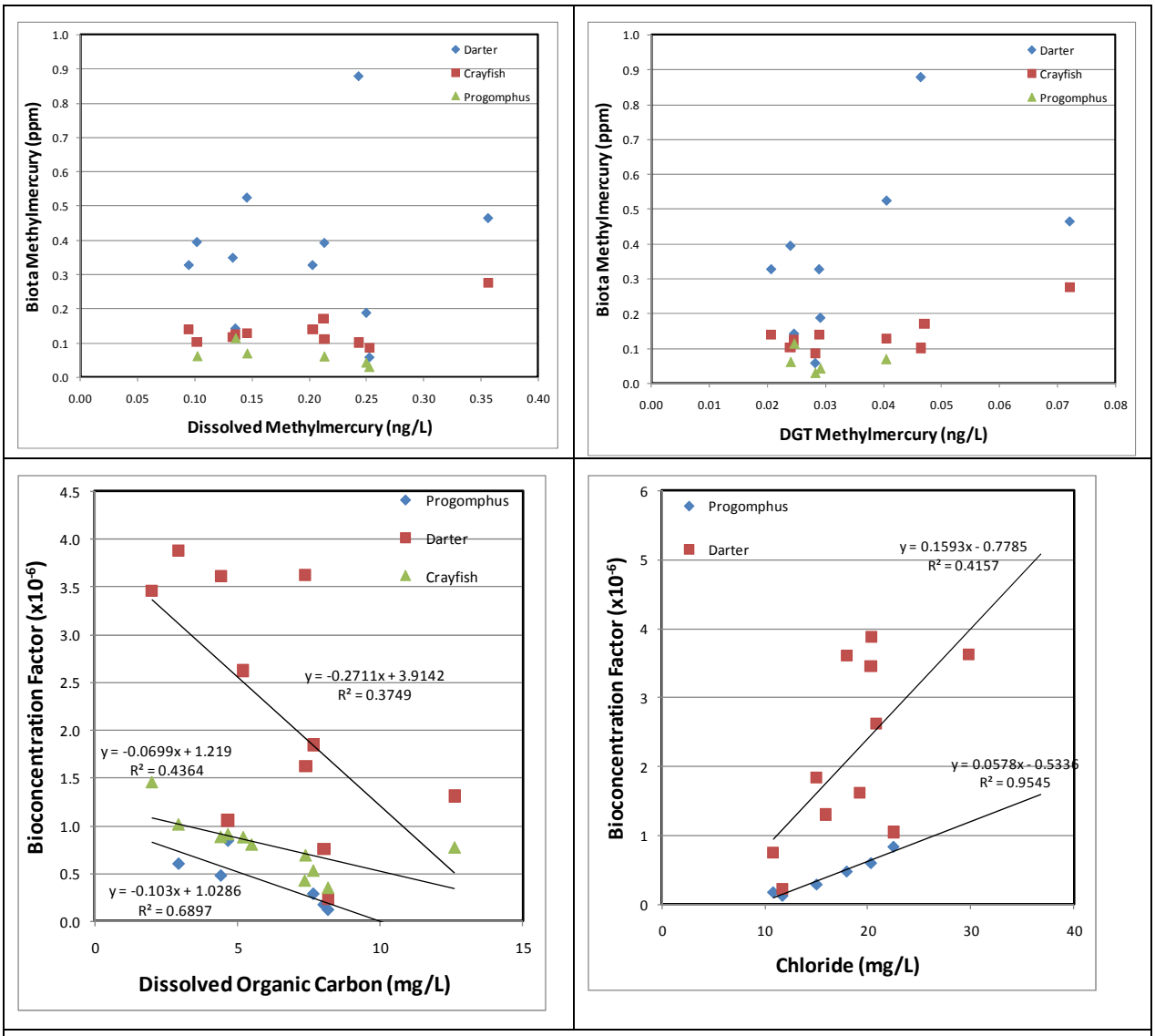

Figure 4. Relationships between MeHg in biota and FMeHg (A: upper left), DGT-MeHg (B: upper right).

6) The relationship of MeHg in biota to FMeHg is weak (Fig. 4A). We hypothesize that this is due to the dependence of MeHg bioavailability on other parameters, such as DOC, Cl, and pH. One approach to investigating this issue is to search for relationships between these parameters and the MeHg bioconcentration factor, which is calculated as the ratio of MeHg in biota to that in FMeHg for the same site. We found that the MeHg bioconcentration factors depend negatively on DOC and positively on Cl (for two species). This is consistent with the standard model for MeHg bioavailability in freshwater, which suggests that MeHg uptake into food webs may be controlled by a set of reactions that can be approximated by:

$$MeHg - DOM + Cl^{-} \longleftrightarrow MeHgCl^{0} + DOM$$

$$MeHgCl^{0} \longrightarrow MeHg_{BIOTA}$$

Although such effects of DOM are not unusual, the enhancement of bioavailability by Cl is rarely reported despite it being a core prediction of the standard model for MeHg uptake into food webs. Therefore, we are excited about the prospect that further careful analysis of these data will shed new light on the bioavailability of MeHg in freshwater ecosystems.

Notable achievements:

1) Using novel analytical techniques developed in our lab at the University of Illinois Urbana-Champaign, we have measured:
   i) The MeHg content of four aquatic organisms (110 individuals) sampled in June 2007 from 12 locations in the Piasa Creek watershed,
   ii) The dissolved MeHg and THg content of 152-163 surface waters samples collected between June 2007 and June 2008 from 12 locations within the Piasa Creek watershed,
   iii) The amount of accumulated MeHg in 30 DGT probes deployed in June 2007 from 10 locations in the Piasa Creek watershed. However, as mentioned above due to a design flaw in the probes these data appear to be compromised.
2) The total Hg and MeHg data are most strongly correlated with measures of dissolved organic matter in the streamwater. The degree of correlation is greatest between FMeHg and UV absorbance, which measures hydrophobic dissolved organic matter.
3) Bioconcentration factors calculated by site for crayfish, stonefly nymphs, and shiners were inversely correlated with DOC and positively correlated with Cl, which is consistent with chemical models for biota-MeHg interactions with DOC.
4) Bioconcentration factors calculated by site for darters were not correlated with DOC, suggesting that darters either possess a unique MeHg uptake pathway, compared to the other organisms analyzed in this study, or are more mobile.

Students Supported:

Brian Vermillion, Department of Natural Resources and Environmental Sciences, University of Illinois, Ph.D. student, degree expected (8/2009).

Chris Ivanovitch was a National Great Rivers Research and Education Center intern in the summer of 2008. His internship was indirectly supported by this project since he worked these data.

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Results were presented at the Illinois State Academy of Science meeting in April 2008 and at the Illinois Water conference in October 2008.

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Modeling of Hydrodynamics and Sediment Transport in St. Clair River

Submitted

To

International Joint Commission (IJC)

International Upper Great Lakes Study (IUGLS)

by

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1. Introduction

The continuous lowering of Lake Michigan-Huron levels has caused increasing concerns. St. Clair River, which drains Lakes Michigan and Huron to Lake St. Clair-Lake Erie, appears to bear much of the blame. Among many others, Baird & Associates (2005) investigated the possible causes. The three most possible ones appear to be: erosion of the St. Clair River bed, relative change in net basin supply (NBS), and differential glacial rebound. These hypotheses are still under investigation.

Dredging activities for navigation and mining of sand and gravel in the river bed can be dated back to the 1800's. Three major dredging projects in the history of the river can be identified: dredging for the 6.1m navigation channel completed in 1906, the 7.6m (25ft) navigation channel completed in 1937, and the 8.2m (27ft) navigation channel completed in 1962. Dredging and erosion so induced appears to have changed the river conveyance. Sand and gravel mining have also contributed to the change of the river bathymetry.

Changes of the cross section at some critical points (due to e.g. shipwrecks) may also have affected the conveyance. These changes of the cross section are due to human settlement and development. The modification of the cross section may have changed the flow in the river and therefore affected the water level in Lake Michigan and Lake Huron.

The sediment supply into the St. Clair River has changed over time. Shoreline protection and numerous harbor structures in Lake Huron, especially around the area near the St. Clair River outlet, appear to have locally reduced the sediment transport rate. The sediment feed rate at the inlet of the St. Clair River, while probably never large due to the presence of Lake Huron, may have been further reduced by e.g. groins. These factors could have caused erosion of the river bed and therefore change in the conveyance.

In our work, an in-house numerical code, HydroSed2D, will be used. HydroSed2D is a two-dimensional depth-averaged hydrodynamic code with sediment transport (Liu and García, 2008). It is based on the shallow water equations. This code was originally developed by Prof. Alistair Bothwick at University of Oxford, UK. The original code uses a quad-tree grid structure. It has been used in many engineering applications, including scour due to dyke breaching in the Yellow River, China. We have adapted HydroSed2D for unstructured meshes and made it easy to be applied to complicated domains. The Godunov scheme is used to solve the governing equations. The details of the code can be found in Liu (2008).

After a high quality mesh is generated and the HydroSed2D model is carefully calibrated, the model is used to investigate the possible causes of the Lake Huron level dropping, namely the bathymetry change and the Lake Huron inlet alignment. Bathymetry data from year 1971 to 2008 are used. Shear stress distribution in the river is plotted and its implication for sediment transport is analyzed.

Sediment transport and armoring analysis is done by combining the HydroSed2D model and the Microsoft Excel tool Acronym for gravel transport. The shear stresses from the HydroSed2D model and the sediment size distributions from image analysis are used as input for armoring calculation.

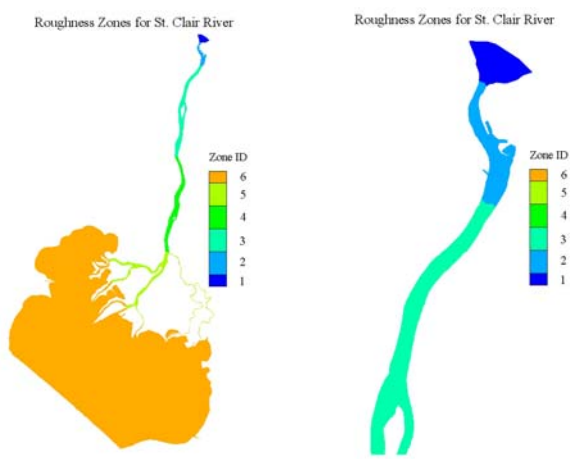
Other factors, such as ice cover/ice jam and navigation, are also investigated. Their effects on the river flow and sediment transport are qualitatively analyzed. Rough estimations are made according to measurement in the literature.

2. Calibrations and Mesh Independence

Before any simulations can be carried out, two things need to be done to control the quality of the results: the calibrations and the mesh independence study.

2.1 Calibrations

The roughness is important since it is the parameter which defines the drag force experience by the flow. On the other hand, the shear force on the river bottom by the flow is the driving force of the sediment movement. The purpose of the calibration runs is to adjust the roughness of the river bed. The roughness of the first two bends area is determined by sediment sizes based on the analysis of the under water images. The rest of the river reach is divided into several zones. The division of the reach is shown in Figure 1. The zones for roughness: (a) the whole river (b) the upstream part In each zone, the Manning's n is adjusted to match the simulated water surface elevations with the measurements. The roughness of the river is not constant. It dynamically changes when the river evolves. The man made changes, such as the gravel mining, navigation, dredging, and ship wreckage, affect the roughness to some extend. The response of the river itself, such as the armoring effect, sediment transport, will also change the roughness. These dynamic changes of the flow resistance involve many unknowns and will be too complicated to be modeled. As such, they are not modeled in the present study.



(a) (b)

Figure 1. The zones for roughness: (a) the whole river (b) the upstream part

2.1.1 Roughness Calculation for the First Two Bends

The bed shear stress can be made dimensionless as

$$C_f = \frac{\tau_b}{\rho U^2}$$

Where C_f is the dimensionless bed resistance coefficient, the dimensionless Chezy resistance coefficient C_z is related to C_f as

$$C_z = C_f^{-1/2}$$

Keulegan (1938) proposed a formulation for the Chezy coefficient:

$$C_z = C_f^{-1/2} = \frac{1}{\kappa}\ln\left(11\frac{H}{k_s}\right)$$

where κ = 0.4 denotes the dimensionless Karman constant and k_s = a roughness height characterizing the bumpiness of the bed.

Manning-Strickler formulation:

$$C_z = C_f^{-1/2} = \alpha_r\left(\frac{H}{k_s}\right)^{1/6}$$

where α_r is a dimensionless constant between 8 and 9. Parker (1991) suggested a value of α_r of 8.1 for gravel-bed streams, which is also used in this research.

Roughness height over a flat bed:

$$k_s = n_k D_{s90}$$

where D_{s90} denotes the surface sediment size such that 90 percent of the surface material is finer, and n_k is a dimensionless number between 1.5 and 3. In this research, the value of n_k is fixed as 2.

The calculation is shown in Table 1.

Table 1. Roughness calculation based on sediment size distribution from images analysis

Image Location	Sediment (use volume)		$K_s=n_k*D_{90}$	C_z		Manning n		Strickler Coefficient	
	D_{50} (mm)	D_{90} (mm)	(mm)	Keulegan (1938)	Manning-Strickler	Keulegan (1938)	Manning-Strickler	Keulegan (1938)	Manning-Strickler
Thalweg 1	27	55	110	16.85	17.18	0.0278	0.0273	35.93	36.63
Thalweg 2	34.4	65.6	131.2	16.42	16.68	0.0286	0.0281	35.02	35.57
Thalweg 3	19	38	76	17.75	18.27	0.0264	0.0257	37.86	38.96
Thalweg 4	26.4	52.5	105	16.96	17.31	0.0276	0.0271	36.18	36.92
					Average:	**0.0276**	**0.0270**	**36.22**	**36.98**

After some initial trial, three sets of roughness conditions are listed in Table 2 as possible candidates. Three sets of hydraulic condition simulations (see Table 3) were done to determine the roughness (Manning's n) for zone 1, 3, 4, 5, and 6 (roughness for zone 2 comes from image analysis). The three sets of simulations represent the low, medium, and high flow conditions. These typical discharges and stages are chosen from measurement data and special care was taken to make sure the river is at almost steady state during these typical periods.

Table 2. Roughness calibration conditions set
(numbers in red for zone 2 is from sediment size analysis)

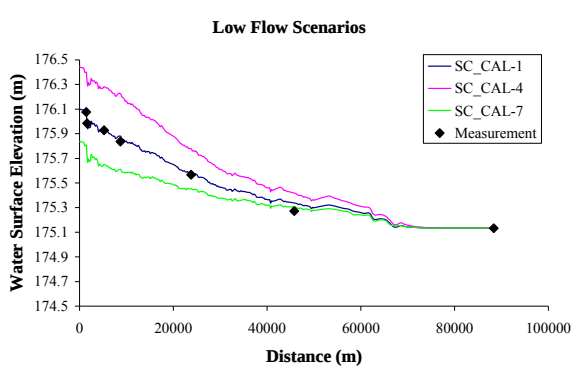
Zone ID	Set 1		Set 2		Set 3	
	Manning's n	Strickler Coefficient	Manning's n	Strickler Coefficient	Manning's n	Strickler Coefficient
1	0.0166	60.2	0.0200	50.0	0.0161	62.0
2	**0.0276**	**36.2**	**0.0276**	**36.2**	**0.0276**	**36.2**
3	0.0250	40.0	0.0333	30.0	0.0167	60.0
4	0.0227	44.0	0.0286	35.0	0.0154	65.0
5	0.0200	50.0	0.0233	43.0	0.0159	63.0
6	0.0213	47.0	0.0278	36.0	0.0192	52.0

Table 3. Three typical hydraulic conditions sets for calibrations

Low Flow Scenario Set 1		Medium Flow Scenario Set 2		High Flow Scenario Set 3	
Discharge (m^3/s)	Lake St. Clair Level (m)	Discharge (m^3/s)	Lake St. Clair Level (m)	Discharge (m^3/s)	Lake St. Clair Level (m)
4645	175.133	5282	174.937	6006	175.513
Date: 4/27/2005		Date: 8/24/2005		Date: 8/1/1998	

Table 4. Nine calibration cases
(combination of roughness sets and hydraulic condition sets)

Case ID	Roughness Condition Set	Hydraulic Condition Set
CAL-1	1	1
CAL-2	1	2
CAL-3	1	3
CAL-4	2	1
CAL-5	2	2
CAL-6	2	3
CAL-7	3	1
CAL-8	3	2
CAL-9	3	3



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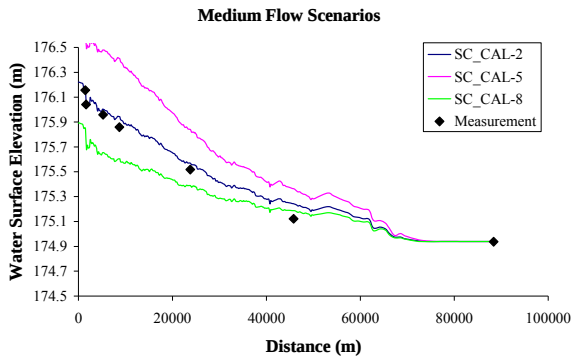

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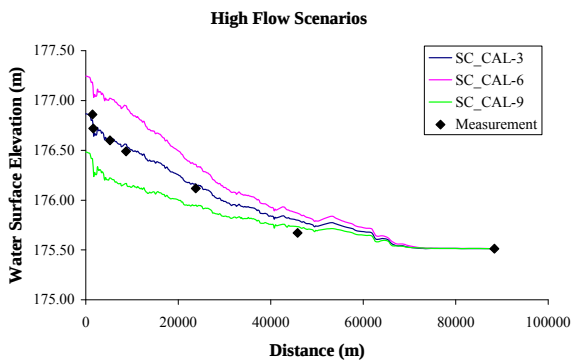


(c)

Figure 2. Comparisons between Simulated Results and Measured Stages for Calibration Runs: (a) Low Flow Scenarios (b) Medium Flow Scenarios (c) High Flow Scenarios

2.2 Mesh Independence Study

For a large, as well as complicated, lake-river system of the Lake Huron-St. Clair River-Lake St. Clair, a decent mesh with high quality is important for the creditability of the simulation results. The mesh need to be as fine as possible to capture most of the geometry and bathymetry details. However, it is unrealistic to use a mesh which is too fine since it will dramatically increase the computational time. In order to use a mesh which is neither too fine nor too coarse, a mesh independence study is warranted.

Three different meshes with different refinement are used. The parameters, such as the mesh size, mesh numbers, are listed in Table 5. The mesh for the domain is shown in Figure 3**.** Special treatment of the meshes is applied to the first two bends. The reason has two folds. First, there are a lot changes around the bends (such as the big scour hole, the tongue features, and historical ship wreckages). This is also the control area for the flow. As shown in the shear stress analysis, the contraction from the Lake Huron to the St. Clair River makes the bottom shear stresses is highest in this area. This implies that sediments in the first two bends have the highest potential of movement. This might lead to the explanation of the tongue features of the sand bars and their

effects in terms of conveyance. Mesh is also refined in the area of the delta in Lake St. Clair. Refined mesh is needed to well represent the narrow navigation channel which controls the water surface elevation throughout the St. Clair River.

Table 5. Three sets of meshes used for mesh independence study

Mesh ID	Cell Numbers	Mesh Size in the First Two Bends (m)	Mesh Size in Other Areas (m)
A	6124	400	800
B	24066	100	200
C	53962	50	200

(a) (b)

Figure 3. Mesh example for the computational domain: (a) mesh for the Lake Huron inlet area (b) mesh for the delta area in Lake St. Clair

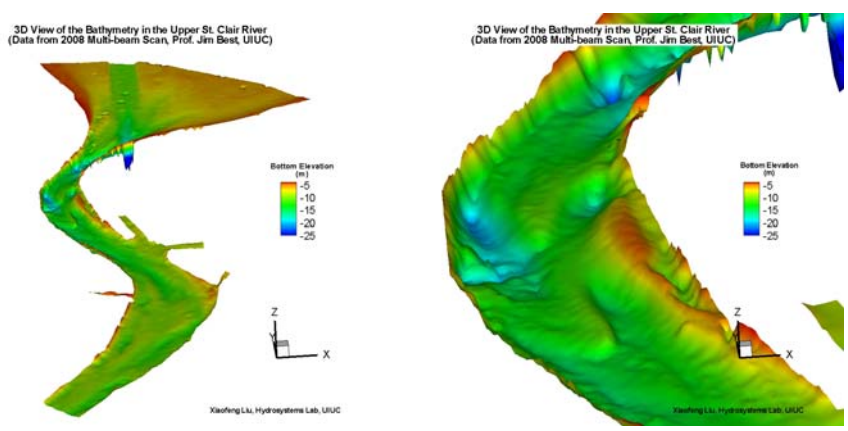
For all three meshes, the simulations were done for 8/24/2005. The bathymetry for year 2005 is from the survey done by USACE. The measured discharge is 5247 m^3/s. The numerical results of stages are compared with the measurement along the St. Clair River. From the simulations, the intermediate mesh (mesh ID B) and the fine mesh (mesh ID C) give almost the same results. However, the fine mesh has more double the cell number than the intermediate mesh which makes the computational time much longer. The coarse mesh (mesh ID A) seems not representing the domain and bathymetry well and it gave a result with high level of error. So in the simulations hereafter, the intermediate mesh (mesh ID B) is used.

3. 3D Numerical Model Verifications

HydroSed2D is a two-dimensional model. As all other 2D models, it has its limitations. The major assumption here is the hydrostatic condition. For our case, the St. Clair River is very shallow. The width-depth-ratio is about 40. So the shallow water equation is generally valid. However, at some local areas, such as the first two bends near the inlet, the effects of local features (secondary flow in the bends, the two tongue features etc., see Figure 4) will change the flow from hydrostatic condition. In order to verify if the 2D model give a relative accurate description of our problem, fully 3D simulations were done. The specific purpose of this exercise is to verify that the shear stress in the first two bends given by the 2D model is in the right range.

The three-dimensional numerical code we used is the open source CFD code OpenFOAM v1.5 (OpenCFD, 2008). OpenFOAM is primarily designed for problems in continuum mechanics. It provides a fundamental platform to solve fluid mechanics problems. The core of the code is the finite volume discretization of the governing equations. The Hydosystems Laboratory at University of Illinois at Urbana-Champaign has used this code in both basic and applied research, such scour around objects (Liu and García, 2008a) and particle settling (Liu and García, 2007).

Due to the limitation of computational resource, only the Lake Huron inlet area and the first two bends are modeled in the 3D simulations. The bathymetry is from the multi-beam scan of Professor Jim Best of University of Illinois at Urbana-Champaign. The 3D view of the 2008 bathymetry is show in Figure 4. The domain is about 8 km long and it has a mesh of around 1.5 million cells. The turbulence is modeled by the k-ε model. It takes more than 24 hours for the model to reach steady state in an 8 nodes computer cluster.



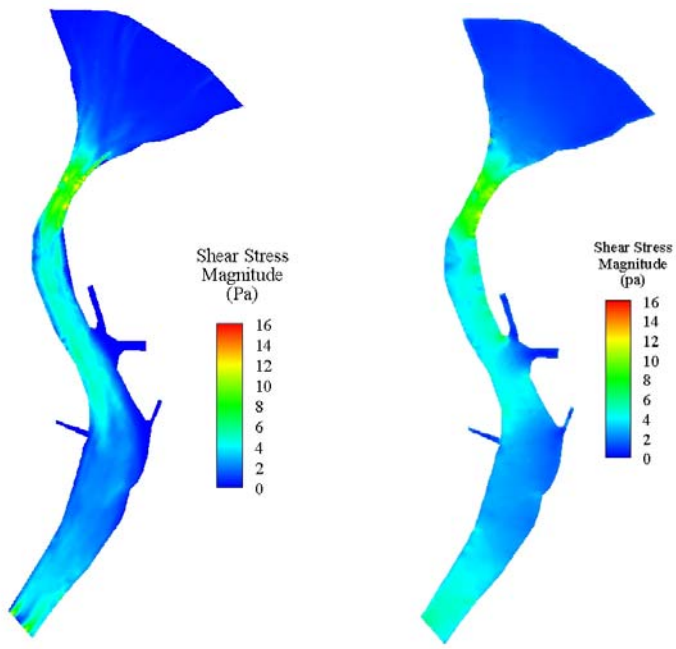
(a) (b)

Figure 4. Bathymetry for the upper reach of the St. Clair River: (a) Overall view of the first two bends (b) Local tongue features at the first bend

The comparison of the bed shear stress between the 2D and 3D models is shown in Figure 5. Although exact match of the shear stresses is not possible, the basic patterns of the shear distribution from both models agree well. For both models, the maximum shear stress is located at

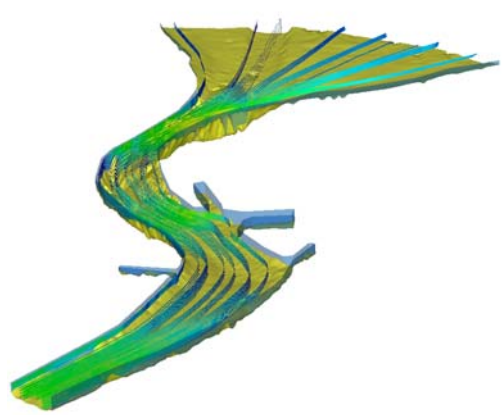
the Lake Huron inlet area and in the second bend, low shear stress is observed. The magnitude of the shear stress also agrees well which means the roughness coefficient we chose and the velocity magnitude the model computed are in the right range. With these, it is safe to say that the HydroSed2D model gives reasonable results.

As an aside, the flow pattern from the 3D model is shown in Figure 6. The stream trace in Figure 6 (a) and (b) helps visualize the flow field. In the first bend, the velocity vectors in several cross sections are shown in Figure 6(c). The secondary flow feature is evident. This might cause the further scour of the deep whole on the outer bend and deposit sediment on the two sand bars in the inner bend. The flow field from the numerical model with 3D ADCP measurement can be used to give a clear picture of what is happening around the bend.



(a) 2D Result (b) 3D Result

Figure 5. Shear stress comparison between 2D (HyroSed2D) and 3D (OpenFOAM) models



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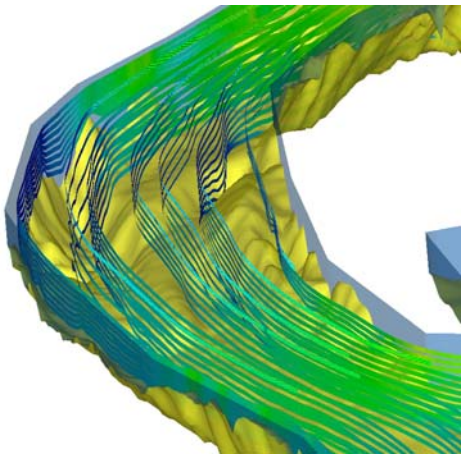

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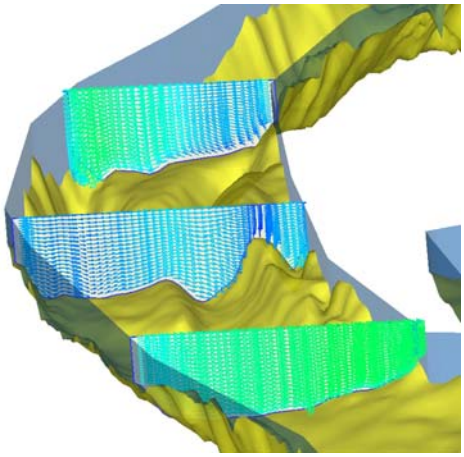


(c)

Figure 6. 3D view of the flow field: (a) Overall view of the streamlines (b) Streamlines in the bend (c) Secondary flow features in the bend over the tongue features

4. HydroSed2D Model Applications

Since the model is carefully calibrated and verified, it is used to investigate the possible cause of the continuous dropping the Lake Huron level. Firstly, the shear stress distribution is analyzed and its implication for the sediment transport is deduced. Secondly, the effects of the bathymetry changes on the Lake Huron level are studied. At the end, the model is used to see the effects of the alignment of the Lake Huron inlet channel.

4.1 Shear Stress Distribution

Bathymetry change in the St. Clair River and the sediment transport supply change from Lake

Huron affect the movement of sediment particles. The interaction between the flow and sediment is a coupled process. The river tries to adjust to a new equilibrium after any change. From the under water videos and images, the sediment has a wide distribution of sizes. Depending on the location in the river, the sediment can range from fine sand to very coarse gravels.

Before doing any numerical simulations, some simple calculation can be done to give the average shear stress in the river. Assume the river has a slope S=2E-5, water depth H=10m, then the average bottom shear stress should be

$$\tau_b = \rho g H S \approx 2Pa$$

Numerical simulations should give an average shear in that order. However, local shear from numerical results could be far apart from this value. In order to see the implications of the shear stress for sediment transport, the critical shear stress needed for the motion of different size of sediment is listed in Table 6. The dimensionless form of this relation, i.e., Shield's diagram, is shown in Figure 7. From this relationship, the average shear stress of 2Pa can only move sediment finer than 5 mm.

The flow condition used for the simulation is the medium discharge condition listed in Table 3. The bathymetry used for the shear stress distribution simulation is from year 2008.

Table 6. Critical shear stress needed for the motion of sediment particles

ψ	D (mm)	Re_p	τ_c^*	τ (pa)
-3	0.125	5.62E+00	3.91E-02	0.08
-2	0.25	1.59E+01	2.20E-02	0.09
-1	0.5	4.50E+01	1.61E-02	0.13
0	1	1.27E+02	1.74E-02	0.28
1	2	3.60E+02	2.11E-02	0.68
2	4	1.02E+03	2.44E-02	1.58
3	8	2.88E+03	2.68E-02	3.46
4	16	8.14E+03	2.82E-02	7.29
5	32	2.30E+04	2.90E-02	15.01
6	64	6.51E+04	2.95E-02	30.49
7	128	1.84E+05	2.97E-02	61.49
8	256	5.21E+05	2.98E-02	123.54

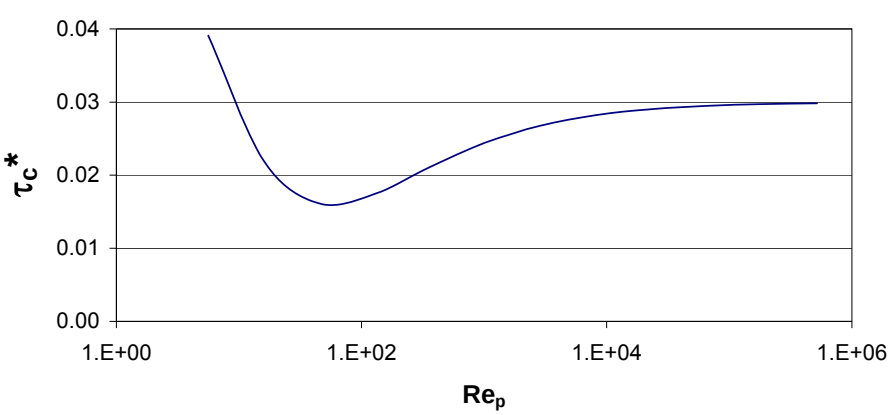
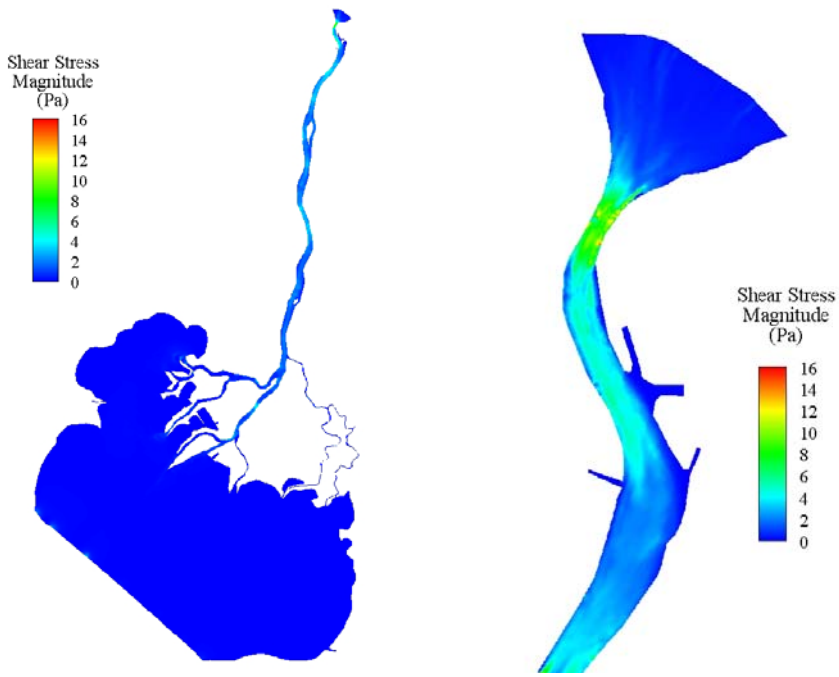


Figure 7. Shield's diagram for the sediment initiation of motion



(a) (b)

Figure 8. Shear stress distribution in the St. Clair River (medium flow condition): (a) shear stress for the whole system (b) shear stress for the upper reach

The simulation results of the shear stress are shown in Figure 8. High shear stress is only observed from in the St. Clair River channel. In the Lake St. Clair, since the velocity is almost zero, the shear stress diminishes. In the St. Clair River, highest shear velocity is located at the Lake Huron inlet area. In this area, the shear stress is about 8 to 10 Pa. This value of shear stress can move sediment finer than 20 mm diameter. Sediment supply (except extremely big particles) from Lake Huron will be moved across this inlet area and be transported downstream. The very possible deposition location is the in the first bend. In the first bend where there is a deep hole and two big sand bars, the shear stress is around 4 to 5 Pa. This value of shear stress can only move sediment finer than 10 mm diameter. The two sand bars might still be evolving because of relatively high shear stress in this area.

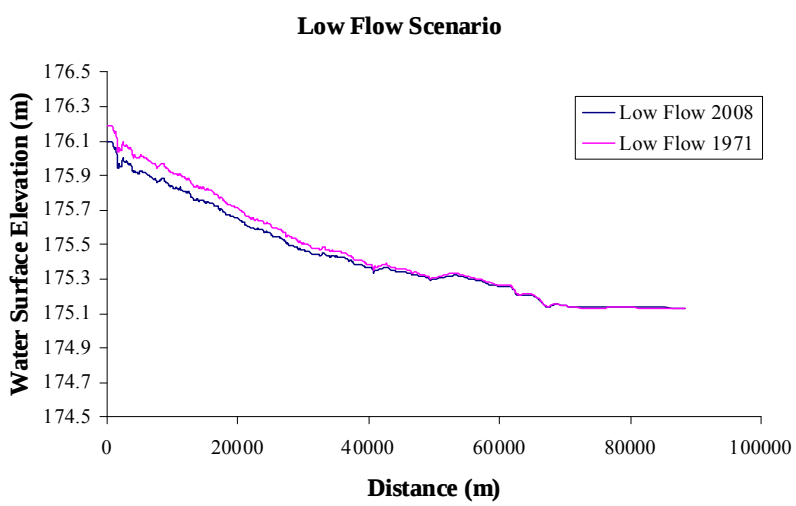
4.2 Bathymetry Change Effects

4.2.1 Two-dimensional Modeling and Analysis

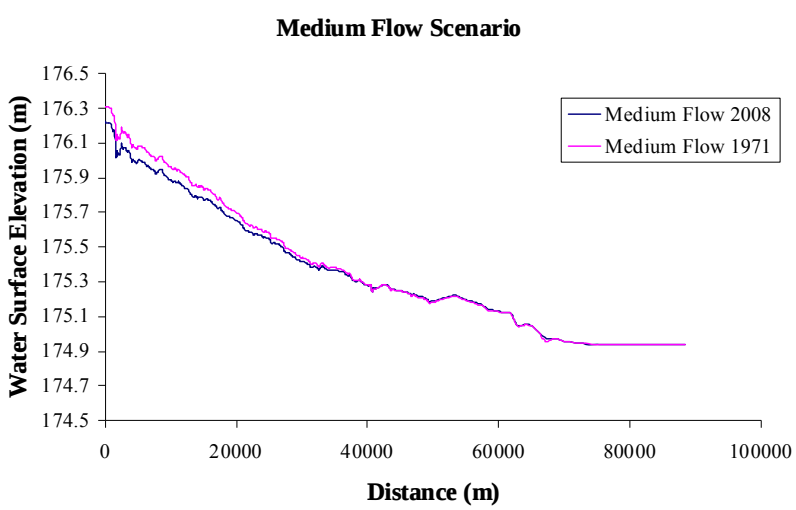
Survey data has shown the bathymetry of the St. Clair River has been modified extensively due to both man made changes and natural processes (such as post-glacial rebound). The bathymetries of 1971, 2000, and 2008 are used to investigate whether the dropping of Lake Huron level is related to the river bottom change. The available bathymetric data include 1971 and 2000 for the full St. Clair River, 2002, 2005, 2006, 2007, and 2008 data for the upper portion of the river, 2002 data for the Lake St. Clair. 2008 data is from the multibeam echo sound mapping by Prof. Jim Best of

University of Illinois at Urbana and Champaign. In this research, for year 1971 and 2000, the data of the whole river of 1971 and 2000, 2002 data for Lake St. Clair, and some data of Lake Huron of 2008 are used. For the year 2008 simulation, the 2008 data for the upper portion of the river, 2000 data for the rest of the river, 2002 data for Lake St. Clair and 2008 data for part of Lake Huron are used. Three sets of hydraulic conditions (low, medium, and high discharges) are simulated (see Table 3).

The water surface elevations of the three hydraulic conditions for both 1971 and 2008 are plotted in Figure 9. For all three hydraulic conditions, the bathymetry changes from 1971 to 2008 make the water surface in the whole river system drop. Table 7 lists the Lake Huron water level dropping due to the river bottom change form 1971 to 2008. The level drop is about 9 to 10 cm for all the cases. This number is also consistent with the results from other studies. The dredging and mining in the St. Clair River started from 19th century. If the bathymetry data is available for those years, the dropping of lake level would be even higher.



(a)



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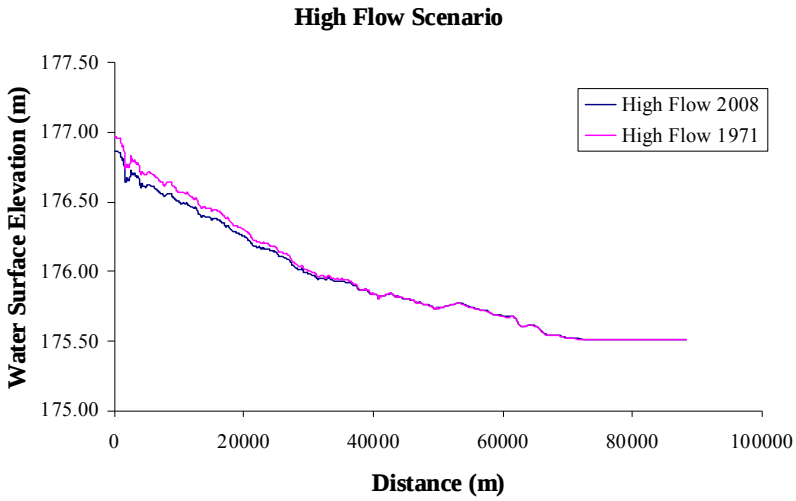


(c)

Figure 9. Comparison of the water surface elevation in the St. Clair River between 1971 and 2008 bathymetry data: (a) Low flow scenarios (b) Medium flow scenarios (c) High flow scenarios

Table 7. Comparison of the Lake Huron level drop between using 1971 and 2008 bathymetry data

Flow Scenarios	Flow Discharge (m^3/s)	Lake St. Clair Level (m)	Lake Huron Level Drop (m)
Low Flow	4645	175.13	0.094
Medium Flow	5282	174.94	0.089
High Flow	6006	175.51	0.098

4.2.2 One-dimensional Backwater Curve Analysis

The St. Clair River is long (~80km) and shallow (width/depth~40). It is believed that even without 2D and 3D numerical models, 1D back water calculation can give some estimation of the water surface change due to bathymetry changes. If one looks at the bathymetry changes from 1948 to 2000 in Figure 10, the major part of the river bottom is been lowered by about 30-50 cm. At the upstream and downstream ends, the river bottom has been dredged for about 3-4 meters due to the 27 feet navigation requirement. According to this, some scenarios of 1D back water curve calculations are done. There scenarios are dredging 4 meters in the downstream 10 km, midstream 10 km, upstream 10 km, and upstream+downstream dredging combined. The river is assumed to be 80 km long, has a slope of 2E-5, and water depth in the Lake St. Clair is fixed at 10 meters.

Figure 11 shows the 1D back water calculation results. For all the cases, no matter where the dredging is taking place, the water surface elevation in the river always goes down. This is true since for a river like this, the mean Froude number is about 0.1, which means the whole river is subcritical. Any change in the St. Clair River will affect the water surface both downstream and upstream. In order to see clearly the effect of dredging, Figure 12 plots the original water surface without dredging and the water surface after both upstream and downstream 4 meters dredging

which is the similar what happened in St. Clair River.

Quantitatively, Table 8 lists the Lake Huron level dropping from the 1D back water curve calculation. For all upstream, midstream, downstream dredging, the Lake Huron level drops about 15 cm. If upstream and downstream dredging combined, the Lake Huron level drops about 29 cm.

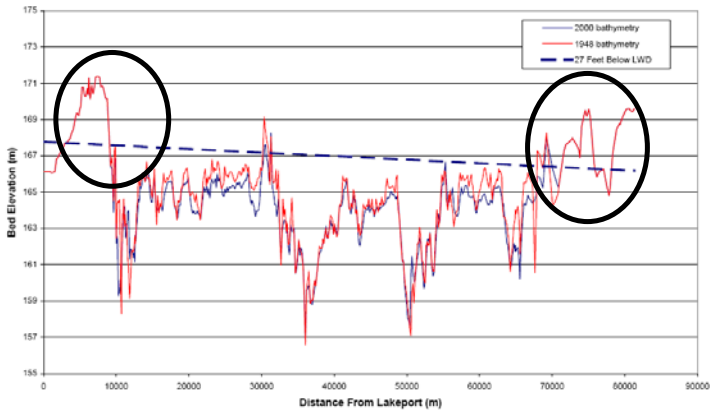
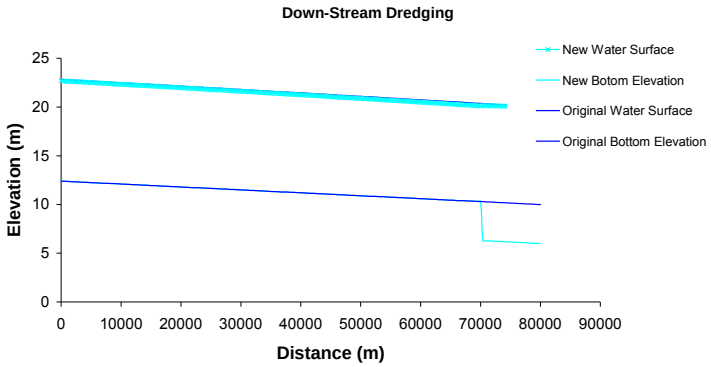
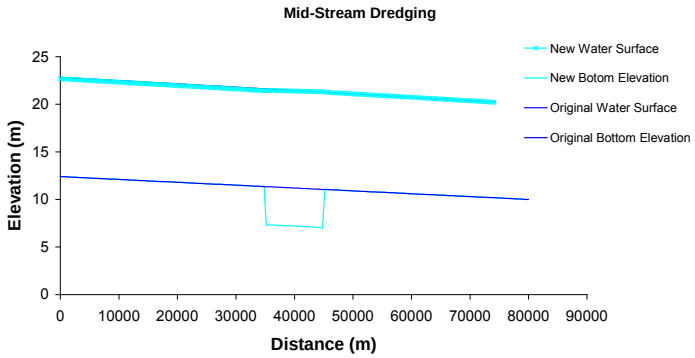


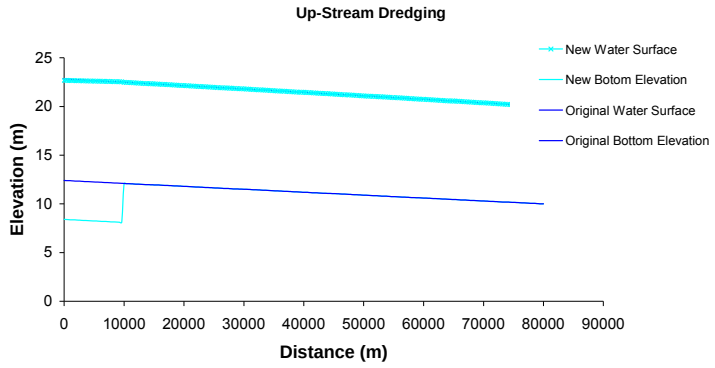
Figure 10. Dredging and bathymetry changes along the St. Clair River (adapted from Baird & Associates, 2005)



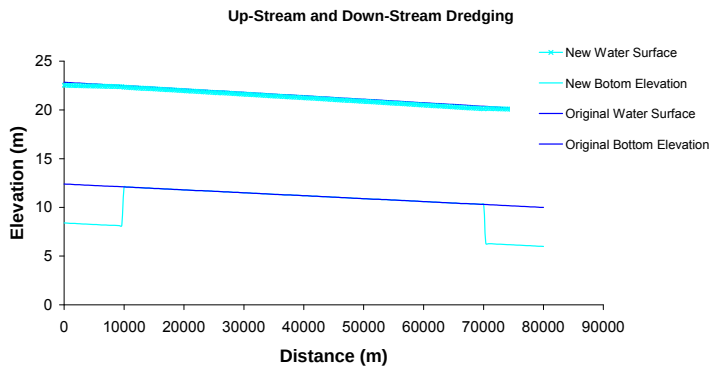
(a)



(b)



(c)



(d)

Figure 11. Dredging Effects on the Water Surface Elevations: (a) Downstream Dredging (b) Midstream Dredging (c) Upstream Dredging (d) Upstream/Downstream Dredging Combined

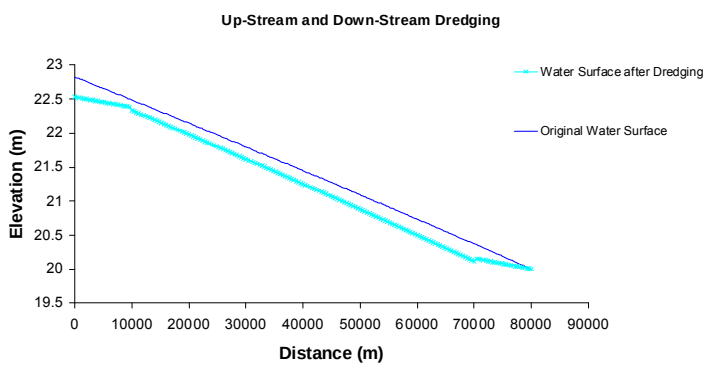


Figure 12. The original water surface and the water surface after both upstream and downstream dredging

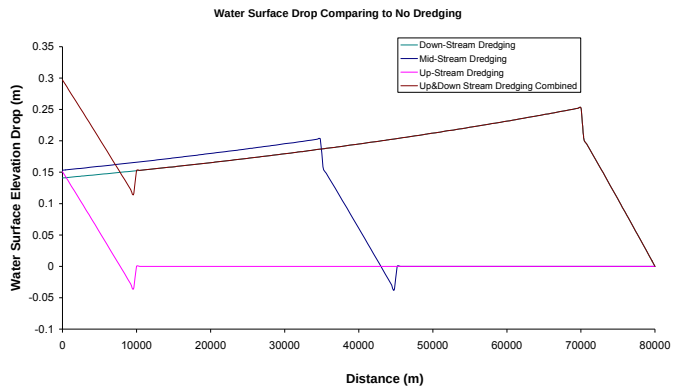


Figure 13. Water Surface Drop due to Bathymetry Changes

Table 8. Effects of Bathymetry Changes on the Lake Huron Level (1D Back Water Curve Calculations)

Bathymetry Changes	Lake Huron Elevation Decrease (m)
Downstream Dredging	0.141
Midstream Dredging	0.153
Upstream Dredging	0.151
Upstream + DownstreamDredging	0.297

4.2.3 Two-lake Problem and Conveyance Change Analysis

The St. Clair River is a canal connecting two lakes, namely Lake Michigan-Huron and Lake St. Clair. The bottom slope of the St. Clair River is negligible. The upper portion of the river even has a negative slope. Therefore the discharge in the river is mainly driven by the level difference between the lakes. This is a typical example of canal delivery of subcritical flows (see Chapter 11 of Chow 1959). Figure 14 shows the scheme of the two-lake problem. Although it is not possible to follow the same analysis in Chow (1959), HydroSed2D is used to generate the Hydraulic Performance Graph (HPG) with the bathymetry of 1971 and 2007.

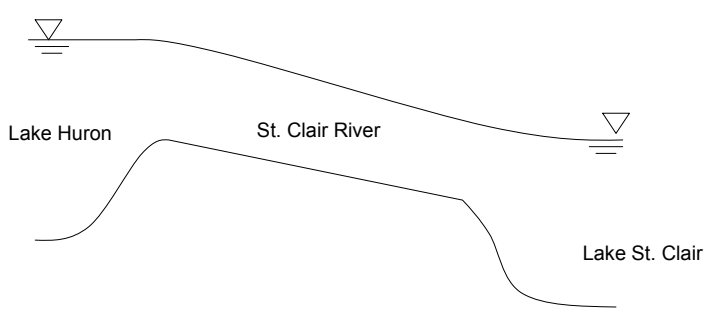


Figure 14. Scheme of the two-lake problem applied to the Lake Huron, St.Clair River, and Lake St. Clair system

Discharge Q constant curves are plotted in Figure 15 for the bathymetry of year 1971 and 2007. For a given combination of Lake Huron and Lake St. Clair levels, a discharge in the St. Clair

River can be obtained from the 2D model. 33 simulations were done for each bathymetry, which results in 66 simulations for year 1971 and 2007. From the comparison, the conveyance has increased from 1971 to 2007. For the same combination of lake levels, the discharge is higher for year 2007 than for year 1971. It is also found that the conveyance change is larger when the lakes have higher water levels.

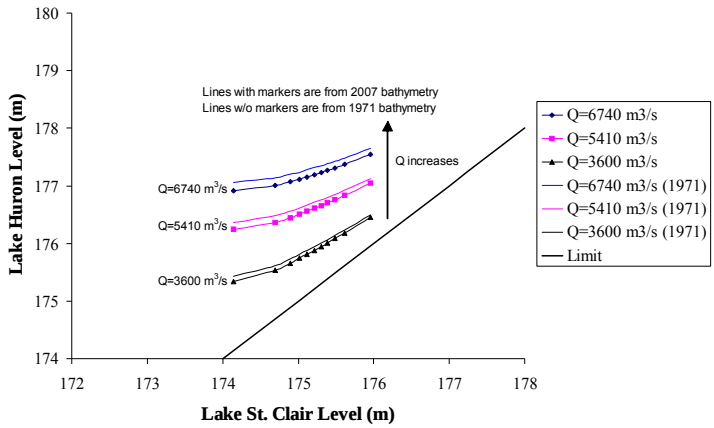


Figure 15. Q constant curves for year 1971 and 2007 as a function of Lake Michigan-Huron and Lake St. Clair Levels. Smooth lines are results for 2007 and lines with markers are for 1971.

The conveyance change in the St. Clair River is used to estimate its effect on the lake levels. The question needs to be answered is how long the Lake Michigan-Huron level will drop 0.8 m assuming there is an increase in the St. Clair River conveyance. Also assumed is that everything else is kept constant (e.g., precipitation, evaporation, etc.). The purpose is to see how relevant the conveyance change is and to what extend.

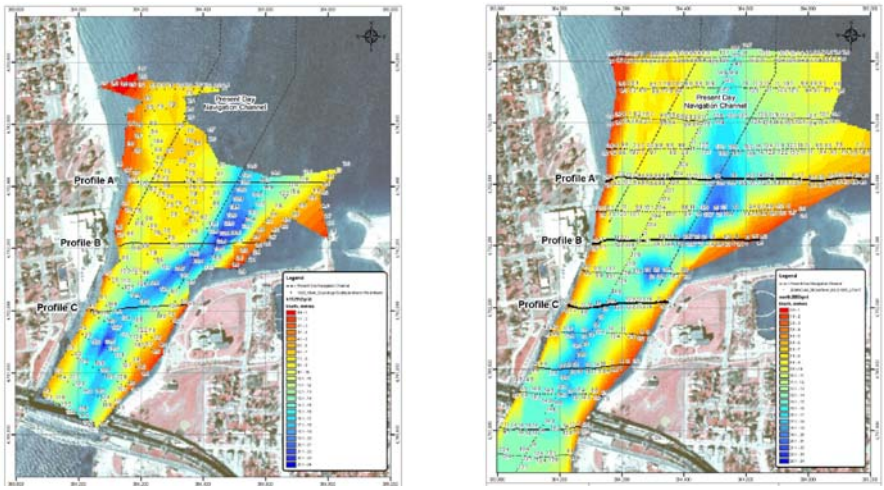
The calculation results are shown in Table 9. For 0.5%, 1%, and 5% changes of the St. Clair River conveyance, it takes 110, 55, and 11 years to lower the lake level by 0.8 m. In that sense, the water level in Lake Michigan-Huron is sensitive to the conveyance change in St. Clair River. A small percentage increase of conveyance will drop the lake level very quickly (in the order of 10-100 years). As a matter of fact, it only takes the mean discharge (5410 m^3/s) about 50 years to drain all the 8,458 km^3 volume of water in the Lake Michigan-Huron system without any inflow. To put things into perspective, it is beneficial to make the following analogy. Lake Michigan-Huron is like a big bath tub full of water. However, it also has a very big drain hole (the St. Clair River). Small percentage change of the drain hole could fluctuate the water level in the bath tub quickly to some substantial extend.

Table 9. Time needed for the Lake Michigan-Huron level to drop 0.8 m (assuming everything else is kept constant). Different conveyance changes are also assumed.

Area of Lake Michigan-Huron (km^2)	Water Level Drop (m)	Water Volume Loss (m^3)	St. Clair River Average Discharge (m^3/s)		0.5% Conveyance change (m^3/s)	1% Conveyance change (m^3/s)	5% Conveyance Change (m^3/s)
117,702	0.8	9.42E+10	5410		27	54	271
					Time needed (years)	Time needed (years)	Time needed (years)
					110	**55**	**11**

4.3 Lake Huron Inlet Alignment Effects

In Baird & Associate (2005), one possibility of Lake Huron level drop is identified as the inlet channel alignment. In Figure 16, the bathymetries of year 1929 and 2000 are plotted. The inlet channel is shifted from east Canada side to the west US side in the part several decades. If comparing to the 2008 bathymetry data, the deep inlet channel is shifted even more toward west.

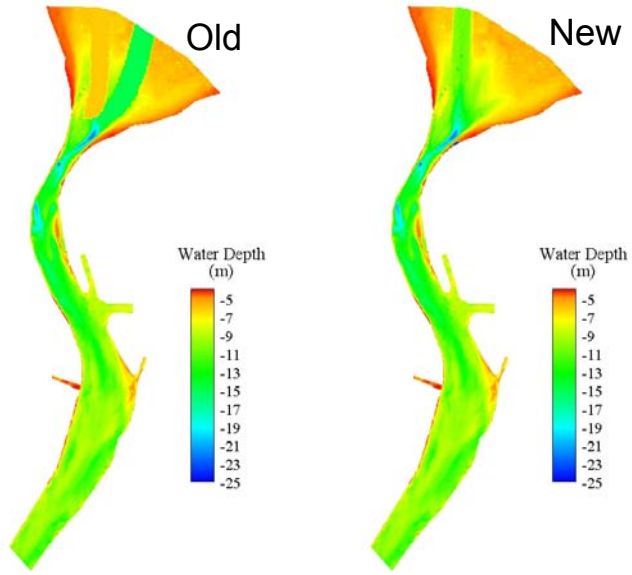


(a) (b)

Figure 16. Bathymetry at the Lake Huron inlet area (adapted from Baird & Associate, 2005): (a) 1929 (b) 2000

In order to see whether this inlet alignment change will affect the Lake Huron level, simulations were done using the old bathymetry where the deep inlet channel is placed toward the east side (see Figure 17). This bathymetry is obtained roughly according the figures in Baird report.

There is no major change of shear stresses distribution due to the inlet alignment change (see Figure 18). The major change is focused in the Lake Huron area. The velocity distribution changes a little bit due to the change of inlet alignment (see Figure 19). Velocity changes mainly happen in the Lake Huron area. For the rest of the river, the velocity is not affected. In terms of Lake Huron level, the new bathymetry even raised the Lake Huron elevation by 3mm (see Figure 20). This is reasonable since for the current bathymetry (year 2008, for example), there is a larger angle between the inlet channel and the St. Clair River. This angle increases the resistance force and the water has to spend some energy to adjust its direction before flows into the river.



(a) (b)

Figure 17. The bathymetries used for the inlet alignment study: (a) Old bathymetry where the inlet is toward the east side (b) New bathymetry where the inlet is toward the west side

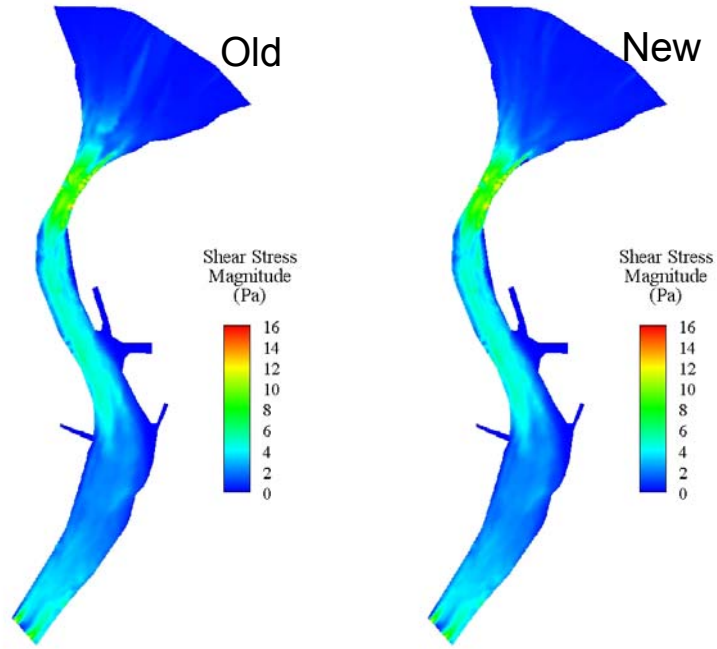


Figure 18. Effects of the inlet alignment on the bottom shear stresses: (a) old bathymetry where the inlet is toward the east side (b) new bathymetry where the inlet is toward the west side

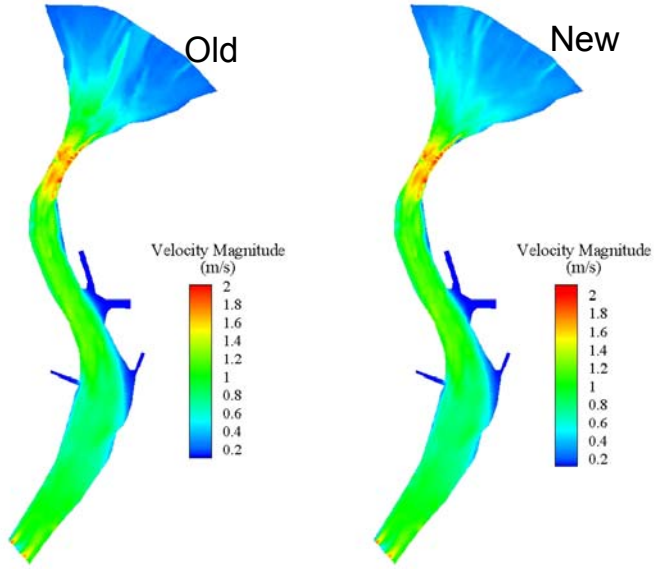


Figure 19. Effects of the inlet alignment on the velocity distribution: (a) old bathymetry where the inlet is toward the east side (b) new bathymetry where the inlet is toward the west side

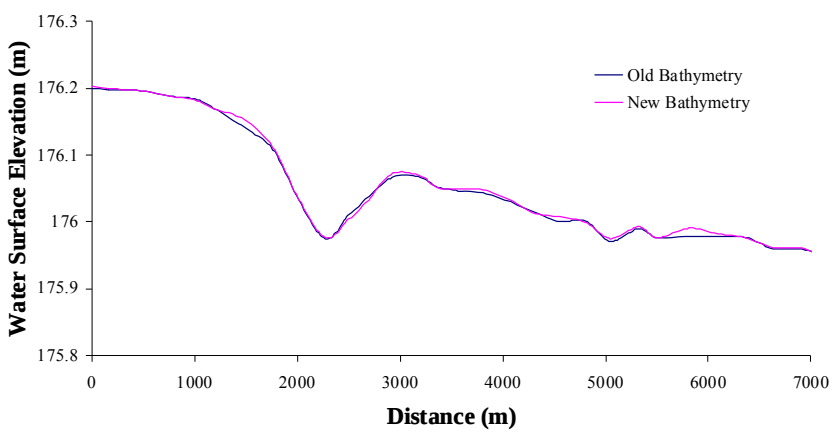


Figure 20. Effects of the inlet alignment on the water surface elevation in the St. Clair River (the new bathymetry even raised the Lake Huron Level by 3 mm)

5. Sediment Transport and Armoring Analysis

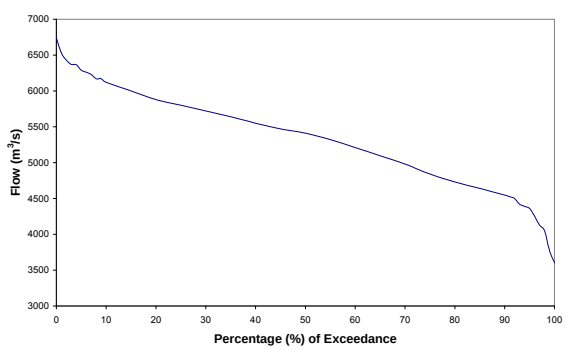
5.1 Gravel Transport

The formula used to do the computation is from Parker (1990), which is implemented in a Microsoft Excel file which can be downloaded from http://vtchl.uiuc.edu/people/parkerg/. This

surface-based bedload transport relation for gravel excludes sand. The finest size of the sediment must be greater than 2 mm. The details of the program can be found in the website and the companion notes. The original program Acronym1 has three different versions: Acronym1, Acronym1_R, and Acronym1_D.

Acronym1 is used to compute the volume bedload transport rate per unit width and the bedload grain size distribution from a specified surface grain size distribution (with sand removed), a bed shear stress, and a specific gravity of the sediment. Acronym1_R uses the Manning-Strickler relation for flow resistance. Given flow discharge, channel width, and channel slope, it first calculates the bed shear stress assuming normal flow condition. Then the same code in Acronym1 is used to calculate the transport rate. Acronym1_D combines the scheme of Acronym1_R with a flow duration curve. The bedload transport rate and bedload grain size distribution are computed for each flow of the curve, and then averaged to yield a mean bedload transport rate and a mean bedload grain size distribution.

In this study, since HydroSed2D is used to calculate the shear stresses on the river bed, normal flow assumption is not necessary. The general analysis process is as follows. After the calibration in the previous section, HydroSed2D is run to get the shear stress distributions under different flow conditions. These flows cover the whole flow duration curve for the river as shown in Figure 21. The flow duration curve is calculated through the monthly averaged flow data from 1963 to 2006. For each flow condition, the shear stresses on the bottom at the 9 river transects (see Figure 22) are extracted. The bed material size distributions at the corresponding cross sections are provided by Environment Canada through the video image analysis. Figure 23 shows the grain size distributions for the different transects analyzed. It is assumed that the given grain size distribution applicable across the entire cross-section. With these as inputs, the Acronym code is run for all the cross sections. Figure 24 shows the general process of combining the HydroSed2D and Acronym code.



Q (m^3/s)	% time exceeded
6740	0
6120	10
5878	20
5720	30
5550	40
5410	50
5210	60
4980	70
4730	80
4547	90
3600	100

Figure 21. Flow Duration Curve for the St. Clair River
(Monthly Average Discharge from 1963 to 2006)

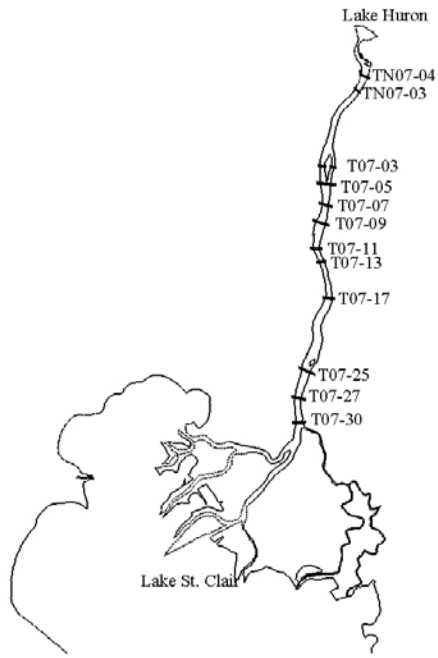


Figure 22. Transects along the St. Clair River

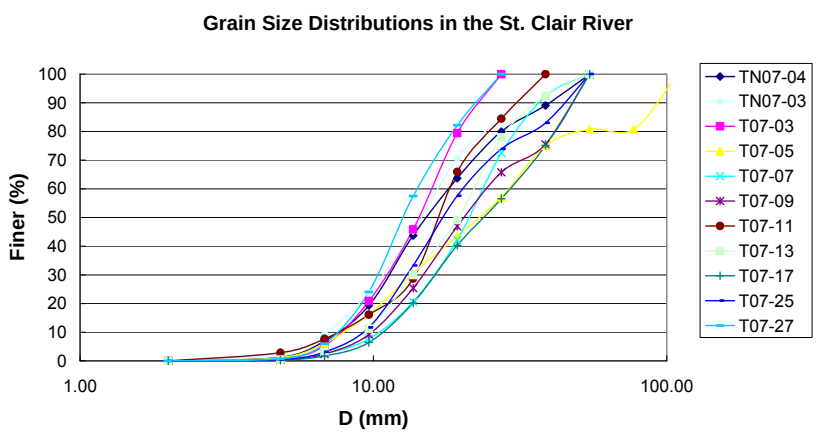


Figure 23. Grain Size Distributions in the St. Clair River for Different Transects

For each transect, it is divided into many small sections as in Figure 25. For section *i*, the shear stress is the average values at the end points which define this section. The transport rates are calculated at each of these sections and an average value is computed for the whole transect. Since the run of Acronym1 code will be repeated for many times, the original code is modified to run in batch mode. Specifically, 11 flows are used to cover the whole flow duration curve and 9 transects are analyzed. For each transect, it is divided into 50 small sections. Therefore, the Acronym code is called 11*9*50=4950 times.

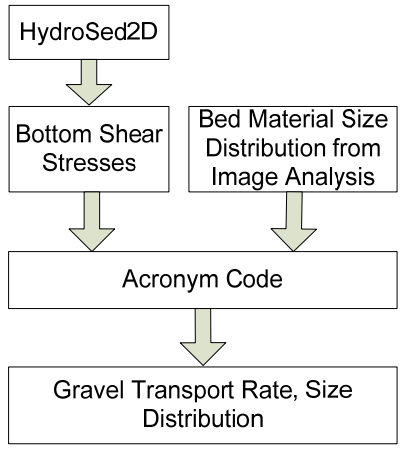


Figure 24. Analysis Process for the Gravel Transport Calculation

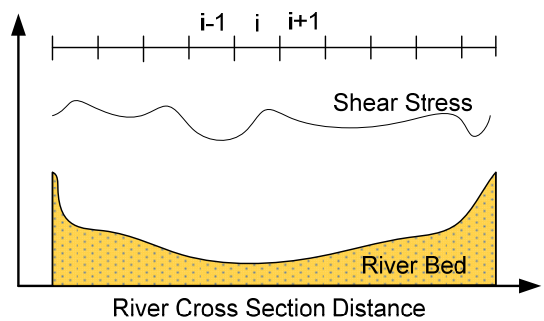


Figure 25. Division of the River Cross Section

TN07-04 is chosen as a typical transect whose calculation results are elaborated. Results for other transects are shown in the Appendix. Figure 26 shows the river bottom shear stress distribution across the transect TN07-04 for the discharge of 5410 m^3/s, which corresponds to 50% on the flow duration curve. The shear stresses range from 3 to 5 Pa, which is not high even this transect is located upstream of the river. Figure 27 shows the size distributions of the sediment in the surface and bedload. The surface geometric mean of the sediment size is 16 mm and the bedload geometric mean is about 9.9 mm. The ratio between them is about 1.62. The river renders itself able to transport the coarse half of its gravel load at the same rate as its finer half by overrepresenting coarse material on its surface, where it is available for transport. The mean annual volume bedload transport rate per unit width for transect TN07-04 is about 1.07×10^{-11} m2/s, which is negligible. This translates to an also negligible annul sediment yield of about 0.54 ton (the river width at this transect is about 600 meters).

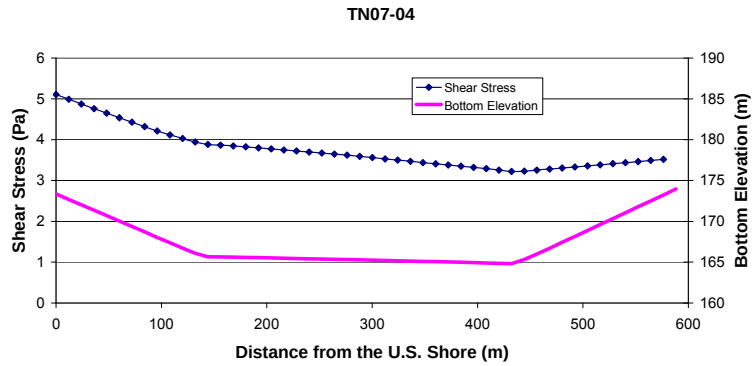


Figure 26. Shear Stress Distribution and River Bottom Elevation for Transect TN07-04 for Discharge of 5410 m^3/s (Corresponding to 50% on the Flow Duration Curve)

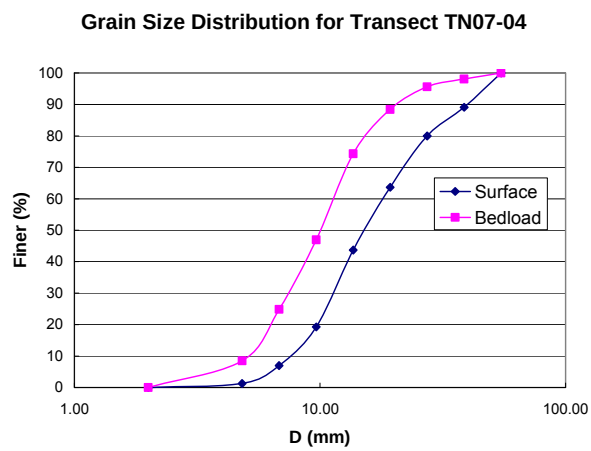


Figure 27. Mean Surface and Bedload Grain Size Distributions for the Transect TN07-04

Through the analysis of all transects, some general conclusions can be drawn for the St. Clair River.

- Although upstream of the river seems to move more sediment than downstream, it is found that the capacity of the river to move gravel-sized material at all transects is extremely limited. The mean annual bedload transport rate we obtained was (for all practical purposes) zero. The effective Shields number was about 0.004 to 0.015, i.e. less than the smallest reasonable guess for a critical Shields number. The results are listed in Table 10 and Table 11.
- The bed should be armored. If the lack of imbrication can be taken as evidence for the lack of armoring, one should look for causes other than significant bedload transport for this: ship propeller wash, ice, bioturbation, etc. Perhaps the first and the second are more likely which will be discussed later.
- One can also make some quick inferences through simple analysis. The bed elevation profile from Fort Gratiot to Port Lambton (42 km reach) shows lots of local variation, but no consistent trend from which we can extract a bed slope (see Figure 28). The linear fitting of the bed long profile shows a

negligible slope of $2x10^{-5}$. We might as well consider this bed slope to be zero, and the flow to be driven entirely by the water surface gradient. The water surface slope shows a significant decline in the downstream direction, with a value near $2.9x10^{-5}$ for the upper half and $1.5x10^{-5}$ on the lower half (see the previous sections). The implication is that the shear stresses upstream should be somewhat higher than downstream. This downstream decreasing of shear stress is evident in Figure 29, which shows the river center shear stresses. Despite a small reach in the upstream, the computed shear stresses are in the range of 2 - 6 Pa. Considering the mean size of gravel material (12 mm to 23 mm), the Shields numbers should not be higher than about 0.03. Again, this implies a very limited capacity to move gravel.

- The calculations so far do not support global mobility of the gravel. The variations in cross-sectional shape and alignment support the possibility of local "clear water scour". Below Dickenson Island, the shear stress drops even lower, i.e. ~ 2 Pa. The photo images show a sand bed here, but we don't know the sizes. Having said this, even if we assume a grain size of 0.5 mm, we obtain Shields numbers that are about 1/8 of typical sand/bed rivers at bankfull flow. So the capacity to move sand does not seem very high, either.
- The local "tongue-like" feature of bed forms at the first two upstream bends does not contradict the global immobility of the gravel. In general, the upstream of the river, especially in the Lake Huron inlet contraction area, the shear stresses are relatively high than the rest of the river. Annual sediment yield across transects in this region is about 0.5 to 1 ton. The "tongue-like" feature has a total of about 10 to 100 tons of sand/gravel. The calculated sediment yield is enough to generate, sustain, and even transform this feature over a period of 10 to 50 years. Local flow conditions due to secondary flow in the bend, ship maneuver, ice cover/ice jam, etc., shall also contribute to some extend.
- For the long-term morphodynamic simulation of bed evolution along the St. Clair River, it is not possible at current stage because of the lack of data for grain size distributions in enough details. The calculations to date, however, do not even warrant such a computation. In the long term, the river is likely stable in the overall sense. (Again, we are considering a scale larger than e.g. scour associated with ships sinking.)

Table 10. Geometric Mean of Sediment Size for Surface and Bedload

Transects	TN07-04	T07-03-Left	T07-05	T07-07	T07-09	T07-11	T07-17	T07-25	T07-27
Mean annual volume bedload transport rate per unit width qbTa (m^2/s)	1.072E-11	3.938E-13	1.065E-18	1.083E-15	7.970E-19	9.106E-15	2.591E-17	8.714E-19	1.410E-15
Mean annual Shields number based on surface geometric mean size tga*	0.015	0.012	0.005	0.009	0.005	0.010	0.006	0.004	0.008
Mean annual shear velocity u*a	0.06188	0.050	0.044	0.053	0.041	0.050	0.045	0.036	0.041

Table 11. Gravel Transport Analysis Results

Transects	TN07-04	T07-03-Left	T07-05	T07-07	T07-09	T07-11	T07-17	T07-25	T07-27
Mean annual volume bedload transport rate per unit width qbTa (m^2/s)	1.072E-11	3.938E-13	1.065E-18	1.083E-15	7.970E-19	9.106E-15	2.591E-17	8.714E-19	1.410E-15
River Width (m)	600	500	1080	600	990	625	700	900	640
Annual Sediment Yield (ton)	5.38E-01	1.65E-02	9.62E-08	5.44E-05	6.60E-08	4.76E-04	1.52E-06	6.56E-08	7.55E-05
Mean annual Shields number based on surface geometric mean size tga*	0.015	0.012	0.005	0.009	0.005	0.010	0.006	0.004	0.008
Mean annual shear velocity u*a	0.06188	0.050	0.044	0.053	0.041	0.050	0.045	0.036	0.041

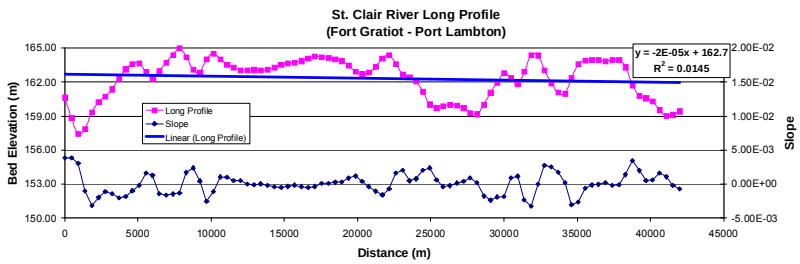


Figure 28. St. Clair River Long Profile and Bottom Slope from Fort Gratiot to Port Lambton

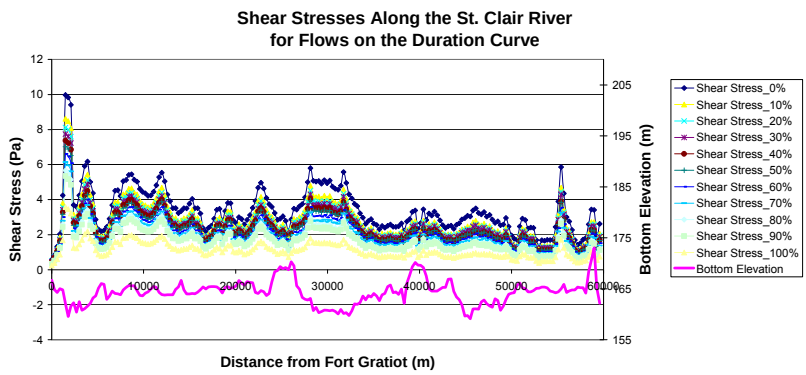


Figure 29. Shear Stresses along the St. Clair River for Flows on the Duration Curve

5.2 Sand Transport

Sand patches have been observed along the St. Clair River. In the upstream, both sides of the river have sand covers due to the sand feed from the shore of the Lake Huron. In the downstream, sand cover expands to larger portion of the cross section. In the delta region into the Lake St. Clair, sand might cover the whole area. In this section, sand transport rate is estimated and its impact on the conveyance is analyzed. To be specific, the theoretical sand transport rate q_s is calculated assuming the whole cross section is covered by sand. Then the sand coverage P_0 for each cross section is estimated by inspecting the under water video images. Finally, the actual sand load q_{sl} is back calculated using the formula

$$P_0 = \frac{q_{sl}}{q_s}.$$

Sand size analysis has been done using the grab samples taken in various locations along the river. Table 12 shows the sand size results for three cross sections which represent the upstream, middle, and downstream of the river bed. For each cross section, samples were taken at left bank, middle, and right bank, which are distinguished by "A", "B", and "C" in the location names. Some cross sectional variations of sand sizes have been observed. For the upstream section, sand patches are located along the side of the river which is evident from the under water videos. The sand has a D_{50} ranging from 340 to 570 microns. In the middle reach of the river, the sand has a D_{50} of about 200 to 300 microns. Very fine sand with D_{50} of 50 to 80 microns has been retrieved from the downstream section. This is consistent with the general downstream fining trend of typical river systems. Despite the variations in the sand size both along the river and across the transect, two typical sand sizes (0.5 mm and 1 mm) are used to calculate the sand transport rates.

Table 12. Sand size results from the grab samples taken for three typical (upstream, middle, and downstream) cross sections

Location	TN07-03A	TN07-03B	TN07-03C	T07-10A	T07-10B	T07-10C	T07-25A	T07-25B	T07-25C
D_{50} (μm)	569	2409	343	375	204	7768	50	1548	83

The method to determine the sand cover percentage for each transect is through the inspection of the under-water videos. These videos were played and the types of sediment cover and vegetations were recorded. Each category is assigned a percentage number which describes the sand coverage. Since the UTM coordinates are recorded on the video image, the length of each sediment cover category can be calculated and therefore a cross-section averaged sand coverage. As an example, Figure 1Figure 30 shows the four different bed material coverage for transect TN07-03. In Table 13, the process of calculation of sand coverage for the entire transect TN07-03 is illustrated. The calculations for other transects are similar.

Three typical transects are selected for the sand transport rate calculation, namely TN07-03, T07-09, and T07-27, which represent upstream, middle, and downstream portion of the river respectively. The sand coverage values for these three transects are about **0.12**, **0.32**, and **0.5** respectively.

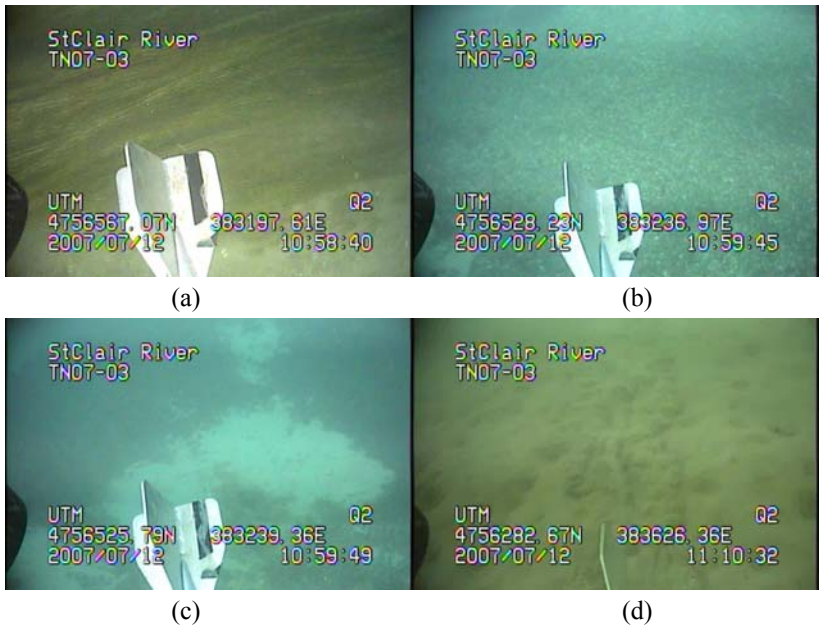
The calculation process for the sand transport rate Q_s is similar to the one used for the gravel transport. The shear stress distributions for each transect covering the flow duration curve are from the *HydroSed2D* model. The Engelund-Hansen (1976) sand transport formula is used, which has the form

$$q^* = \frac{0.05}{C_f}\left(\tau^*\right)^{\frac{5}{2}},$$

where $q^* = q_s/(\sqrt{RgD}D)$ is the dimensionless sediment transport rate, R is the submerged

specific gravity of the sediment, g is the gravitational acceleration, D is the mean diameter of the sand, C_f is the friction factor, $\tau^* = \tau/(\rho g R D)$ is the Shield's number.

Table 14 shows the calculation results of sand transport rate Qs (assuming full sand coverage) and estimated sand load Q_{sl} (back calculated = P_0*Q_s).



(a) (b)

(c) (d)

Figure 30. Images of different sand coverage for the transect TN07-03: (a) Vegetation dominant (b) Small gravel dominant (c) Thin layer of gravel on top of bed rock (d) Sand dominant

Table 13. Example calculation of sand coverage for transect TN07-03

Image Number	UTM Coordinates North	East	Distance	Sand cover percentage	Distance*Sand _Cover	Description
0	4756580	383189	0	0		start
1	4756578	383189	1.94	0	0.00	vegetation
2	4756566	383197	16.12	0	0.00	vegetation
3	4756524	383240	75.74	0.2	11.92	small gravel with algae, some wood debri, some bed rock exposure
4	4756292	383622	520.03	0.1	44.43	small gravel with a lot of shells (shells are not moving), some bed rock exposure, the layer of gravel is very thin
5	4756282	383623	526.46	0.9	5.79	sandy and muddy bed, the bed is easlily disturbed
				Average sand coverage P_0	0.12	

Table 14. Sand transport rate Q_s (assuming full sand coverage) and sand load Q_{sl} (back calculated=P_0*Q_s) for each transect

D_{50} (mm)	TN07-03			T07-09			T07-27		
	P_0	Q_s (Mt/yr)	Q_{sl} (Mt/yr)	P_0	Q_s (Mt/yr)	Q_{sl} (Mt/yr)	P_0	Q_s (Mt/yr)	Q_{sl} (Mt/yr)
0.5	0.12	5.80	0.70	0.32	2.30	0.74	0.50	2.50	1.25
1	0.12	1.45	0.17	0.32	0.58	0.19	0.50	0.58	0.29

From Table 14, even though the sand load Q_{sl} in the upstream and middle of the St. Clair River is less than that of the downstream, one can not conclude that the downstream portion of the river is under degradation. The reason simply lies in the fact that the estimation in Table 14 includes a large error margin. The sand coverage derived from the underwater video is rough and the change of this value could alter the conclusion completely. As a demonstration, the average sand load Q_{sl} along the river is about (0.70+0.74+1.25)/3 = 0.89 Mt/yr for D_{50} = 0.5 mm. If assuming the whole river is in equilibrium sand transport state, i.e., the amount of sand coming into the river equals that going out. It is also assumed that this equilibrium sand load is 0.89 Mt/yr which is the average calculated sand load. The required sand coverage and the original ones are shown in Table 15. It is clear that the change of sand coverage is not so high. With the large error margin of the sand coverage values derived from the videos, it can be concluded that the river sand transport might be in the equilibrium state and it will not affect the overall hydraulics of the river. Moreover, nowhere along the river is fully covered by sand, which means the river is under capacity in transporting sand. This further confirmed that the sand has minor effect on the hydraulics of the river.

Table 15. Demonstration of the sensitivity of the sand coverage P_0. The result (for D_{50} = 0.5 mm) shows a small change of sand coverage P0 could alter the conclusion.

Sand Coverage	TN07-03			T07-09			T07-27		
	P_0	Q_s (Mt/yr)	Q_{sl} (Mt/yr)	P_0	Q_s (Mt/yr)	Q_{sl} (Mt/yr)	P_0	Q_s (Mt/yr)	Q_{sl} (Mt/yr)
Original	**0.12**	5.80	0.70	**0.32**	2.30	0.74	**0.50**	2.50	1.25
Changed	**0.154**	5.80	0.89	**0.39**	2.30	0.89	**0.36**	2.50	0.89

5.3 Glacial Till Erosion Test and Analysis

(To be finished by Jose Mier)

6. Ice Cover and Ice Jam Effects

Ice cover and ice jam affect the sediment transport in a river on different time and spatial scales (chap 13 of García, 2006). Generally, for long time and large spatial scales, the ice cover/ice jam will increase and redistribute river channel's resistance and reduce the sediment transport rate. However, on the local scale, an ice cover can redistribute the flow laterally which may cause both sediment scour and deposition. During the surge of water and ice following an ice jam breakup, the water discharge and sediment transport rate can jump to a relatively high value. Although a lot of researches have been done, these postulations about the ice effect are still not fully verified. In this section, the effects of ice cover and ice jam are briefly reviewed. The interpretations for the St. Clair River are also provided.

6.1 Flow Redistribution Effect under an Ice Cover

The shallow portion of a cross section usually has low flow velocity and it provides a place for the ice frazil to accumulate (Figure 31**Figure 31 Flow redistribution in a river cross section**

(adapted from Ettema and Daly, 2004)). This will block the flow in the shallow area and focus it to the deep portion. Higher velocity there might cause sediment scour and further deep the channel. This may contribute to the deep the whole in the first bend when there is an ice cover on top of it.

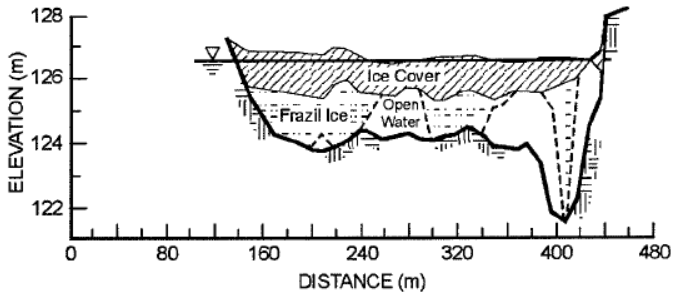


Figure 31 Flow redistribution in a river cross section (adapted from Ettema and Daly, 2004)

Ice cover may also contribute the bed forms. According to Hains and Zabilansky (2004), bed forms tend to be observed under rough ice cover. This might be a factor which needs to be considered to explain the bed forms shown in the multi-beam bathymetry data.

6.2 Could the record St. Clair River ice jam of 1984 cause significant erosion?

It is useful to list some facts about the 1984 ice jam. In April, 1984, the record 24-days ice jam in St. Clair River causes major impact on the water levels and flows. The level of Lake St. Clair dropped about 0.6 m. At the peak of the ice jam, the flow in the St. Clair River was reduced by about 65%. Computer models predicted that the effects on the lake levels should take about one to three years to recover to the pre-jam conditions (Derecki and Quinn, 1986).

At the initial stage of the ice jam, the drifting ice flow downstream to the lower river (delta area) and started to jam. After that, the ice jam progressed upstream rapidly. No record shows whether the ice jam developed upstream to the Lake Huron inlet area. In this report, we assume that the ice jam of 1984 did not.

During the ice jam, large amount of ice floated downstream to the point where the ice movement stopped. Depending on the location, the characteristics of flow and sediment transport are different. The readers are advised to refer to Figure 32 for the definitions of upstream and downstream of the ice jam.

- Upstream of the ice jam, the flow discharge was significantly reduced and the stages were elevated. Globally, sediment upstream of the jam point can not be moved during this period. Sediment particle could move locally due to

mechanisms such as ice grounding, although these effects are deemed as minimal.

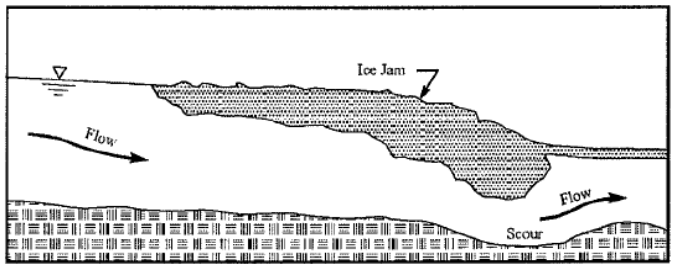


Figure 32. A Schematic view of an ice jam (adapted from Ettema and Daly, 2004)

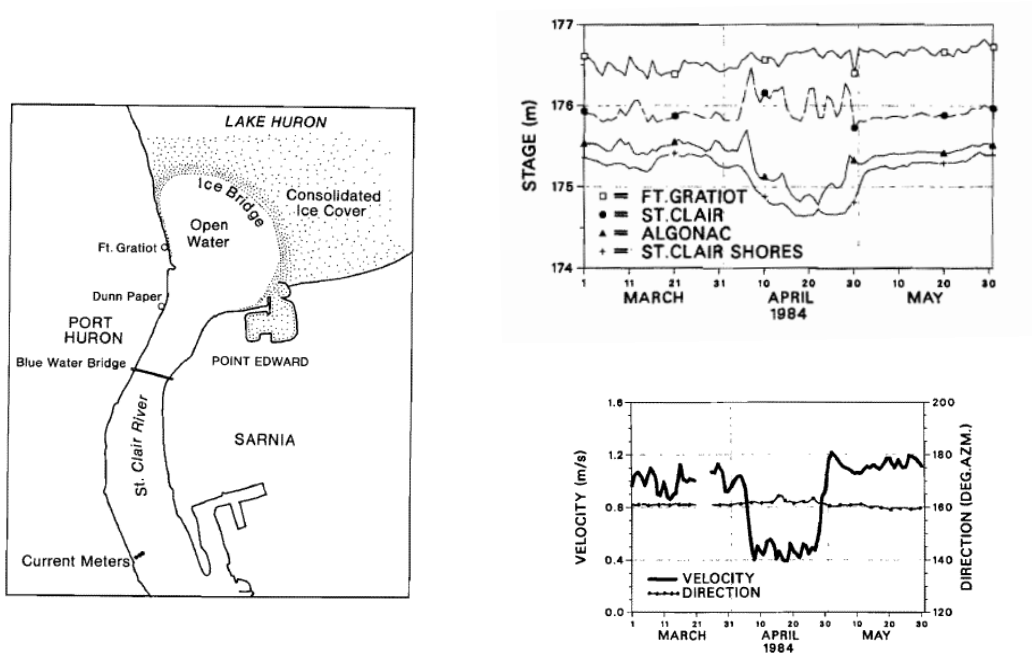


Figure 33. St. Clair River ice jam of 1984: (a) Locations of the ice-bridge and current meters (b) Stages in the river during the ice jam (c) Flow velocity and direction during the ice jam (adapted from Derecki and Quinn, 1986)

- At the ice jam, local scour and deposition could be trigged since at the toe, the ice is thickest and the flow is most restricted. The induced high flow at the toe will cause local scour and deposition the sediment downstream. Recurrent of ice jam in the river may cause substantial scour in the river.
- Downstream of the ice jam, the river is covered with ice over some distance. For this reach of the river, depending on whether the ice cover is fixed or freely floating, the flow and shear stress on the bed is different from open channel flow.
  - If the ice cover is fixed in space, i.e., it can not move up and down, the

river is pressurized (Figure 34). Two controlling parameters here are the pressure head and the roughness of the ice cover (Hains and Zabilansky, 2004). The pressure head is determined by the blocking effect of the ice jam. Higher pressure head means higher flow velocity under the ice cover and higher bed shear stress. For the roughness, experiments have shown that the increase of the ice cover roughness will push the maximum velocity location toward the bed and therefore increase the bed shear stress.

- If the cover is freely floating, than the ice cover roughness is important.

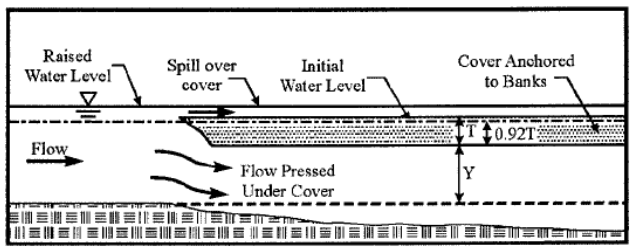


Figure 34. Pressurized flow under an ice cover (adapted from Ettema and Daly, 2004)

After the ice jam breakup, a surge was observed due to the sudden release of water built upstream. The current meter measurement just downstream the first bend shows a surge of flow velocity from about 0.4 m/s to 1.2 m/s as shown in Figure 33. Velocity higher than 1.2 m/s might have occurred somewhere else which was not captured by the current meter. Without the ice jam, the velocity at the measurement location is about 0.8 – 1.0 m/s (from the HydroSed2D simulation and ADCP measurement). We can assume that the sediment transport rate is $q_s \sim \tau_b^{3/2} \sim u^3$, where τ_b is the bed shear stress, u is the velocity magnitude. The surge will cause the sediment transport rate increase 73%-237%.

Since there are very limited measurements during an ice jam event or when the river is covered with ice, the best conclusion we can make is through some rough estimations. We can not conclude with definite answers to the effects of ice on the sediment transport in the St. Clair River. However, the episodic events such as the 1984 ice jam must have played a role which can not be neglected.

6. Navigation Effects

Wuebben et al (1984) has investigated the effects of ship propeller wash, ship waves, and ship drawdown/surges. Some conclusions from Wuebben et al. (1984) are as follows:

- For ship propeller wash, it only gave general guidance by asserting that for most part of the St. Clair River, the ship propeller will suspended the sediment and

cause scour. No detailed calculation was done.

- For ship drawdown/surges, it claimed that downbound ship, not matter what ship class, will not cause erosion. On the other hand, upbound ship (the worst case is a class 10 vessel traveling upbound), will cause substantial scour for a large portion of the river. Particularly, it specified the portion between St. Clair flats and Stag Island as the most possible erosion area due to ship drawdown/surges.
- For ship waves, it concluded that the worst case for a loaded class 10 vessel traveling upbound with low water level. Base on the 0.5 ft wave height as the critical value for sediment movement, the authors concluded that only the area near the downstream delta slightly exceed this criteria.

In this report, the ship propeller wash is suspected to have contributed to the big hole in the first bend where ships need to maneuver and accelerate/decelerate. Huge surge has been observed by people walking along the river bank near the first bend when a vessel is passing by. This surge of water hit the sheet piles on the bank and spilled over to the road. At that time, wind was not strong. As a rough estimation, Wuebben et al. (1984) calculated the near bed maximum velocity due to the propeller. The efflux velocity may be calculated as

$$V_0 = nD\sqrt{\frac{2K_T D^2}{F}}$$

where n is the propeller revolutions per minute, D is the propeller diameter, K_T is the thrust coefficient (0.25-0.50), F is the area of propeller perpendicular to its horizontal axis. For a 17.5 ft diameter propeller rotating at 90 rpm, V_0 is about 7.32 m/s (24 ft/s). When the water leaves the propeller, it accelerates and then decelerates. The maximum horizontal velocity happens at $V_{x,max}$, where

$$\frac{V_{x,\max}}{V_0} = A\left(\frac{X}{D}\right)^a .$$

Here X is the horizontal distance from the propeller, a has a value of -0.6 which accounts for the channel bottom effect on the jet, A is a coefficient which depends on the degree of jet limitation. Also assuming that the jet expands at an angle of 13 degree with the horizontal axis, the maximum flow velocity due to the propeller is estimated to be about 5.5 m/s (18 ft/s) for this type of vessel. Although it is hard to calculate the wall shear stress based on this velocity, a comparison is useful. When there is no ship movement, the river has a maximum velocity of about 2 m/s in area of Lake Huron inlet. This velocity corresponds to a maximum shear stress of about 7-8 Pa. Assume a linear relationship between the wall shear and flow velocity (which might not be so accurate), the ship induced wall shear stress will be about 20 Pa. This propeller induced wall shear, together with the ambient bottom shear by the river, is capable of moving sediment size of *64* mm, which is the upper limit of d_{50} of the gravel found in the river.

Another aspect of the navigation effect worth consideration is the so-called downstream-biased sediment transport due to ship propeller (Figure 35). This is due to two reasons. First is that when a vessel is traveling upstream, the thrust needed is more than that of traveling downstream. Higher

bed shear stress will be produced to move the sediment downstream when a vessel heading upstream. The second reason is that on average, when the sediments are entrained and resuspended by the propeller, the river will carry them downstream. These effects might not be so significant by the pass of a single vessel. However, in long term, the cumulative effect shall not be overlooked.

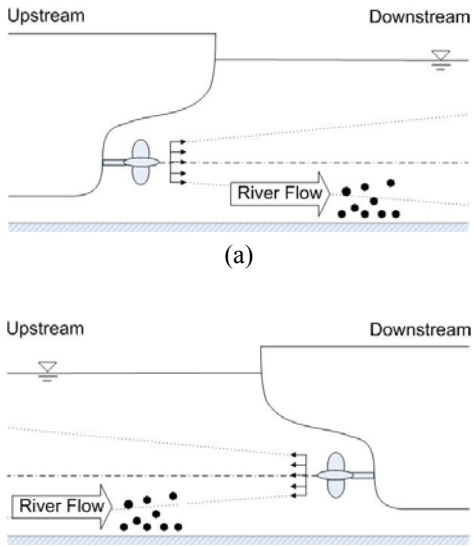


Figure 35. Downstream-biased sediment transport due to ship propeller wash in a river: (a) vessel moving upstream (b) vessel moving downstream

8. Conclusions

HydroSed2D model is carefully calibrated by changing the resistance coefficients in the river. It is also verified by 3D numerical model. Then the HydroSed2D model is used as a tool to study the different aspects of the St. Clair River problem.

Firstly, the calibrated model was used to investigate the factors affecting Lake Huron level. The most important factor is the bathymetry change. From the model results, the river bottom change from 1971 to 2008 contributes about 9-10 cm of Lake Huron level dropping. Simple 1D back water curve calculations also confirm the conclusion regarding the dredging effects for the subcritical St. Clair River. The Lake Huron inlet alignment is found to be not important. The inlet alignment today in the Lake Huron even slightly raises the Lake Huron level.

Secondly, a preliminary shear stress analysis was done to see their implications of sediment transport. The average shear stress in the St. Clair river is about 3-4Pa. It can not move the mean size sediment. Maximum shear stress (~10Pa) is located at the Lake Huron inlet area where scour is possible and the tongue features might be due to that.

Thirdly, a detailed sediment transport and armoring analysis was done by combining HydroSed2D

and the Microsoft Excel tool Acronym. The main conclusion from this analysis confirms the preliminary shear stress analysis and shows that the capacity of the river to move gravel-sized material at all transects is extremely limited. The river should be armored if solely based on the calculation. The lack of imbrication as an evidence of armoring might be explained by causes, such as ship propeller, ice, bioturbation, etc. The local "tongue-like" feature of bed forms at the first two upstream bends does not contradict the global immobility of the gravel. The calculated sediment yield is enough to generate, sustain, and even transform this feature over a period of 10 to 50 years. Long-term morphodynamic simulation of bed evolution along the St. Clair River is not necessary simply because the overall stable status of the river bed.

Lastly, the effects of ice and navigation were reviewed. Ice cover could local redistribute the flow along a cross section and trigger the initiation of bed forms. The record St. Clair River ice jam of 1984 should have caused some scour and deposition locally around the jam. During the ice jam breakup, the sudden release of water caused a surge of flow velocity from about 0.4 m/s to 1.2 m/s. The surge caused the sediment transport rate increase 73% to 237%. Propeller wash induced maximum flow velocity is estimated to be 5.5 m/s which could cause a shear stress of about 20 Pa. This shear stress is capable of moving sediment size of 64 mm, which is the upper limit of d_{50} of the gravel found in the river. A so-called downstream-biased sediment transport due to navigation is hypothesized. Due to the thrust difference between upstream and downstream moving vessels and the preferential downstream movement of the river flow, sediment movement due to navigation is downstream-biased. The cumulative effect of this downstream-biased sediment movement over a long time period might be significant.

Appendix A

In this appendix, the armoring analysis results for all transects are listed.

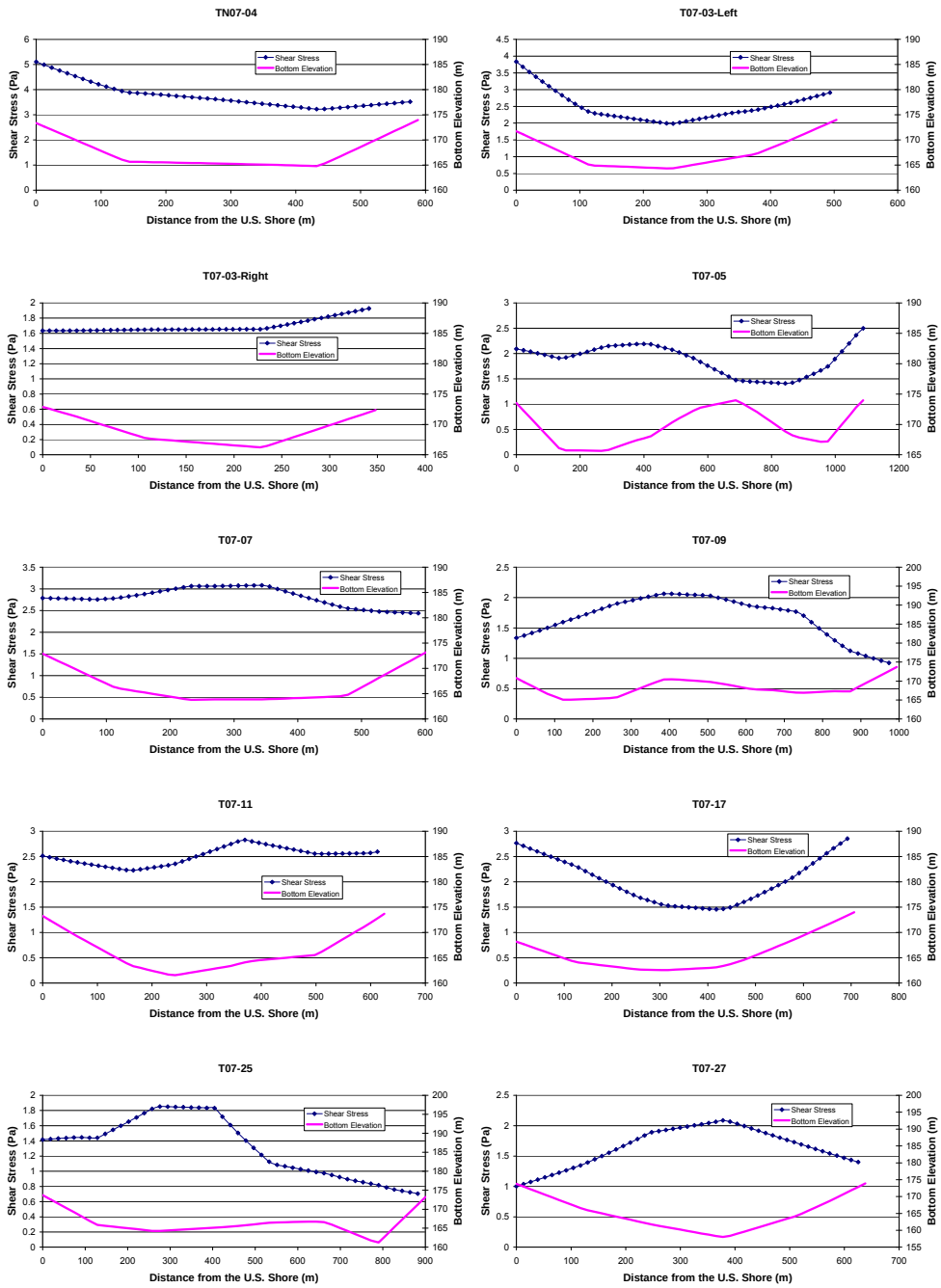
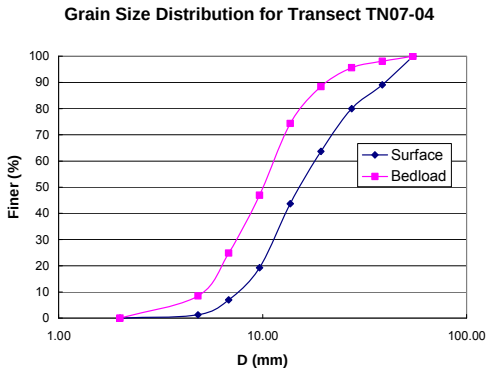
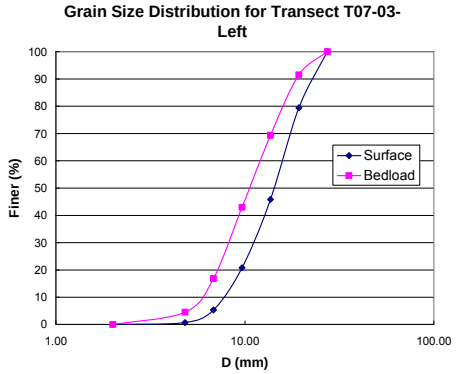
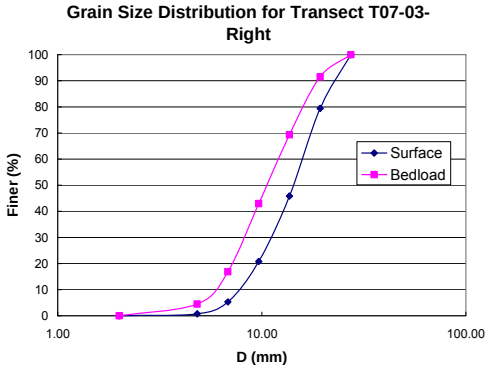
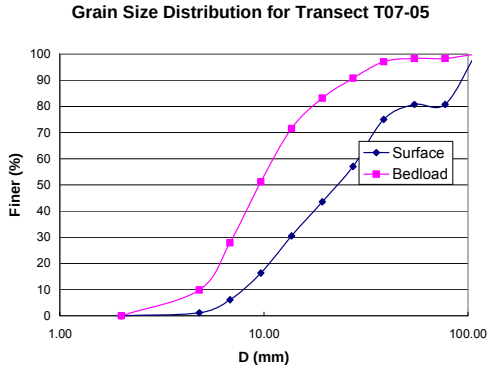


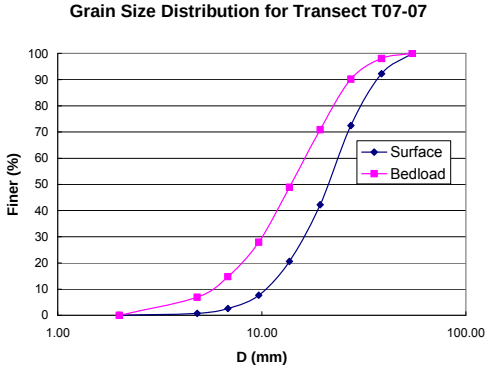
Figure 36. Shear Stress Distributions along the Transects Analyzed for the St. Clair River for Discharge of 5410 m^3/s (Corresponding to 50% on the Flow Duration Curve)

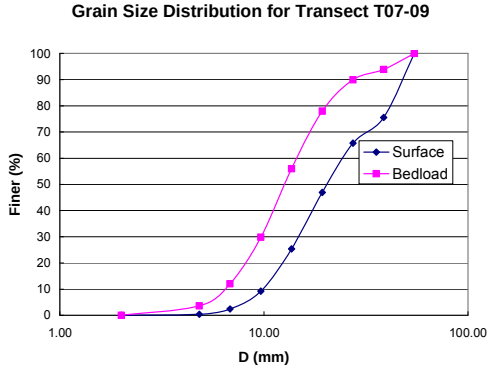

Grain Size Distribution for Transect TN07-04
Finer (%)
D (mm)
Surface
Bedload

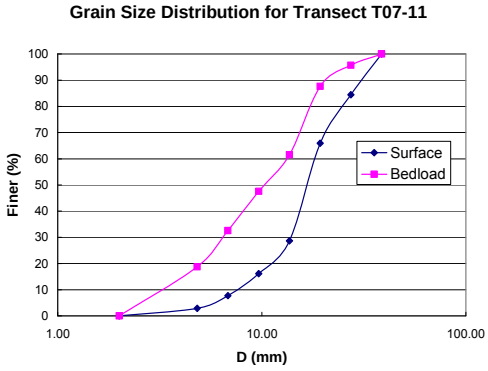

Grain Size Distribution for Transect T07-03-Left
Finer (%)
D (mm)
Surface
Bedload

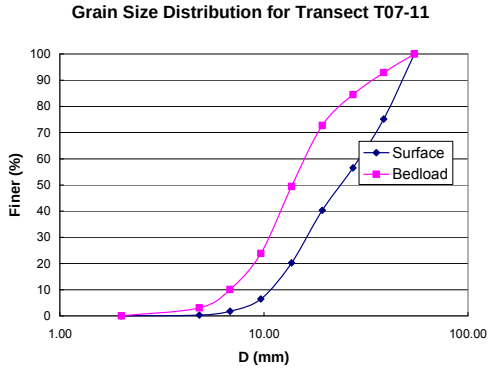

Grain Size Distribution for Transect T07-03-Right
Finer (%)
D (mm)
Surface
Bedload


Grain Size Distribution for Transect T07-05
Finer (%)
D (mm)
Surface
Bedload


Grain Size Distribution for Transect T07-07
Finer (%)
D (mm)
Surface
Bedload


Grain Size Distribution for Transect T07-09
Finer (%)
D (mm)
Surface
Bedload


Grain Size Distribution for Transect T07-11
Finer (%)
D (mm)
Surface
Bedload


Grain Size Distribution for Transect T07-11
Finer (%)
D (mm)
Surface
Bedload

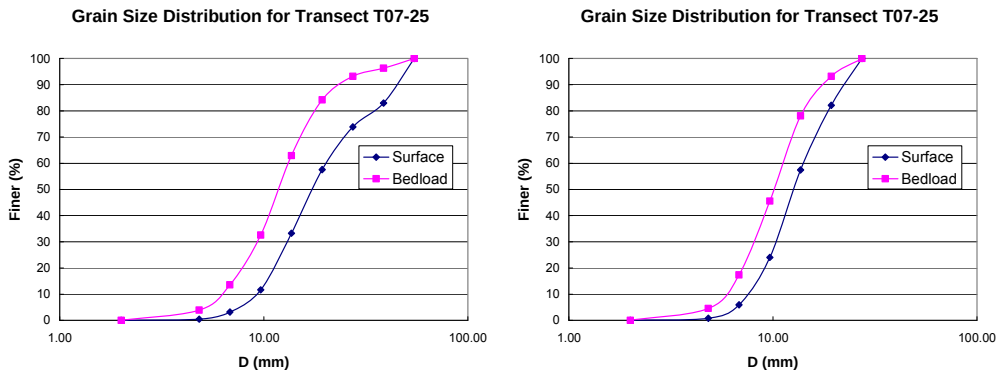


Figure 37. Surface and Bedload Sediment Size Distributions for the Transects along the St. Clair River

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Information Transfer Program Introduction

None.

IWRC Web Site

Basic Information

Title:	IWRC Web Site
Project Number:	2005IL156B
Start Date:	1/1/2005
End Date:	1/1/2011
Funding Source:	104B
Congressional District:	15th
Research Category:	Not Applicable
Focus Category:	Education, None, None
Descriptors:	web site, outreach, education
Principal Investigators:	Lisa Merrifield, Lisa Merrifield

Publication

1. Fackler, Jennifer, ed., 2006, Illinois Water Resources Center Web Site, www.environ.uiuc.edu/iwrc.
2. Fackler, Jennifer, ed., 2007 Illinois Water Resources Center Web Site, www.extension.uiuc.edu/iwrc.
3. Lisa Merrifield, ed., 2008. Illinois Water Resources Center Web site, http://web.extension.uiuc.edu/iwrc/.
4. Lisa Merrifield, ed. 2008. University Council on Water Resources 2009 Conference Web Site. http://www.isws.illinois.edu/hilites/confinfo/ucowr/

The IWRC web site has long been an access point for people seeking information about water resources in Illinois. In 2008, our primary website focus has been digitizing our library of publications and making them available as PDFs via the site. Users can now visit http://web.extension.uiuc.edu/iwrc/scientists_research.html to download research reports 1-240. Special publications, such as conference proceedings and reports are currently being digitized and should be available in the coming year.

In addition to making the publications available via the IWRC website, we are working with the University of Illinois to be included in their efforts to digitize University collections. The publications will be available via the IDEALS web site in the coming year which can be accessed at http://www.ideals.uiuc.edu/. The benefits to participating in this effort include a guarantee that the publication format will be updated as software changes and the addition of our publications to a searchable database that will allow users to find these materials more easily.

IWRC Newsletter

Basic Information

Title:	IWRC Newsletter
Project Number:	2005IL157B
Start Date:	1/1/2005
End Date:	1/1/2011
Funding Source:	104B
Congressional District:	15th
Research Category:	Not Applicable
Focus Category:	Education, None, None
Descriptors:	newsletter, education, outreach
Principal Investigators:	Lisa Merrifield, Jennifer Fackler

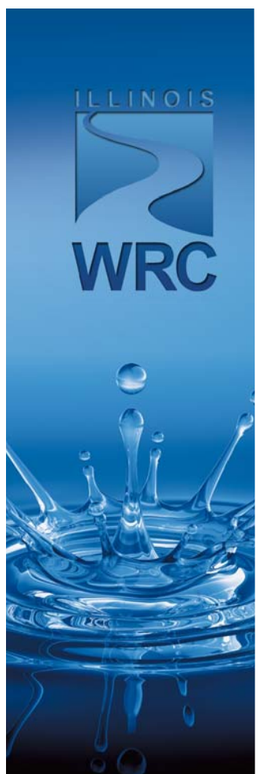
Publication

1. Miles, Irene, Jennifer Fackler, Lisa Merrifield, eds., Fall 2005, Illinois Water Resources Center Newsletter.
2. Illinois Water Resources Center, 2006, Illinois Water Resources Center Newsletter, Illinois Water Resources Center, Urbana, Illinois, 4 pages.
3. Merrifield, Lisa, ed., Fall 2007, Illinois Water Resources Center Newsletter, p. 4.
4. Merrifield, Lisa, ed, Fall 2008, Illinois Water Resources Center Newsletter, p. 4.

Once per year, usually in late summer, the Illinois Water Resources Center publishes a newsletter detailing our research and outreach activities over the previous year. The newsletter is distributed to over 700 people on our mailing list and is made available on our website. Following is a copy of the 2008 newsletter.

Dates to Remember

October 8-9, 2008	Illinois Water, Champaign, Illinois. See cover page.
October 24, 2008	Proposals due for IWRC funding. See page 2.
December 4, 2008	UCOWR Papers submissions due. See page 3.
July 7-9, 2009	UCOWR Meeting, Chicago, Illinois. See page 2.
October 20-22, 2009	Governor's Conference on Management of the Illinois River System, Peoria, Illinois.



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UNIVERSITY OF ILLINOIS EXTENSION

Illinois Water Resources Center

Summer 2008 Bulletin

Illinois Water Conference Celebrates 10 Years of Water Science

IWRC will host our 10th anniversary biennial Conference on Illinois Water, October 8-9 in Champaign, Illinois. Begun in 1998, the mission of the conference is to showcase the latest research findings and policy issues related to Illinois waters.

This year's conference provides opportunities to reflect on the past and look to the future. What has changed in the last ten years, what are our successes, and what problems do we still face? To help out the past decade, we have invited Richard Sparks, former director of the Illinois Water Resources Center and founder of this conference series, to give us his perspective on the changes that have occurred in the past ten years and the issues he sees on the horizon. Now the director of research for the National Great Rivers Research and Education Center, Dr. Sparks is actively involved in preserving and restoring our waterways.

Also on the conference agenda are plenary sessions on the Water Resources Development Act, climate change, nutrients, water supply, and energy/ biofuels.

Papers have been submitted by about 40 scientists and students and will include topics such as groundwater research, technology, water quality, watershed-scale science, planning, and environmental measurements.

"We invite all members of the water community in Illinois to join us at the Illinois Water 2008 conference," says conference coordinator Lisa Merrified. "Topics will define the critical issues currently facing Illinois waters and explore the current research advancements in our scientific communities."

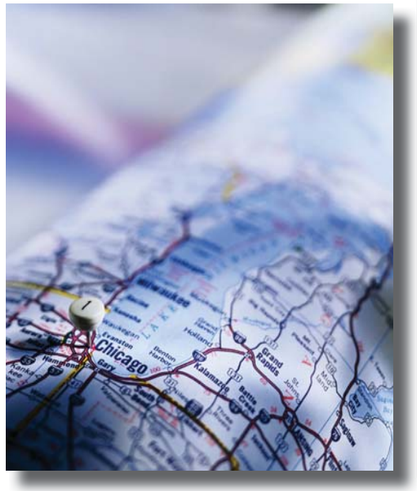
If you are interested in learning more about this year's conference or attending, please visit www.iisgcp.org/ilwater/.

Conference early registration fees are $155 ($85 for one day). After September 7, rates increase to $185 for the full conference and $105 for a single day.

Student rates and scholarships are available.

Researchers Shed Light on Groundwater in Northeastern Illinois

Managing water resources in northeastern Illinois is complicated by interstate treaties and multiple demands on available supply. The aquifers underlying much of the region do not make the situation any easier. They are characterized as fractured dolomite aquifers which means that the water flows through cracks in the rocks. The cracks are highly variable, making the rate of flow and transportation of contaminants difficult to understand. It is not unusual for neighboring wells to produce very different amounts of water due to the number of fractures the well intersects. Further, as the water flows through the fractures in the rock, very little filtration occurs, making it possible for surface contaminants to travel long distances with little alteration.



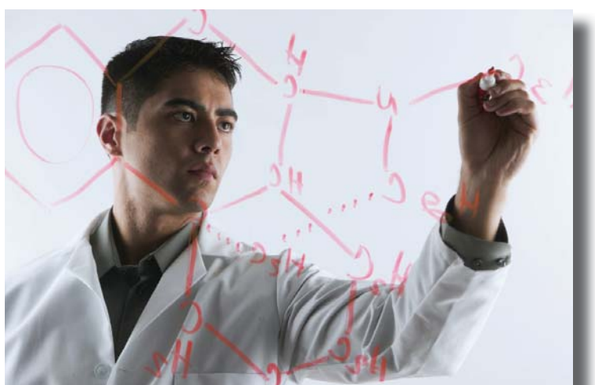
This year, two IWRC funded researchers completed projects to help us better understand the aquifer structure and function in the region.

With funding from the National Institutes of Water Resources program, Researchers Yu-Feng Lin and Albert Valocchi, University of Illinois, and Randall Hunt, USGS Wisconsin Water Science Center, have developed a tool that can more quickly and easily allow decision makers to understand the implications of different options on the aquifer. They have developed a GIS plug-in called Pro Grade that can quickly generate aquifer recharge and discharge rates using widely available data. The tool is available online at www.sws.uiuc.edu/gws/sware/prograde.

Researcher Douglas Walker, University of Illinois, with funding from IWRC's base grant program, has spent the last two years looking at how to model the flow rates from these aquifers. As the aquifers are highly variable, determining impacts is difficult. Given the high demand on water in the region, more accurate methods for modeling these types of aquifers are critically needed. Dr. Walker's revised models now show markedly different flow rates than those more commonly used. His findings, while preliminary, have created a great deal of interest and discussion within the groundwater community and could lead to new interpretations of how water flows under the Chicago area.

IWRC Seeks Graduate Students

In the early fall, look for IWRC's latest call for proposals. "Encouraging and supporting new scientists is one of the most important tasks our center does," says research coordinator, Dr. Phil Mankin. "During this RFP cycle, our focus will be on supporting students with a strong interest in water issues."



This year IWRC requests proposals to fund a graduate student who is conducting research on topics of importance to Illinois water resources. We will provide one 50 percent, nine- to twelve-month research assistantship to an MS or PhD student at a university in Illinois whose work is in support of a thesis.

Funding will begin as early as May 2009 and end by August 2010. Faculty members should submit a plan of work that describes the problems, methods, role for the graduate student, and expected outcomes. Proposals will be evaluated on the strength of the science as well as the academic record of the student. They are due October 24, 2008.

IWRC is issuing this call on a trial basis. With sufficient interest, Mankin expects to make this an annual funding opportunity. "We hope that many professors and graduate students around the state will see this as an opportunity to help reach their research and career goals," Mankin says.

A full request for proposals is available at web.extension.uiuc.edu/iwrc/.

Urban Water Management Conference Comes to Chicago; Seeks Papers

The University Council on Water Resources (UCOWR) has selected Chicago for its annual conference to be held during the summer of 2009. The conference theme will be urban water management and IWRC will serve as the local host.

IWRC director, Dr. Richard Warner, said "We are very excited to help host this conference and to showcase research and outreach related to the complexities of water management in densely populated coastal settings."

With Chicago as a backdrop, the location provides abundant opportunities to showcase our successes and challenges as we deal with infrastructure decay, pharmaceuticals and other chemicals in waterways, climate change, water supply planning, energy, and other critical issues.

UCOWR director, Dr. Christopher Lant is enthusiastic about bringing this annual conference to Chicago. "Following annual conferences in Santa Fe, New Mexico, Bosie, Idaho, and Durham, North Carolina, the 2009 UCOWR conference in downtown Chicago promises to draw from public and private sectors as well as academic participants in a dynamic exchange of ideas, issues, and solutions to urban water management problems in an exciting environment with good food and good fun," Lant said.

Conference organizers are currently soliciting papers from anyone interested in presenting.

Topics include:

- Urban water quality
- Urban water quantity
- Pharmaceuticals and other pollutants
- Urban stream restoration
- Climate change
- Urban flash flooding
- Storm water management
- Monitoring
- Water reuse/gray water
- Public education and participation
- Water security/disaster preparedness
- Water and energy: biofuels, thermoelectric use
- Local, regional and watershed planning and economics

Abstracts are due December 4, 2008. Guidelines are available at www.ucowr.org.

Papers due December 4, 2008

Conference coming Summer of 2009

Illinois Water Resources Center

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UNIVERSITY OF ILLINOIS EXTENSION

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Program Coordinator/
Newsletter Editor

Midwest Technology Assistance Center

Basic Information

Title:	Midwest Technology Assistance Center
Project Number:	2005IL158B
Start Date:	1/1/2005
End Date:	1/1/2011
Funding Source:	104B
Congressional District:	15th
Research Category:	Water Quality
Focus Category:	Water Supply, Water Quantity, Water Quality
Descriptors:	small water systems, Midwest
Principal Investigators:	Dick Warner, Jennifer Fackler, Lisa Merrifield

Publication

1. Lau, Boris L. T., Gregory W. Harrington, Marc. A. Anderson, 2006, Arsenic and Bacteriophage MS2 Removal from Groundwater by Nanoparticulate Aluminum Oxide Coated Granular Filter Media: A Pilot-Scale Evaluation on the Effect of pH and Coating Density, Illinois State Water Survey, (FS06-01).
2. Moore, Michelle, 2006, Chlorine's Effect on Corrosion in Drinking Water Systems, Illinois State Water Survey, NDWC, Tech Brief #3, Item # DWBRPE52.
3. Winstanley, Derek, James R. Angel, Timothy P. Bryant, H. Vernon Knapp, Michael A. Palecki, Amy M. Russell, H. Allen Wehrmann, 2006, Drought Planning for Small Community Water Systems, Illinois State Water Survey,(FS06-02).

The Midwest Technology Assistance Center for Small Public Water Systems (MTAC) is a consortium led by the University of Illinois and the Illinois State Water Survey, in partnership with the land grant universities of Indiana, Iowa, Kansas, Michigan, Minnesota, Missouri, Nebraska, Ohio, and Wisconsin. MTAC serves small public water systems and public systems serving Native American Tribes. The participation of each state is led by its Water Resources Research Institute (WRRI), established under authority of the Water Resources Research Act of 1964 on the campus of the land grant university as a federal-state partnership to conduct applied research and technology transfer.

The Center cooperates closley withother regional technology assistance centers established by the USEPA, and with other partner agencies and organizations in order to ensure efficient response to the highest priority needs of small public water systems and Native AmericanTribal systems in the Midwest.

Beginning in January, 2009, MTAC was awarded a grant to build an online tool to help small water supply system operators connect to online resources designed for them. Research has shown that many do not have access to the internet at their place of work and thus do not utilize the materials available to them.

IWRC's role in this effort is to identify the 20 operators to test and use the site, get them set up with laptops and internet access, and collect information for the website.

Water 2008

Basic Information

Title:	Water 2008
Project Number:	2007IL169B
Start Date:	11/1/2006
End Date:	11/1/2008
Funding Source:	104B
Congressional District:	15th
Research Category:	Not Applicable
Focus Category:	None, None, None
Descriptors:	Conference highlighting Illinis water issues
Principal Investigators:	Lisa Merrifield, Jennifer Fackler

Publication

1. Jennifer Fackler, ed. 2008. Illinois Water Conference Proceedings. 62 pages.

At the 2008 Illinois Water Conference—held on October 8th and 9th in Champaign—speakers examined and discussed the challenges presented by long-term water supply planning, among other topics. (Conference details follow.)

"There is great uncertainty in the future," Gary Clark, director of the Office of Water Resources at the Illinois Department of Natural Resources (IDNR), said of water supply planning, "It requires consideration of uncertainties in climate, geology, hydrology and a host of social and economic factors."

Using three water demand scenarios for Illinois over the next 50 years—constructed by Ben Dziegielewski from Southern Illinois University at Carbondale—the Illinois State Water Survey (ISWS) is examining the ability of resources to meet those demands and the impacts of those demands on the environment.

According to ISWS, the scenarios—less resource intensive, the current trend, and more resource intensive—are meant to "provide estimates of how much more or less water will be available on the surface and in aquifers, and how much more or less water will be needed by consumers if climate changes by specified amounts."

"Uncertainty creates a dilemma for planners, because there are costs and harm caused by either over-estimating or under-estimating the effects of drought or climate change on water supplies," said Richard Sparks, director of research at National Great Rivers Research and Education Center, and keynote speaker at the conference.

Clark noted that future temperatures will most likely increase due to climate change, causing water demand to increase and water availability to decrease. However, he said it is unclear whether climate conditions will become wetter or drier.

"Droughts are the issue," Clark said. "They have caused the most problems in the past and will cause the most in the future."

According to research from the ISWS, Illinois has not experienced a major multi-year drought in the last 40 years. However, Allen Wehrmann, head of the Center for Groundwater Science at ISWS, stressed the importance of planning for them anyway.

"It's not a matter of if," Wehrmann said of droughts. "It's a matter of when."
Conference speakers focused primarily on the regional planning efforts resulting from Governor Rod Blagojevich's 2006 Executive Order, which initiated a three-year water supply planning process for Illinois.

The Chicago Metropolitan Agency for Planning (CMAP), commissioned by IDNR to carry out regional planning for an 11-county area in northeastern Illinois (one of two pilot-planning areas in Illinois) is trying to mitigate water supply concerns through water conservation.

In a recent regional water demand study, CMAP found that without planning intervention, demand in their 11-county region could increase by 64 percent by 2050. Tim Loftus, CMAP

senior planner for water resources, pointed to wastefulness as the issue rather than scarcity. Conservation, according to Loftus, is the most logical and ethical first response.
"If we can become more conservative with the use of a resource and increase efficiency, why wouldn't we?" Loftus said. He noted that conservation must be economically favorable to be looked at as a primary option.

"This is an early-phase planning effort that has been undertaken within a relatively short period of time," Loftus said. "As regional planning matures, we will explore all options more fully than time and resources will allow us to right now. In the meantime, conservation has proven elsewhere to be a cost effective and efficacious means for managing demand."
Loftus presented 14 conservation measures—including improved plumbing efficiency, public information and school education—that they plan to adopt throughout regional planning.

CMAP's progress was deterred recently when Gov. Blagojevich cut funding for the final year of his three-year initiative in an effort to close a $2 billion gap in FY 2009 budget. As a result, CMAP has had to scale back staff resources and other project components.

Illinois Water Conference 2008

Wednesday, October 8, 2008

8:00 am - 9:00 am — Registration/Check-in (Conference Center Foyer)

9:00 am - 9:10 am — Welcome and Opening Comments (Boilermaker Room)
Richard Warner, Director, Illinois Water Resources Center

9:10 am - 10:10 am — Featured Speaker (Boilermaker Room)
Richard Sparks, Research Director, National Great Rivers Research and Education Center
Where We Have Been and Where We Are Going: A Personal Retrospective and Outlook on Water Resources in Illinois

10:10 am - 10:25 am — Break/Exhibits (Illini Ballroom)

10:25 am - 12:15 pm — Plenary Session (Boilermaker Room)

Water Resources Development Act of 2007 - Recent Experiences in Illinois
Moderator: Timothy Feather, CDM Federal Programs

Gary Clark, Illinois Department of Natural Resources, Office of Water Resources
Federal Water Resources Development Act: Illinois' Interest and Influence

John Zimmerman, U.S. Army Corps of Engineers
WRDA: What It Is and What It Can Do For You

Claudia Emken, The Nature Conservancy
WRDA 2007—A 7 Year Quest for The Nature Conservancy

12:15 pm - 1:30 pm — Lunch (Illini Ballroom)

1:30 pm - 3:00 pm — Themed Session I (concurrent sessions)

Water Supply (Fighting Illini Room)
Moderator: Gary Clark, Illinois Department of Natural Resources

Allen Wehrmann, Illinois State Water Survey
Water Supply Planning in Illinois – A Progress Report from the State Surveys

Tim Loftus, Chicago Metropolitan Agency for Planning
21st Century Water Conservation in Northeastern Illinois

Gary Clark, Illinois Department of Natural Resources
Uncertainties and Challenges in Regional and Statewide Water Supply Planning and Management

Nutrients (Golden Gopher Room)
Moderator: Gregg Good, Illinois Environmental Protection Agency

Mark David, University of Illinois at Urbana-Champaign
Overview of Nutrients in Illinois Waters from Sources to Downstream Contributions

Paul Terrio, U.S. Geological Survey
Nutrient Standards for Illinois Surface Waters - A Progress Update

Nick Menninga, Illinois Association of Wastewater Agencies
Costs of POTW Nutrient Removal in Illinois

Dennis McKenna, Illinois Department of Agriculture
Agricultural Nutrient-Reduction Alternatives and Costs

3:00 pm - 3:30 pm Break/Exhibits (Illini Ballroom)

3:30 pm - 5:00 pm Technical Session I (concurrent sessions)

Environmental Measures (Fighting Illini Room)
Moderator: David Larson, Illinois State Geological Survey

Teresa Chow, Illinois Sustainable Technology Center
Evaluation of Analytical Methods for Pharmaceuticals and Personal Care Products

Michael Plewa, University of Illinois at Urbana-Champaign
Induction of Mammalian Cell Chronic Cytotoxicity and Acute Genomic DNA Damage by Drinking Water Disinfection Byproducts

Charles Pederson, Eastern Illinois University
Use of Photopigments as a Descriptor of Phytoplankton Assemblages

Lewis Parish, University of Illinois at Springfield/Illinois Department of Public Health
GIS Mapping of Surface Discharge Septic Systems

Groundwater Research (Golden Gopher Room)
Moderator: Stacy James, Prairie Rivers Network

Edward Mehnert, Illinois State Geological Survey
Refining Estimate of Shallow Groundwater Recharge Using Hydrologic and Geologic Information

Thomas Holm, Illinois State Water Survey
Spatial Variability of Arsenic in Glacial Aquifers

William Dey, Illinois State Geological Survey
Mapping The Mahomet Aquifer Beneath Champaign County, Illinois

5:15 pm - 7:30 pm Reception (Illini Ballroom)
Poster Session 5:15 pm - 6:15 pm

6:30 pm - 7:30 pm Student Career Panel (Fighting Illini Room)

Thursday, October 9, 2008

8:00 am - 8:30 am Registration (Conference Center Foyer)

8:30 am - 10:30 am Themed Session II (concurrent sessions)

Water and Energy/Biofuels (Fighting Illini Room)
Moderator: Steve John, Agricultural Watershed Institute

Vijay Singh, University of Illinois at Urbana-Champaign
Water Use in Bioethanol Production

Allen Wehrmann, Illinois State Water Survey
Water and Ethanol Production in Illinois

Gregory McIsaac, University of Illinois
Perennial Grass, Corn and Soybean Effects on Soil Moisture and Inorganic Nitrogen Leaching in Central Illinois

David Riber, Avenine Renewable Energy, Inc.
Ethanol Production and Water Usage

Climate Change (Golden Gopher Room)
Moderator: Jim Angel, Illinois State Water Survey

Ximing Cai, University of Illinois at Urbana-Champaign
Impact of Climate Change on Crop Yield? A Case Study of Rainfed Corn in Central Illinois

Joseph Kozak, Metropolitan Water Reclamation District of Greater Chicago
The Energy and Carbon Footprint of Wastewater Treatment and Waterway Management in Greater Chicago

Jim Angel, Illinois State Water Survey
Future Climate Change Scenarios for Lake Michigan Levels

10:30 am - 10:45 am Break and Exhibits (Illini Ballroom)

10:45 am - 12:15 pm Technical Session II (concurrent sessions)

Hydrology/Hydraulics (Fighting Illini Room)
Moderator: Phil Mankin, Illinois-Indiana Sea Grant

David Soong, U.S. Geological Survey
Illinois StreamStats — A Basin Characteristics and Flood-peak Frequencies Determination Tool

Jorge Abad, University of Illinois at Urbana-Champaign
Linking the Detailed Physical Understanding of Meandering Channels into the River Restoration Rramework

Diego Oviedo-Salcedo, University of Illinois at Urbana-Champaign
Balancing Irrigation and Instream Water Requirements under Drought Conditions: A Study of Kankakee River Watershed

Andrea Zimmer, University of Illinois at Urbana-Champaign
Critical Rainfall and Infrastructure Dependencies as CSO Triggering Thresholds

Watershed Planning (Golden Gopher Room)
Moderator: Glynnis Collins, Prairie Rivers Network

Patrick Mills and Tim Bryant, U.S. Geological Survey
Estimating Water Use in Illinois — Present Realities, Future Visions

Barbara Minsker, University of Illinois Urbana-Champaign
Harnessing the Power of Sensors and Cyberinfrastructure Towards Environmental Sustainability: The WATERS Network Vision and Testbedding Research in Illinois

Luiz Freitas, University of Illinois at Urbana-Champaign
Adoption of Green Technologies: The Case of Chicago Rain Barrels

Christopher Slemp, Southern Illinois University Carbondale (SIUC)
Stakeholder Visions of Community and Environmental Health in the Lower Kaskaskia River Watershed

Water Quality (Spartan Room)
Moderator: Thomas Holm, Illinois State Water Survey

Charnsmorn Hwang, Southern Illinois University Carbondale
Effects of Urbanization on Water Quality in the Lower Kaskaskia Watershed in Southern Illinois

Timothy Straub, U.S. Geological Survey
Sediment Issues in Illinois

David Kovacic, University of Illinois at Urbana-Champaign
Constructed Wetland Size Requirements for Effective Nutrient Removal in Agricultural Watersheds

Agenda

12:15 pm - 1:30 pm — Lunch (Illini Ballroom)

1:30 pm - 3:00 pm — Technical Session III (concurrent sessions)

Technology Updates (Fighting Illini Room)
Moderator: Phil Mankin, Illinois-Indiana Sea Grant

Yovanni Catao, University of Illinois at Urbana-Champaign
Laboratory Testing of a Vortex Flow Restrictor

Paul Horvatin, U.S. EPA Great Lakes National Program Office
Monitoring — U.S. EPA Great Lakes National Program Office Nearshore Monitoring Using the Triaxus Towed Instrument Platform

Robert Hudson, University of Illinois at Urbana-Champaign
Methylmercury Dynamics in Streams and Wetlands in Illinois and Indiana: Geochemical Survey and Method Comparison Results Obtained Using a Novel Analytical Method

Mostafa Noureldin, Illinois Institute of Technology
Biosolids Dewatering Using Super Absorbent Polymers

Watershed Scale Science (Golden Gopher Room)
Moderator: Bill White, Illinois State Water Survey

Walton Kelly, Illinois State Water Survey
Nitrate and Chloride in the Illinois River Basin

Ryan Jackson, US Geological Survey, Illinois Water Science Center
Density Currents in the Chicago River: Characterization, Effects on Water Quality, and Potential Sources

Erin Bauer, Illinois State Water Survey
15 Years of Hydrologic and Nutrient Monitoring of the Lake Decatur Watershed: Floods, Droughts and In Between

Julia Friedmann, Southern Illinois University Carbondale
Effects of Agricultural Land Cover on Water Quality at the Watershed Scale

3:00 - 3:15 pm — Closing Comments (Fighting Illini Room)
Richard Warner, Director, Illinois Water Resoureces Center

Richard Sparks

Where We Have Been and Where We Are Going: A Personal Retrospective and Outlook on Water Resources in Illinois

The six proceedings of the biennial Water Illinois conferences (including this year's) provide a 10-year history of major issues that have engaged the water community throughout Illinois. The very first conference (1998) now seems eerily prescient of our current concerns about terrorism, because the title of the featured presentation (by Dr. Yacov Haimes) was "The Risk of Willful Hazard to Water Infrastructure." Dr. Haimes urged advance planning to reduce vulnerabilities to either willful or natural hazards (storms, floods and droughts). The latter have been the subject of many presentations during the last 10 years. The 1998 conference had one paper on the after-effects on water and sediment quality of the Great Midwest Flood of 1993 and the second conference (2000) followed the drought of 1998-1999. The featured speaker in 2000 (Dr. Don Wilhite, Director of the National Drought Mitigation Center) argued persuasively for drought assessment, planning and management, something the Illinois State Water Plan Task Force, the Interagency Coordinating Committee on Groundwater, and the Water Survey took to heart. A second drought in 2005 stimulated many papers in the 2006 Conference and impelled the Governor to issue an executive order that speeded the development of plans for areas that were most at risk for water shortages and conflicts. The potential effects of climate change on water availability, irrigation use, and streams were addressed in just one paper in 1998, but are the subject of a Plenary Panel in this year's program, indicating growing concern about longer term trends.

On a par with water availability, water quality has been a persistent theme. The process of identifying surface waters in Illinois that are not attaining their designated beneficial uses, and then correcting the problem by developing total maximum daily loadings of contaminants that will be allowed in those streams has been going on for at least 10 years. This regulatory process has spurred research on sources and fate of contaminants and nutrients in watersheds, development of predictive models, and experimentation with treatment systems, including constructed wetlands. In the water realm below ground, concerns about natural and human-induced contamination, as well as concerns about depletion, have also spurred innovations in analytical techniques and predictive modeling.

Where are we going? It is likely that the effects of climate change on water resources will be increasingly discernable above the "noise" of annual variation. Evidence from Illinois includes: (1) increases in precipitation and river flows during the spring in the Illinois River basin when the past four decades are compared to the previous seven; (2) increasing abundances of some typically "southern" species of fishes, turtles, and amphibians; (3) some explanatory simulation models that predict wetter winter seasons, but the same or drier growing seasons. Implications are that we might see more frequent large floods, especially if we do not change the trend toward more impervious surfaces in rapidly-developing areas around our cities. Water will be the nexus among policies regarding climate change, energy, food, and land use. For example, some biofuels may reduce carbon emissions and our dependence on fossil fuels (effectiveness depends on whether corn or cellulosic feedstocks are used), but the water and land requirements may present problems (see the Plenary Panel II at this conference). We contribute to the downstream flows of nutrients and contaminants to the Gulf of Mexico and we are subject to continuing invasions of harmful species and fallout of toxicants from distant coal-burning plants. Our abilities to assess, validate, and enhance carbon uptake, contaminant reduction, and nutrient retention or conversion will continue to improve, and we'll see markets develop for these and many other ecosystem services. Although the Illinois water conferences will continue to focus on issues in our state, we will find ourselves increasingly connected with, and responsive to, the larger world.

Richard Sparks *(cont.)*

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In 1998, the outgoing Director of Illinois Water Resources Center, Dr. John Braden, and the incoming Director, Dr. Richard Sparks, formed a planning committee that organized the very first of the biennial Illinois Water Conferences. From 1998 to 2002, Dr. Sparks was Director of the Illinois Water Resources Center, Research Coordinator for the Illinois-Indiana Sea Grant College Program, and a faculty member in the Department of Natural Resources and Environmental Sciences at the University of Illinois in Urbana-Champaign. For 26 years prior to that, he directed the Illinois Natural History Survey's Large River Research Program on the Illinois and Upper Mississippi Rivers from the field station on the Illinois River at Havana. Dr. Sparks is currently the Director of Research, National Great Rivers Research and Education Center, Alton, Illinois, which is a partnership of the University of Illinois at Urbana-Champaign, Lewis and Clark Community College, the Illinois State Natural History Survey, and several other institutions and agencies concerned with river management and with education and research on rivers and watersheds. He co-authored "The Flood Pulse Concept in River-Floodplain Systems", a much-cited paper which described the role of seasonal flood cycles in maintaining the ecological structure and function of large floodplain-river ecosystems. He has served on several U.S. National Research Council committees, including the Committee on Restoration of Aquatic Ecosystems and the Committee to Assess U.S. Army Corps of Engineers Water Resources Project Planning Procedures. In Argentina, Brazil, India, and China he provided advice on management of floodplain ecosystems and large rivers.

Moderator: Timothy Feather

Dr. Feather is CDM's national water resources strategy leader. He focuses on development of interdisciplinary solutions to environmental challenges and has been involved in projects nationwide servicing federal and state water resource agencies with special planning and policy studies. Dr. Feather has supervised development of a range of projects including resource valuation, consensus-based watershed planning, environmental law review/assessment, outdoor recreation analysis, and water demand and conservation analysis. He is the current Illinois Section President of the American Water Resources Association and Chairman of the Environmental and Water Resources Planning Committee of the American Society of Civil Engineers.

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Claudia Emken

WRDA 2007—A 7 Year Quest for The Nature Conservancy

The Nature Conservancy is the single largest cost-share partner of the Corps of Engineers for its environmental restoration programs in regard to the number projects across the country. Two Conservancy projects along the Illinois River, Emiquon and Spunky Bottoms, are good examples of the rewards and challenges in working through complex federal processes. The Illinois River has been a priority for The Nature Conservancy since the early 1990s and since 1999, the Conservancy has partnered with the Corps of Engineers on these two floodplain restoration projects in Brown and Fulton counties. When the Conservancy entered into these partnerships with the Corps, we identified legal authorities under which to proceed and collaboratively began investigations and planning. In 2000, we identified the need for legislative changes in order to proceed with our Spunky Bottoms project, so we began working with our Congressional delegation to secure the correct language in WRDA. Thus began our seven year journey to get critical authorizations to proceed at Spunky Bottoms. In 2000, the Conservancy purchased nearly 7,000 acres in Fulton County, now called Emiquon Preserve, and a second partnership with the Corps was begun. And again we needed to seek legislative changes to proceed. Working on federal re-authorizations is not for the short-winded. After years of lobbying, the proper authorizations passed in WRDA 2007 and now we focus on appropriations to pay for the work authorized.

The Nature Conservancy
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Claudia Emken has been with The Nature Conservancy in Illinois since March 1997. She was first hired as Director of Government Relations and in 2007, was promoted to Associate Director of Conservation. In that capacity she supervises land acquisition, land conservation, and policy work for the chapter. She works directly on federal policy.

Emken's degree in political studies is from Sangamon State University (now University of Illinois, Springfield), class of 1993. She served as Constituency Liaison for the Illinois Department of Conservation/Department of Natural Resources from 1990 to 1997.

Gary Clark

Illinois Dept. of Natural Resources,
Office of Water Resources
Director, Office of Water Resources
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Mr. Clark started his career as a civil engineer with the State of Illinois Department of Natural Resources, Office of Water Resources in 1974. On July 1, 2003, Mr. Clark was appointed as the Director of the Office of Water Resources. During his career with the Office of Water Resources, Mr. Clark has served as the Chief of the Planning and Research Section and as manager of the Division of Program Development. During his career, his areas of professional responsibilities included the administration and conduct of research and planning in the areas of instream flow protection, statewide water supply management, groundwater modeling, drought management, groundwater and surface water law and state water planning. Mr. Clark is a graduate of the University of Wisconsin, with a B.S. Civil Engineering in 1972, and a M.S. in Civil and Environmental Engineering in 1974. He is a licensed Professional Engineer in the State of Illinois and Wisconsin. In June of 2005 Mr. Clark was credentialed as a Diplomate, Water Resources Engineer by the American Academy of Water Resources Engineers.

Federal Water Resources Development Act: Illinois' Interest and Influence

The Water Resources Development Act (WRDA) is periodic federal legislation that authorizes the Corps of Engineers' programs and projects. WRDA is a very significant federal action that is closely monitored by all State Natural Resources Agencies under the leadership of DNR's Office of Water Resources. DNR's Office of Water Resources has actively worked on all WRDA's since the mid 1970's. This program for covering Illinois' interests and significant provision of WRDA's over the last three decades will be highlighted.

John Zimmerman

WRDA: What it is and what it can do for you.

An overview of how the Water Resources Development Act (WRDA) is formulated and approved will be provided, with particular commentary on what it is and what it is not. Highlights of WRDA 2007 will be provided as will discussion of what is being considered in WRDA 2009. Comments on WRDA and impacts in Illinois will be offered.

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U.S. Army Corps of Engineers
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Lead Plan Formulator
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A registered Professional Engineer and Surveyor in Kentucky and Tennessee, Mr. Zimmerman has been with the U.S. Army Corps of Engineers for the last 28-plus years, mostly with the Louisville District, Lakes and River Division and at Headquarters, Washington, D.C. on several long term assignments. At Louisville, he has served in a variety of positions as both a Military and Civil Project and Construction Manager. During this time he has managed and constructed more than $800 million dollars in improvement projects spanning Navigation, Flood Control, Ecosystem Restoration, Recreation and numerous Military programs.

Thank You!

Sponsors

The organizers wish to thank these organizations for helping make this conference possible with their generous donations.

Sustaining
Illinois EPA
Illinois-Indiana Sea Grant
Illinois State Geological Survey
American Water Works Association

Supporting
Metropolitan Water Reclamation District of Greater Chicago
Prairie Rivers Network

Contributing
Illinois Farm Bureau
Illinois Water Authority Association

General
Agricultural Watershed Institute
Hach Environmental
Illinois Water Environment Association

Planning Committee

Representatives of these organizations committed hours of work to develop and execute this biennial conference. The Illinois Water Resources Center thanks them for their efforts.

Jackie Adams - Illinois-Indiana Sea Grant, U.S. EPA Great Lakes National Program Office
Gary Clark - Illinois Department of Natural Resources
George Czapar - University of Illinois, Springfield Extension Office
Sam Dennison - Metropolitan Water Reclamation District of Greater Chicago
Denise Devotta - Center for Watershed Science, Illinois State Water Survey
Nancy Erickson - Natural and Environmental Resources, Illinois Farm Bureau
Jennifer Fackler - Illinois Water Resources Center, University of Illinois
Tim Feather - CDM Federal Programs
Bob Frazee - U of I Extension, East Peoria Extension Center
Gregg Good - Bureau of Water, Illinois EPA
George Groschen - WRD, U.S. Geological Survey, Illinois Water Science Center
Beth Hinchey Malloy - Illinois-Indiana Sea Grant, Purdue University, U.S. EPA Great Lakes National Program Office
Bev Herzog - Illinois State Geological Survey
Vern Knapp - Illinois State Water Survey
Bill Kruidenier - National Great Rivers Research and Education Center
Dave Larson - Illinois State Geological Survey
Phil Mankin - Illinois-Indiana Sea Grant, University of Illinois
Dennis McKenna - Department of Agricultural
Lisa Merrifield - Illinois Water Resources Center, University of Illinois
Jim Nelson - Association of Illinois Soil and Water Conservation Districts
Frank Pisani - Illinois Department of Natural Resources
Dorland Smith - Illinois Water Authority Association
Art Schmidt - Department of Civil & Environmental Engineering , University of Illinois
Dick Warner - Extension and Outreach, University of Illinois
Jennifer Wasik - Metropolitan Water Reclamation , District of Greater Chicago
Karl Williard - Southern Illinois University
Al Wehrmann - Center for Groundwater Science, Illinois State Water Survey
Bill White - Illinois State Water Survey, Illinois Department of Natural Resources

Staff

Water 2008 is coordinated by the Illinois Water Resources Center with guidance from organizations and agencies in Illinois.

Director - Richard E. Warner
Research Coordinator - Phil Mankin
Program Coordinator - Lisa Merrifield
Program Specialist - Jennifer Fackler

Illinois Water Supply Plan Task Force

Basic Information

Title:	Illinois Water Supply Plan Task Force
Project Number:	2007IL170B
Start Date:	1/15/2006
End Date:	1/15/2010
Funding Source:	104B
Congressional District:	15th
Research Category:	Not Applicable
Focus Category:	Management and Planning, None, None
Descriptors:	Committee on management of water supply
Principal Investigators:	Dick Warner

Publication

The Illinois Water Supply Planning Task force meets quarterly in Springfield, Illinois and provides an opportunity to interact and network with representatives from agencies and programs around the state of Illinois who are grappling with similar issues. On the committee are representatives from the following groups:

Illinois Department of Agriculture
Illinois EPA
Illinois Department of Public Health
DNR Office of Resource Conservation
DNR Office of Water Resources
Illinois State Geological Survey
Illinois State Water Survey
Illinois Water Resources Center
University of Illinois Extension
USDA – NRCS
U. S. Geological Survey

Members are each given an opportunity to update members on ongoing activities and upcoming events. Some of the topics of discussion over the last year have included:

Flooding
Regional Water Supply Planning
Dam Safety
Water Resource Assessment Projects
Fox River Accounting Model
Ground water
Gulf hypoxia
Levee safety summit
Budges and Legislation

IWRC provided updates on our 2008 conference regularly at these meetings.

Information Transfer to Illinois Constituents

Basic Information

Title:	Information Transfer to Illinois Constituents
Project Number:	2008IL167B
Start Date:	3/1/2008
End Date:	2/28/2011
Funding Source:	104B
Congressional District:	15th
Research Category:	Not Applicable
Focus Category:	None, None, None
Descriptors:	
Principal Investigators:	Dick Warner

Publication

1. Robert Reber, ed. 2008. Illinois Steward. Winter 2008-2009.
2. Robert Reber, ed. 2008. Illinois Steward. Spring 2008.
3. Robert Reber, ed. 2008. Illinois Steward. Summer 2008.

IWRC engages in a number of information transfer activities. Most have been covered under specific areas in this annual report. A few other activities we have engaged in include:

- Director, Richard Warner, is in the third year of his term on the board of the University Council on Water Resources.

- IWRC has provided support for Illinois Steward Magazine, which has the following mission:

  "The Illinois Steward is an award-winning nature magazine that is grounded in the "land ethic" of Aldo Leopold. *The Illinois Steward* features articles about stewardship, conservation, preservation, and restoration of natural areas in Illinois. Article topics include native plants, wildlife, natural areas in Illinois, nature photography, and Illinois' historical past."

  The magazine is published quarterly and regularly includes articles on water resources issues because of IWRC support.

  Articles over the past year include:

  Spring 2008

  - "The Rites of Passage: Spring Migration of Waterfowl," by Steve Havera and Michelle Horath. Chronicles the waterfowl migration along the Illinois River.
  - "The Future of Wetland Birds in Northeastern Illinois," by Mike Ward, Brad Semel, and Jim Herkert. Discusses the changing nature of wetlands in northeastern Illinois and how these changes are affecting different bird species.

  Summer 2008

  - "Restoring Our Ribbons of Life: The Conservation Hopes of Prairie Rivers Network," by Eric Freyfogle and Anne Phillips. Chronicles the history, work, and challenges of the network.
  - Series of articles (approx. 1200 words each) on each of 4 rivers, the Sangamon, the Fox, the Kankakee, and the Macinaw, by R. J. Reber. Discusses the particular problems faced by each river (siltation, pollution, storm pulses, etc.) and how these problems are affecting particular species of aquatic life.

  Fall 2008

  - "At the Confluence: The National Great Rivers Research and Education Center," by Lyle Guyon. Discusses the history, work, future projects, and challenges facing the center.

  Winter 2008-2009

  - "Emiquon Corps of Discovery: Rebirth of Backwater Lakes, Bottomland Forest, Wetland, and Prairie," by Jane Garrison Ward. Relates a naturalist's view of the progress at Emiquon.

- IWRC has partnered with the National Great Rivers Research and Education Center (NGREEC) to support the Illinois RiverWatch stream monitoring effort. This program trains volunteers to collect water quality data around the state.

  IWRC is specifically contributing to building the first official volunteer data management system in Illinois. The system will have the capacity to store, manage, retrieve, interpret, and report on volunteer data.

- IWRC maintains close relations with players in the water and natural resources communities on the University of Illinois campus through shared appointments of staff.
  - Director, Richard Warner, accepted a position as Director of the University of Illinois Office of Sustainability in 2008. This office is housed under the Vice Chancellor for Public Engagement.
  - Assistant Director, Lisa Merrifield, and Program Specialist, Jennifer Fackler, have joint appointments with Illinois-Indiana Sea Grant, which resides in the College of Agricultural, Consumer and Environmental Sciences Cooperative Extension unit.

Universities Council on Water Resources Conference

Basic Information

Title:	Universities Council on Water Resources Conference
Project Number:	2008IL199B
Start Date:	2/1/2008
End Date:	9/1/2009
Funding Source:	104B
Congressional District:	15 th
Research Category:	Not Applicable
Focus Category:	Education, None, None
Descriptors:	
Principal Investigators:	Lisa Merrifield, Jennifer Fackler, Dick Warner

Publication

IWRC was selected to host the 2009 Universities Council on Water Resources/National Institute for Water Resources conference in Chicago, Illinois. In 2008, IWRC staff began planning the conference. IWRC achievements have included finding an affordable and appropriately equipped venue, planning tours and activities beyond the meeting, soliciting a call for papers and organizing technical sessions, outfitting a steering committee to select and invite plenary speakers and guide overall conference planning, securing conference co-sponsors, and designing, maintaining and updating the conference web site and registration forms.

Following are excerpts from preliminary program.

Urban Water Management:
Issues and Opportunities

Universities Council On Water Resources

NIWR The National Institutes for Water Resources

Southern Illinois University Carbondale

University of Illinois Extension

Sea Grant Illinois - Indiana

Metropolitan Water Reclamation District of Greater Chicago

The Ivanhoe Foundation

SPECIAL EVENTS

See page 13 for details.

MONDAY July 6

Stickney Water Reclamation District 1:30PM-4:00PM

Metropolitan WRD Cruise 4:00PM-7:00PM

Registration 4:00PM-7:00PM

TUESDAY July 7

Welcome Reception and Poster Session

6:00PM-8:00PM

WEDNESDAY July 8

UCOWR Awards & Banquet

Marriott Ballroom
Cash Bar 6:30PM
Banquet 7:00PM-9:00PM

THURSDAY July 9

Racine Pumping Station
1:30PM-3:30PM

TUESDAY July 7

REGISTRATION 7:00AM-4:00PM

Cont. Breakfast 7:30AM-8:00AM

PLENARY SESSION 1
8:00AM-10:00AM

Welcome and Keynote Speakers
- Michael Sturtevant
- David Naftzger

Break 10:00AM-10:30AM

TECHNICAL SESSIONS 1
10:30AM-12:00PM

2 Stormwater Management I
3 Human Impacts on Water Resources
4 Agricultural Methods, Practices and Policy

Lunch on Your Own 12:00PM-1:30PM

TECHNICAL SESSIONS 2
1:30PM-3:00PM

5 Stormwater Management II
6 Ecosystem Impacts and Management Practices
7 International Water Supply Policies and Practices

Break 3:00PM-3:30PM

TECHNICAL SESSIONS 3
3:30PM-5:00PM

8 Balancing Urban Water Supply and Demand
9 Stormwater Management Models
10 Pharmaceuticals and Personal Care Product Impact on Water Quality

WELCOME RECEPTION AND POSTER SESSION

Marriot Lower Foyer
6:00PM-8:00PM
TUESDAY JULY 7

2009 Conference at a Glance

WEDNESDAY July 8

REGISTRATION 7:30AM-4:00PM

Cont. Breakfast 7:30AM-8:00AM

PLENARY SESSION 2
8:00AM-10:00AM

Keynote Speakers
- Mary Ann Dickinson
- Ed Archuleta
- Alice Miller Keyes

Break 10:00AM-10:30AM

TECHNICAL SESSIONS 4
10:30AM-12:00PM

13 Streamflow and Urban Water Management
14 Planning for Water Sustainability
15 Impacts of Organic and Inorganic Contaminants on Water Quality

Lunch on Your Own 12:00PM-1:30PM

TECHNICAL SESSIONS 5
1:30PM-3:00PM

16 Monitoring Water Quality and Quantity
17 Water Policy: Planning, Implementation and Management
18 Groundwater Conservation and Management

Break 3:00PM-3:30PM

PLENARY SESSION 3
3:30PM-5:00PM

Keynote Speakers
- Jim Heaney
- David Douglas

UCOWR BANQUET AND AWARDS CEREMONY

Marriott Ballroom
CASH BAR 6:30PM
BANQUET 7:00PM-9:00PM
WEDNESDAY JULY 8

THURSDAY July 9

REGISTRATION 7:30AM-9:00AM

Cont. Breakfast 7:30AM-8:00AM

TECHNICAL SESSIONS 6
8:30AM-10:00AM

20 Dissertation Winners & Other Research
21 Water Supply Planning and Policy in Illinois
22 International Water Resource Problems

Break 10:00AM-10:30AM

TECHNICAL SESSIONS 7
10:30AM-12:00PM

23 Water Quality Monitoring, Modeling and Management
24 Approaches to Stormwater Management
25 Methods for Augmenting Water Supply

END OF TECHNICAL PROGRAM

TECHNICAL TOURS

Racine Pumping Station

1:30PM-3:30PM

2009 UCOWR AWARD WINNERS

Warren A. Hall Medal

Gerald E. Galloway
Univeristy of Maryland

Friends of UCOWR

Gretchen Rupp and M. J. Nehasil
Montana Water Center

Ronald D. Lacewell and Michele Zinn
Texas A & M University

Ph.D. Dissertation
Natural Science and Engineering

To be announced

Ph.D. Dissertation
Water Policy and Socioeconomics

To be announced

Education and Public Service

Alliance for Water Efficiency

Illinois-Indiana Sea Grant

2009 UCOWR AWARD WINNERS

Welcome

Urban Water Management: Issues and Opportunities is the theme of the 2009 UCOWR/NIWR Annual Conference in exciting downtown Chicago. With the term "infrastructure" in the news and on everyone's minds, are we entering a time of renewal of our aging drinking water, waste water, and storm water systems? Will we, community by community, meet the urban water challenges of the 21st Century? This important conference will include presentations on these topics as well as others as critical as pharmaceuticals in our drinking water and the water resource demands of "green" energy sources such as biofuels.

I would like to invite you to join us in downtown Chicago at the Marriott Courtyard hotel for an exciting and professionally rewarding conference – as well as our reception, annual awards banquet, technical, and recreational tours in the urban heart of the Midwest.

Jay Lund
President, Universities Council on Water Resources

CONFERENCE COMMITTEE

Dick Warner, University of Illinois Urbana-Champaign, Chair
Martin Jaffe, University of Illinois-Chicago
Tim Loftus, Chicago Metropolitan Agency for Planning
Jay R. Lund, University of California-Davis
Ari Michelsen, Texas AgriLife Research Center

Christopher Lant, SIUC, UCOWR Executive Director
Rosie Gard, SIUC, UCOWR Conference Coordinator
Lisa Merrifield, UIUC, Local Conference Coordinator
Farhat Jahan Chowdhury, SIUC, Publications Designer
Stanley Mubako, SIUC, Publications Designer

Universities Council on Water Resources (UCOWR) is an organization of universities, non-academic institutions, and international affiliates leading in water resources education, research, and public service. UCOWR institutional members and delegates are at the forefront of water resources related research and education. In addition to our annual national conference, UCOWR publishes ***The Journal of Contemporary Water Research and Education***. If you would like to join UCOWR, please visit our website at: www.ucowr.siu.edu or call (618) 536-7571.

National Institutes for Water Resources (NIWR) are the 54 university-based centers that were established by the federal Water Resources Research Act. They are charged with arranging for research that addresses water problems or expands understanding of water and water-related phenomena, aiding the entry of new professionals into the water resources fields, helping to train future water scientists and engineers, and transmitting research results to water managers and the public.

Plenary Speakers

Plenary Session 1 .....Chicago and the Great Lakes Compact.....Tuesday July 7, 8:30-10:00am

Michael Sturtevant has worked in the water industry for 28 years and has been with the Department of Water Management for the past 15 years. He presently is head of the Planning and Operations Section within the Bureau of Engineering Services. Prior to that he worked as a project manager for the engineering consulting firm, Pitometer Associates for 13 years where he conducted numerous hydraulic engineering studies with various utilities throughout the country. Michael graduated from Michigan Technological University with a Bachelor of Science in Civil Engineering. He is a member of AWWA and ASCE is a registered professional engineer in Illinois.

David Naftzger serves as Executive Director of the Council of Great Lakes Governors. David facilitated the negotiation of the Great Lakes-St. Lawrence River Basin Water Resources Compact. He also oversees six foreign trade offices promoting State exports; the regional biomass energy program; and, the regional tourism partnership. Previously, David was the National Conference of State Legislatures' director for agriculture and international trade in Washington, D.C. David earned a Master's degree in Government from the London School of Economics. He holds a Bachelor's degree in Political Science from DePauw University and studied at the University of Freiburg, Germany.

Plenary Session 2.....Drought Preparedness across the Country.....Wednesday July 8, 8:00-10:00am

Mary Ann Dickinson is the founder and Executive Director of the Alliance for Water Efficiency, a non-profit organization dedicated to promoting the efficient and sustainable use of water in the United States and Canada. Based in Chicago, the Alliance works with water utilities, water conservation professionals in business and industry, planners, regulators, and consumers. Mary Ann has over 35 years of experience in water resources and water efficiency. She is a fellow at the Water Resources Center at the University of California at Santa Cruz, a Trustee and past Chair of the American Water Works Association National Water Conservation Division, and has presented numerous papers on water conservation in Spain, France, Australia, Korea, Jordan, Israel, Italy, Chile, China, Romania, Canada, and all across the United States.

Edmund G. "Ed" Archuleta has been manager of the El Paso Water Utilities Public Service Board since January 1989. A registered Professional Engineer in Texas, New Mexico, and Iowa, he is responsible for all aspects of water, wastewater, reclaimed water service, and storm water to the greater El Paso metropolitan area. He is an American Academy of Environmental Engineers Diplomat. He was appointed in June 2006 by President George W. Bush to the National Infrastructure Advisory Council. In 2008, he was appointed a Committee Member of the National Research Council, National Academy of Science and Engineering to assess water reuse as an alternative for meeting future water supply needs.

Alice Miller Keyes has served as advisor on water conservation and efficiency to the EPD Director since 2004. She helped develop Georgia's comprehensive statewide water management plan and coordinated the development of Georgia's Water Conservation Implementation Plan. Alice has 15 years of experience in water policy and planning. She serves as a charter board member of the Alliance for Water Efficiency and the Georgia WaterWise Council. She has a Master's in Conservation Ecology/Sustainable Development from University of Georgia and a Bachelor's in Biology from University of Southern Mississippi.

Plenary Session 3...Cutting Edge Research and Water for the Poor...Wednesday July 8, 3:30-5:00pm

Jim Heaney received his PhD in environmental and water resources engineering from Northwestern University. Currently, he is Professor and Chair of the Department of Environmental Engineering Sciences at the University of Florida. He specializes in the application of decision support systems to developing more sustainable urban water infrastructure systems including water supply, wastewater, and stormwater. Dr. Heaney is a former President of UCOWR. He has served on numerous committees of the National Academy of Sciences dealing with water and environmental issues. He is a Diplomate of the American Academy of Environmental Engineers and a Diplomate of the American Academy of Water Resources Engineers.

David Douglas

WELCOME AND INTRODUCTIONS 8:00am - 8:30 am

Jay R. Lund, UCOWR President, University of California, Davis
Upton Hatch, NIWR President, North Carolina WRRI; North Carolina State University

PLENARY 1 Chicago and the Great Lakes Compact 8:30 am – 10:00 am

Michael Sturtevant, Head, Planning and Operations, Bureau of Engineering Services, Chicago
David Naftzger, Executive Director, Council of Great Lakes Governors

---------- BREAK 10:00 am – 10:30 am ----------

CONCURRENT TECHNICAL SESSIONS 10:30 am – 12:00 pm

Session 2 Stormwater Management I

Survey of Stormwater BMP Maintenance Practices. ***John S. Gulliver,*** University of Minnesota, Minneapolis, MN; Andrew J. Erickson, _____; Joo-Hyon Kang, _____; Peter T. Weiss, _____; C. Bruce Wilson _____.

Improving Urban Stormwater Quality: Applying Fundamental Principles. ***Allen P. Davis,*** University of Maryland, College Park, MD; Robert G. Traver, Villanova University, Villanova, PA; William F. Hunt, North Carolina State University, Raleigh, NC.

Watershed Retrofit and Management Evaluation for Urban Stormwater Management Systems in North Carolina. ***William F. Hunt,*** Upton Hatch, Olha Sydorovych, and Kathy DeBusk, North Carolina State University, Raleigh, NC.

Application of the Analytic Hierarchy Process to Stormwater BMP Selection. ***Kevin Young,*** Tamim Younos, Randy Dymond, and David Kibler, Virginia Tech, Blacksburg, VA.

Session 3 Human Impacts on Water Resources

Human Interferences to Streamflow Dynamics: A Case Study of Urban Watersheds. ***Dingbao Wang,*** Ximing Cai, and Murugesu Sivapalan, University of Illinois, Urbana, IL.

Calibrating Hydrologic/Hydraulic Models of an Urban Watershed - Upper Salt Creek. ***Wade Moore,*** MWH Americas, Chicago, IL.

Comparative Modeling of Streamflow Response in an Intensively Managed Urban Watershed. ***Hongyi Li,*** Jiing-Yun You, Ximing Cai, and Murugesu Sivapalan, University of Illinois, Urbana, IL.

Integrating Science into Policy: The Use of Climate Information in Municipal Water Resources Management. ***Christine Kirchhoff,*** University of Michigan, Ann Arbor, MI.

Session 4 Agricultural Methods, Practices, and Policy

Rate Analyses for Irrigation Districts in South Texas. ***Allen Sturdivant*** and Edward Rister, Texas A&M University, Weslaco, TX; Ronald D. Lacewell, Texas A&M Agriculture Office of Federal Relations, College Station, TX.

Water Resource Requirements of Corn-Based Ethanol. ***Stanley Mubako*** and Christopher Lant, Southern Illinois University Carbondale, Carbondale, IL.

Water Policy in the Southern High Plains: A Farm Level Analysis. ***Justin Weinheimer*** and Phillip Johnson, Texas Tech University, Lubbock, TX.

Agency Problems in Irrigation Water Transfer: Who Works for What? ***John Wiener,*** University of Colorado, Boulder, CO.

---------- LUNCH ON YOUR OWN 12:00 pm – 1:30 pm ----------

CONCURRENT TECHNICAL SESSIONS 1:30 pm – 3:00 pm

Session 5 Stormwater Management II

Infiltration Pond Design Considerations for Cold Weather Conditions. ***Steve S. Nelson,*** Michael E. Barber, and David R. Yonge, Washington State University, Pullman, WA.

Implementing Watershed-Based Green Infrastructure for Stormwater Management: Case Study in Blacksburg, Virginia. ***Meredith Warren*** and Tamim Younos, Virginia Tech, Blacksburg, VA.

Integration of Education, Scholarship, and Service through Stormwater Management. ***Robert G. Traver,*** Andrea Welker, and Bridget Wadzuk, Villanova University, Villanova, PA.

Stormwater Management for a Record Rainstorm in Chicago. ***Stanley A. Changnon,*** University of Illinois, Champaign, IL.

Session 6 Ecosystem Impacts and Management Practices

Toward Identifying Optimal Best Management Practices for Watershed Management of Water Quality. ***M. Edward Rister,*** Ronald D. Lacewell, Taesoo Lee, Raghavan Srinivasan, Balaji Narasimhan, Texas Agrilife Research, College Station, TX; Allen W. Sturdivant, Texas AgriLife Research and Extension Center, Weslaco, TX; Clint Wolfe, David Waidler, Texas AgriLife Research and Extension Urban Solutions Center, Dallas, TX; Darrel Andrew, Mark Ernst, Jennifer Owens, Tarrant Regional Water District, Fort Worth, TX.

Impacts of Road Salt on Water Resources in the Chicago Region. ***Walton Kelly,*** Samuel V. Panno and Keith C. Hackley, Illinois State Geological Survey, Champaign, IL.

McDowell Grove Dam Removal. ***Kristine Meyer,*** Christopher B. Burke Engineering West, Ltd., St. Charles, IL.

Determining Optimal Reservoir Release for Both Water Supply and Ecosystem Restoration. ***Yi-Chen Yang*** and Ximing Cai, University of Illinois, Urbana, IL.

Session 7 International Water Supply Policies and Practices

Sustainable Control of Water-Related Infectious Diseases: A Review and Proposal for Interdisciplinary Health-Based Systems Research. ***Stuart Batterman,*** Jonathan Bulkley, Joseph Eisenberg, Rebecca Hardin, Margaret Kruk, Elisha Renne, Maria Lemos, Bhramar Mukherjee, Anna M. Michalak, Howard Stein, Cristy Watkins, and Mark Wilson, University of Michigan, Ann Arbor, MI.

Water in Pune District, Maharashtra State, India: Economic, Environmental and Management Issues. ***Subhash Bhagwat,*** University of Illinois Institute for Natural Resources Sustainability, Champaign, IL.

Community Mobilization Models for Safe Water Supply: Experiences from the Developing World. ***Farhat Chowdhury,*** Southern Illinois University Carbondale, Carbondale, IL.

Ergonomic Aspects in the Bottled Water Delivery in Ciudad Juarez, Chihuahua, Mexico. ***Marana-Teresa Escobedo,*** Salvador Noriega Morales, and Jorge A. Salas Plata Mendoza, Universidad Autonoma de Ciudad Juarez.Ciudad Juarez, Chihuahua, Mexico.

---------- BREAK 3:00 pm – 3:30 pm ----------

CONCURRENT TECHNICAL SESSIONS 3:30 pm – 5:00 pm

Session 8 Balancing Urban Water Supply and Demand

Urban Water Demand Analysis of Five Border Cities of Northwestern Mexico. ***Josue Medellin-Azuara,*** University of California-Davis, Davis, CA.

Water Sustainability: Results of the Army Installation Water Study. ***Natalie Myers,*** US Army Corps of Engineers, ERDC/CERL, Champaign, IL.

Water Demand and Supply Outlook for the Greater Chicago Area. ***Benedykt Dziegielewski,*** Southern Illinois University Carbondale, Carbondale, IL.

Revealing the Trade-Offs When Aiming for a Quantitative Balance in England's River Rother. ***John Joyce,*** IPA Energy + Water Economics, London, England; Benoit Grandmougin, ACTEON, Colmar, France.

TUESDAY, JULY 7, 2009

Session 9 Stormwater Management Models

Hydrologic and Hydraulic Modeling of the Tunnel and Reservoir Plan System in Northeastern Illinois. ***Arthur Schmidt*** and Marcelo H. Garcia, University of Illinois, Urbana, IL; Kevin Fitzpatrick, Joseph P. Sobanski and Richard Lanyon, Metropolitan Water Reclamation District of Greater Chicago, Chicago, IL.

Hydrologic Modeling of the Racine Pumping Station Service Area. ***Yovanni Catano,*** Marcelo H. Garcia, University of Illinois, Urbana, IL.

Flow Structure and Hydraulic Capacity for Dropshafts: Application to Tunnel and Reservoir Plan Project, Chicago, Illinois. ***Jorge Abad,*** Yovanni A. Catano-Lopera, and Marcelo H. Garcia, University of Illinois, Urbana, IL.

Laboratory and CFD Modeling of a Vortex Flow Restrictor. ***Andrew Waratuke,*** Yovanni Catano, and Marcelo H. Garcia, University of Illinois, Urbana, IL.

Session 10 Pharmaceuticals and Personal Care Product Impact on Water Quality

Pharmaceuticals and Personal Care Products (PPCPs), Hormones, and Alkylphenol Ethoxylates (APEs) in the North Shore Channel of the Chicago River - Part 1: Concentrations in Fish Tissue and Analysis of Reproductive Impairment. ***Elizabeth Murphy*** and Todd Nettesheim, USEPA Great Lakes National Program Office, Chicago, IL. (et al.)

Pharmaceuticals and Personal Care Products in the North Shore Channel of the Chicago River: Part II - Concentrations in Effluent and the Receiving Stream. ***Todd Nettesheim*** and Elizabeth Murphy, USEPA Great Lakes National Program Office, Chicago, IL. (et al.)

Pharmaceutical Compounds in Water and Wastewater: An Overview. ***P.T. Srinivasan,*** Metropolitan Water Reclamation District of Greater Chicago, Chicago, IL.

RECEPTION AND POSTER SESSION 6:00 pm – 8:00 pm

Marriott Lower Level Foyer

The DuPage River Salt Creek Workgroup: Applied Science in Action, ***Andrea Cline*** and Stephen McCracken, DuPage River Salt Creek Workgroup, Naperville IL.

Evaluation of Urban Stormwater Best Management Practices: Chicago Streetscapes Program. ***James Duncker,*** U.S. Geological Survey, Urbana, IL.

Microbial Pathogens in Tap Water at Rural Communities of North Mexico. ***Juan Pedro Flores-Margez,*** Universidad Autonoma de Ciudad Juarez, Ciudad Juarez, Chihuahua, Mexico. (et al.)

Beneficial Uses of Saline Electric Plant Cooling Tower Reject Water, ***Girisha Ganjegunte,*** Robert Braun, Amy Eddins, Oscar Guerrero, and Elias Montoya, Texas AgriLife Research Center, El Paso, TX; Calvin Trostle, Texas Agrilife Research and Extension Center, 1102 E. FM 1294, Lubbock, Texas 79403.

Enhancing Community Welfare and Sustainability through Improved Water Management within an Integrated Agro-Environmental System, ***Brian Hurd,*** Alexander Fernald, and Carlos Ochoa, New Mexico State University, Las Cruces, NM; Jose Rivera, Janie Chermak, and William Fleming, University of New Mexico, Albuquerque, NM; Steve Guldan, New Mexico State University, Alcalde, NM; Vince Tidwell, Sandia National Laboratory, Albuquerque, NM; Marquita Ortiz, New Mexico Acequia Association, Santa Fe, NM.

Before the Flood: Public (Mis)perception of Flood Risk in the Sacramento San Joaquin Delta. ***Jessica Ludy,*** University of California, Berkeley, Berkeley, CA.

Map of Groundwater Recharge for the Twin Cities Metropolitan Area. ***John Nieber,*** Roman Kanivetsky, University of Minnesota, Saint Paul, MN; Boris Shmagin, South Dakota State University, Brookings, SD.

Linking Social Perceptions and Ecological Realities through Watershed Health Integrated Research. ***Christopher Slemp,*** Charnsmorn Hwang, Mae Davenport, Karl Williard, Jon Schoonover, and Erin Seekamp, Southern Illinois University Carbondale, Carbondale, IL; Joan Brehm, Illinois State University, Normal, IL

WEDNESDAY, JULY 8, 2009

PLENARY SESSION II Drought Preparedness across the Country 8:00am – 10:00am

Mary Ann Dickinson, Executive Director, Alliance for Water Efficiency

Edmund G. "Ed" Archuleta, President and CEO, El Paso Water Utilities

Alice Miller Keyes, Manager, Georgia State Water Conservation

---------- BREAK 10:00 am – 10:30 am ----------

CONCURRENT TECHNICAL SESSIONS 10:30 am – 12:00 pm

Session 13 Streamflow and Urban Water Management

Hydrologic Modeling of Chicago's CSO Networks: An Innovative Approach. ***Joshua Cantone*** and Arthur Schmidt, University of Illinois, Urbana, IL.

Optimizing Streamflow Monitoring Network for the Salt Creek Watershed in Chicago Area. ***Jihua Wang,*** Ximing Cai, and Xiao Bao, University of Illinois, Urbana, IL.

Detailed Unsteady Flow Model Development for the Little Calumet River Watershed. ***Daniel Bounds,*** CDM, Chicago, IL; John P. Murray, Metropolitan Water Reclamation District of Greater Chicago, Chicago, IL.

Session 14 Planning for Water Sustainability

Water Resources Sustainability in the Twin Cities Metropolitan Area. ***Heidi Peterson*****,** John Nieber, and Roman Kanivetsky, University of Minnesota, Saint Paul, MN; Boris Shmagin, South Dakota State University, Brookings, SD.

Planning for Growth: Evaluating the Performance of California's Water Utilities. ***Ellen Hanak,*** Public Policy Institute of California, San Francisco, CA.

Understanding Target Audiences in Water Resources Programs. ***Karlyn Eckman,*** University of Minnesota, Saint Paul, MN.

Wastewater Management Options for a Divided City: The Case of Jerusalem. ***Nir Becker,*** Tel Hai College, Tel Hai, Israel.

Session 15 Impacts of Organic and Inorganic Contaminants on Water Quality

Organic Chemical Contaminants in Sediments of Urbanized Waterways. ***Joseph Delfino,*** University of Florida, Gainesville, FL.

Microbial Impact of Wastewater from Drains on the Rio Grande River. ***Juan Pedro Flores-Margez*** and Evangelina Olivas Enriquez, Universidad Autonoma de Ciudad Juarez, Ciudad Juarez, Chihuahua, Mexico; Jaime Iglesias Olivas, Texas A&M University, Clint, TX.

Comparing Band Ratio, Semi-Empirical, and Modified Gaussian Models in Predicting Cyanobacterial Pigments in Eutrophic Inland Waters. ***Anthony Robertson,*** Indiana University Purdue University Indianapolis, Indianapolis, IN.

Evaluation of Leaching from High Capacity Arsenic Sorbents under Simulated Landfill Conditions. ***Mohammed A. Keshta,*** Wendell Ela, and A. Eduardo Saez, University of Arizona, Tuscon, AZ.

---------LUNCH 12:00 pm – 1:30 pm -------

WEDNESDAY, JULY 8, 2009

CONCURRENT TECHNICAL SESSIONS 1:30 pm – 3:00 pm

Session 16 Monitoring Water Quality and Quantity

Michigan's Water Withdrawal Assessment Tool. ***John Bartholic,*** Jeremiah Asher and Saichon Seedang, Michigan State University, East Lansing, MI.

CSOs and Stream Water Quality: Solving the Puzzle with Automated Data Management. ***Alena Bartosova,*** William Gillespie, Michal Ondrejcek, and Tze Ling Ng, University of Illinois, Urbana, IL; John Frerich and Carrie Carter, Walter E. Deuchler Associates, Inc., Aurora, IL.

U.S. EPA Great Lakes National Program Office Nearshore Monitoring Using the TRIAXUS Towed Instrument Platform. ***Jacqueline Adams*** **a**nd Elizabeth K. Hinchey Malloy, Illinois-Indiana Sea Grant, Chicago, IL; Paul J. Horvatin, Glenn Warren, and Jeffrey May, USEPA Great Lakes National Program Office, Chicago, IL.

Smart Pipe – Nanosensors for Monitoring Water Flow in Public Water Systems. ***Yu-Feng Lin,*** University of Illinois, Urbana, IL; Chang Liu, Northwestern University, Evanston, IL.

Session 17 Water Policy: Planning, Implementation, and Management

Implementing Executive Order 2006-1: Water Supply Planning in Northeastern Illinois. ***Tim Loftus*** and Amy M. Talbot, Chicago Metropolitan Agency for Planning, Chicago, IL.

Development of the Cook County Watershed Management Ordinance. ***William Sheriff*** and John P. Murray, Metropolitan Water Reclamation District of Greater Chicago, Chicago, IL.

Looking towards 2014: Transboundary River Governance in the Columbia River Basin. ***Lynette de Silva*** and Aaron T. Wolf, Oregon State University, Corvallis, OR; Barbara Cosens, University of Idaho, Moscow, ID.

Water Policy in Mexico: A Perspective. ***Jorge Salas Plata,*** Universidad Autonoma de Ciudad Juarez, Ciudad Juarez, Chihuahua, Mexico.

Session 18 Groundwater Conservation and Management

Ogallala Aquifer Conservation: Water Policy Alternatives for the Texas Panhandle. ***Lal Almas,*** West Texas A&M University, Canyon, TX.

The Impact of Urban Form on Groundwater Sustainability: Modeling and Policy Implications. ***Moira Zellner,*** University of Illinois at Chicago, Chicago, IL; Howard W. Reeves, USGS Michigan Water Science Center, Lansing, MI.

A Spatial-Dynamic Model of the Economics of Groundwater Contamination. ***Yusuke Kuwayama*** and Nicholas Brozovic, University of Illinois, Urbana, IL.

Effects of Urbanization on Groundwater Systems – Implications for Urban Water Management. ***John Sharp,*** University of Texas, Austin, TX.

---------- BREAK 3:00 pm – 3:30 pm ---------

PLENARY SESSION III Cutting Edge Research and Water for the Poor 3:30– 5:00 pm

Jim Heaney**,** Professor and Chair, Department of Environmental Engineering Sciences University of Florida

David Douglas, Founder and President, Water Advocates

BANQUET & AWARDS CEREMONY 7:00 pm – 9:00 pm

Marriott Ballroom **Cash Bar Opens at 6:30pm**

CONCURRENT TECHNICAL SESSIONS 8:30 am – 10:00 am

Session 20 Dissertation Award Winner Presentations and Other Research

Presentation by winner of 2009 Ph.D. Dissertation Award in Natural Science and Engineering (tba)

Presentation by winner of 2009 Ph.D. Dissertation Award in Water Policy and Socioeconomics (tba)

Economic Impacts of Rio Grande Salinity. ***Ari M. Michelsen*** and Zhuping Sheng, Texas AgriLife Research, Texas A&M University, El Paso, TX; Tom McGuckin and Bobby Creel, New Mexico State University, Las Cruces, NM; Ron Lacewell, Texas A&M University, College Station, TX.

Session 21 Water Supply Planning and Policy in Illinois

Providing the Basis for Understanding a Geologically and Hydrogeologically Complex Region. ***David Larson,*** Steve Brown, and Jason Thomason, Illinois State Geological Survey, Champaign, IL.

Water Rates and Rate Structures in Northeast Illinois. ***Margaret Schneemann,*** Illinois-Indiana Sea Grant, Champaign, IL.

Residential Water Demand Analysis in the Chicago Metropolitan Area. ***Taro Mieno*** and John Braden, University of Illinois, Urbana, IL.

Reconciling the Needs of Water Utilities and Attitudes of the General Public with Regional Water-Supply Planning in Northeastern Illinois. ***Sandy Perpignani*** and Timothy T. Loftus, Chicago Metropolitan Agency for Planning, Chicago, IL.

Session 22 International Water Resource Problems

Economic Impact of Water Conservation in Local Harvesting Structure – An Analysis. ***Anuradha Baskaran,*** N.K. Ambujam, and K. Karunakaran, Anna University, Chennai, India; B. Rajeswari, Queen Mary's College, Channai, India.

Cleaning of Cooling Tower Water Using EDTA-Modified Natural Fibers. ***Jamil Rima*** and Maurice Abourida, Lebanese University, Fanar, Lebanon.

Characterizing Intentional Contamination Events in Water Distribution Systems: Application of Support Vector Machines. ***Mehdy Amirkhanzadeh Barandouzi*** and Reza Kerachian, University of Tehran, Tehran, Iran.

--------- BREAK 10:00 am – 10:30 am ---------

CONCURRENT TECHNICAL SESSIONS 10:30 am – Noon

Session 23 Water Quality Monitoring, Modeling and Management

Illinois Urban Manual Update Initiative: The Process of Revising a Book of Technical Standards to Keep up with NPDES Phase II Regulations and the Growing Industry of Erosion and Sediment Control. ***Jim Nelson,*** Association of Illinois Soil and Water Conservation Districts, Springfield, IL; Kelsey Musich, Kane DuPage Soil and Water Conservation District, DuPage, IL.

Qualitative Evaluation and Review of Economic Impacts of Water Quality Standards in the Truckee River Basin, Nevada. ***Alan McKay,*** Desert Research Institute, Reno, NV.

Three-Dimensional Water Quality Modeling of the Chicago River. ***Xiaofeng Liu,*** Sumit Sinha, Nahil Sobh, and Marcelo H. Garcia, University of Illinois, Urbana, IL.

Short and Long Term Two-Dimensional Water Quality Modeling for Bubbly Creek, Chicago, Illinois. ***Davide Motta,*** Jorge D. Abad, and Marcelo H. Garcia, University of Illinois, Urbana, IL.

Session 24 Approaches to Stormwater Management

Frozen Soil Impacts on Stormwater Infiltration Treatment BMP Designs. ***Michael Barber,*** Washington State University, Pullman, WA; Zain Al-Houri, Applied Science Private University, Amman, Jordan.

Chicago's Deep Tunnel - History, Progress and Challenges. ***Marcella Landis,*** Kevin Fitzpatrick, and Justine Gembala, Metropolitan Water Reclamation District of Greater Chicago, Chicago, IL.

Stormwater Management and Water Conservation at Institutions of Higher Learning: Models for Urban Water Issues. ***Tammy Parece,*** Tara McCloskey, and Tamim Younos, Virginia Polytechnic Institute and State University, Blacksburg, VA.

The Application of Innovative Stormwater Management Approaches to Develop the Calumet-Sag Detailed Watershed Plan. ***Tim Coleman,*** CH2M Hill, Chicago, IL; Jonathan Grabowy, Metropolitan Water Reclamation District of Greater Chicago, Chicago, IL.

Session 25 Methods for Augmenting Water Supply

Potential of Rainwater Harvesting to meet Urban Water Demand in the Texas Panhandle. ***Lal Almas*** and Tamara R. Sagniere-Guerrero, West Texas A&M University, Canyon, TX.

Rainwater Harvesting in Urban Environments: Opportunities and Challenges. ***Tamim Younos,*** Caitlin Grady, and Tara McCloskey, Virginia Polytechnic Institute and State University, Blacksburg, VA.

Rule-Based Storage Accounting: Injecting Transparency into Water Supply Operations. ***Michael C. Farmer,*** Texas Tech University, Lubbock, TX.

Managed Underground Storage of Recoverable Water Systems to Augment Urban Water Supplies. ***Zhuping Sheng*** and Yi Liu, Texas Agrilife Research Center, El Paso, TX.

END OF TECHNICAL PROGRAM

TECHNICAL TOURS (SEE OPPOSITE PAGE FOR DETAILS)

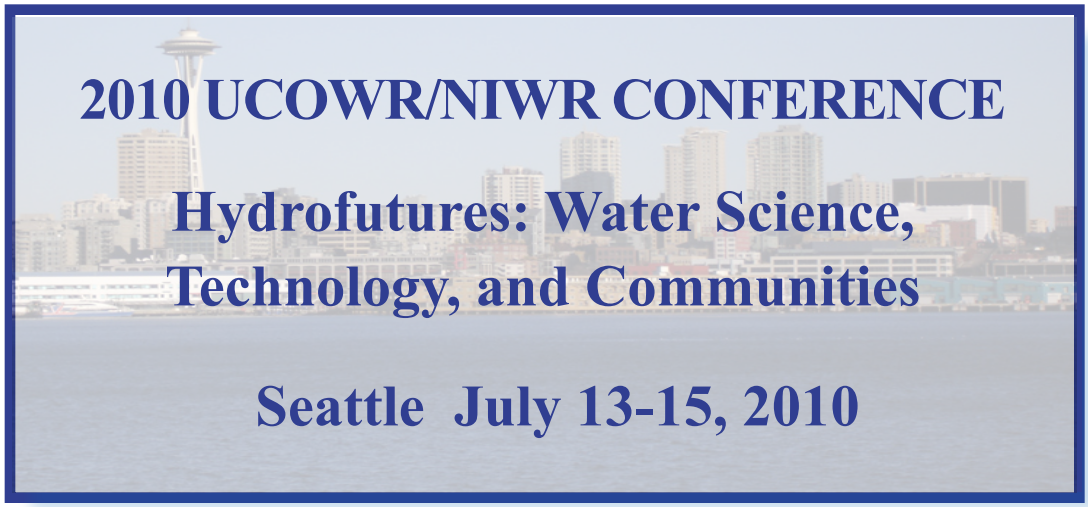
Stickney Water Reclamation District/Biosolid Drying Fields/McCook Water Reservoir
Monday July 6, 2009, 1:30 PM - 4:00 PM

Metropolitan Water Reclamation District Boat Cruise
Monday July 6, 2009, 4:00 PM - 7:00 PM

Racine Pumping Station
Thursday July 9, 1:30-3:30 PM

SUGGESTED RECREATIONAL TRIPS (SEE PAGE 14 FOR DETAILS)

H20=Life exhibit at the Field Museum
Chicago Architecture River Cruise



Governor's Conference on the Illinois River

Basic Information

Title:	Governor's Conference on the Illinois River
Project Number:	2008IL200B
Start Date:	2/1/2008
End Date:	11/1/2009
Funding Source:	104B
Congressional District:	15th
Research Category:	Not Applicable
Focus Category:	Education, None, None
Descriptors:	
Principal Investigators:	Lisa Merrifield, Jennifer Fackler

Publication

The Governor's Conference on the Illinois River is held biennially in odd years. The next conference will be held on October 20-22, 2009 in Peoria, Illinois. IWRC cosponsors the conference by serving on the planning committee and designing the abstract book and conference proceedings. This year, IWRC staff member, Lisa Merrifield, has also participated in the Local Action subcommittee and secured a speaker on implementing pharmaceutical take back programs. Merrifield will also be moderating a session on local action success stories with respect to the Illinois River.

The Governor's Conference on the Illinois River web site is available at http://www.conferences.uiuc.edu/ilriver/.

USGS Summer Intern Program

None.

Student Support					
Category	**Section 104 Base Grant**	**Section 104 NCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	2	0	0	0	2
Masters	1	3	0	0	4
Ph.D.	2	2	0	0	4
Post-Doc.	0	0	0	0	0
Total	5	5	0	0	10

Notable Awards and Achievements

Approximately 200 people attended Water 2008 in Champaign, Illinois to network and discuss the latest water resources science and its application to Illinois water ways.

Research recently completed by John Nicklow, Southern Illinois University, resulted it a model that provides watershed management institutions with a useful tool for watershed planning and development by providing an optimal design, as well as multiple, near-optimal design alternatives to accommodate unmodeled objectives.