

Stream chemical interactions within the urban environment: assessing the fate of nitrogen and mercury in a stream impacted by combined sewer overflows

Basic Information

Title:	Stream chemical interactions within the urban environment: assessing the fate of nitrogen and mercury in a stream impacted by combined sewer overflows
Project Number:	2009CT207B
Start Date:	3/1/2009
End Date:	2/28/2011
Funding Source:	104B
Congressional District:	2
Research Category:	Water Quality
Focus Category:	Nutrients, Surface Water, Wastewater
Descriptors:	None
Principal Investigators:	Joseph T Bushey

CONNECTICUT INSTITUTE OF WATER RESOURCES

Project Title: Dynamics of nitrogen loading and speciation in urban combined sewer catchments: An assessment of the effects of flow conditions

QUARTERLY REPORT

Period: April 2010 – May 2011

Submitted: June 2, 2011

PRINCIPAL INVESTIGATOR

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ADDITIONAL PROJECT PARTICIPANTS

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OVERVIEW:

Due to challenges encountered with the pore water samplers in the Park River, efforts during the second year of the project (April 2010 – May 2011) have focused on characterizing shifts in DOC quality according to source and then to assess the influence of those DOC shifts on mercury (Hg) binding. The nature of the bed sediment in the North Park River and vandalism prevented accurate collection of pore water samples from the range of sites. Field equipment vandalism combined with graduate student interest in DOC quality led to the shift in emphasis. Monthly stream water samples are still being collected to assess base flow changes along with event sample collection associated with separate project. Regarding DOC quality characterization, $SUVA_{254}$ is being used as a surrogate for quality during events. This is to be supplemented by fluorescence and electron emission spectroscopy (EEMS) on select samples. Finally, DOC hydrophilic and hydrophobic fractions have been isolated for characterization and will be utilized in laboratory sorption experiments to assess potential shifts in Hg mobilization and bioavailability with source.

While the focus of the project has shifted towards DOC characterization, a methodology has been developed by another student for laboratory assessment of denitrification potential for the sediments in the North Park River and to examine the potential influence of shifts in N-source on denitrification in a laboratory setting. To date, materials have been ordered and a methodology is being established to perform laboratory work and to assess shifts in microbial populations.

Accomplishments to date:

- Finalized sampling site selection
- Obtained site access
- Hired and trained a graduate student to execute sampling and chemical analysis
- Established method for DOC characterization and fractionation
- Collection of monthly stream water samples (November 2009)
- Collected sediment samples (May 2010)
- Installed water level loggers (June 2010)
- Set up sorption experiments for Hg-DOC interactions (June 2011)

RESEARCH AND EDUCATIONAL ACTIVITIES:

Field Deployment:

Dr. Bushey and Mr. Perkins from the University of Connecticut Center for Environmental Sciences and Engineering made an initial evaluation of perspective field sites in April 2009 in association with a related project for The Metropolitan District Commission. This was followed by two additional site visits by Dr. Bushey during Summer 2009 and by Dr. Bushey and Ms. Mendes in November 2009. Based on these initial discussions regarding The MDC study, a stream reach was selected to bracket the influence of combined sewer overflows (CSOs) and untreated wastewater on water quality in the North Park River (NPR), in Northwestern Hartford (CT). Concerns remained regarding the suitability of the field sampling sites relative to (1) the CT IWR study objectives, (2) the physical potential to install and maintain porewater samplers, and (3) site access approval. Based on preliminary site visits, four sites were selected within the initial stream reach for stream water sampling: UConn Law School, Albany Avenue, University of Hartford and Portage Road moving upstream, respectively (Figure 1). These four sites were approximately equally-distributed along the reach with two each above and below the uppermost CSO. Site access for the respective sites was obtained in Fall 2009 during discussions with homeowners (Portage Rd), the University of Hartford, the University of Connecticut Law School and Hartford and MDC personnel (Albany Ave). Additional site selection for DOC characterization was finalized in Fall 2010 to include the Hartford WPCF influent and effluent streams, impervious surface runoff and a forested site in the headwaters of the NPR.

Equipment

Following site selection, the samplers and flow monitoring devices were ordered. Equipment was ordered and porewater samplers were designed based on an installation approach. The installation approach was selected over composite sampling using a temporary pumping probe due to the consistent potential for the permanent devices. A sediment sampler, flow-meter and two water chemistry probes were ordered and prepared for use. Sufficient 1-ft and 2-ft plastic sediment core sleeves were ordered to collect the proposed number of sediment cores from the sites.

For porewater sampling, 30 mL Teflon vials were ordered with one transfer port on the tip. Holes were drilled into the sides of the vials to allow for uniform water flow into the vials during sampling. The smallest possible drill bit was used to minimize the entrainment of solids during sampling. Additionally, the sediment corer was retrofitted to enable easy installation of the porewater samples at the appropriate depth (Figure 2). A prototype temporary porewater sampling device also was explored and constructed due to potential issues with the permanent installations and site channel sediment composition and security as discussed below.

Student Training

In addition to the set up of instrumentation, a graduate student, Mykel Mendes, has been hired and trained. Due to the timing of the grant, the student did not begin until August 2009. However, in this short time frame, the student has been trained by Dr. Bushey and CESE personnel on laboratory protocol as well as the analysis of dissolved organic carbon (DOC), anions and mercury (Hg). Ms. Mendes has also investigated DOC characterization techniques and set up instrumentation for fractionating and isolating DOC in the UConn laboratory. As with N speciation shifts, the investigation of DOC quality in an urban setting is lacking. Additionally, Ms. Mendes (MS) has become familiar with sampling and field work as well as obtained knowledge of the relevant research in the field.

A second student (Nakita Horrell, MS) was hired in association with the MDC/DEP project and has established a methodology for examining the influence of N shifts on denitrification in a laboratory setting. The lack of suitability of the NPR for in-situ sediment assessment required a shift in the approach towards a laboratory setting, particularly a microbiological assessment. However, the cores previously collected in association with the CTIWR project will be utilized to assess denitrification potential via microbial population dynamics.

Sampling and piezometers installation

Stream water sampling was initiated in November 2009 following the granting of site access. Samples were collected at each of the four sampling sites for Hg speciation, DOC characterization, anions and metals. Monthly stream samples have been collected through April 2011 and are planned to continue to establish a seasonal baseline for the watershed.

Bed type and suitability were examined for porewater samplers during the initial stream water sampling at the four sites in November 2009 (Figure 1). The Portage Road site was eliminated for porewater samplers due to the bedrock stream bed characteristics. At the UConn Law School site, the stream channel is composed of a thick clay layer. However, a sandy layer exists near rip-rap installed to protect a recently modified MDC sewer pipe crossing beneath the channel. Three samplers were installed in this sandy layer as these relatively exchangeable sites are Denitrification and methylation hotspots. The transect of three porewater samplers at the Albany Avenue site was installed perpendicular to the channel (Figure 3) at an approximate depth of 4 in to the top of the sampler. This depth was deeper than initially intended but necessary to prevent the sampler from washing downstream during high flow. The two transects at the University of Hartford site included two samplers in the stream channel at 4 in depth with four samplers installed in sand/gravel bar on a bend in the river (Figure 4). Two samplers were installed at different depths of the bar, one shallow (8 in below surface) and one deep (22 in below surface). The transects at the UConn Law School stream channel site were installed similarly to those at Albany Ave.

At the UConn Law School, a small side channel which floods during elevated discharge conditions was instrumented with porewater samplers as a thick littoral layer existed over the clay layer. However, two of the lysimeter tubes were vandalized in the month following installation while the others filled with clay making pumping difficult. The stream bank samplers and one of the stream transects at the University of Hartford location were also vandalized. Finally, a decision was made not to install porewater samplers in the small pond on the University of Hartford campus in lieu of sediment core collection. Due to vandalism we are re-exploring the temporary porewater collection device as described by the USGS. Permanent samplers are difficult and costly to install particularly given the lack of protection from vandalism afforded at the urbanized sites. However, initial pumping tests in April-May 2010 also demonstrated the difficulty in obtaining accurate porewater samples from the installed lysimeters. Due to the clay lens dominating the stream bed we had selected relatively rocky locations in which to install our samplers. In each case, surface water quickly is drawn into the porewater samplers during pumping. Therefore, we have since shifted to a laboratory-based microbial assessment of the influence of shifts in N speciation.

Initial discharge readings were to be calculated from readings across the channel, with channel morphology noted. However, this has proved difficult and inconsistent. A set of water level loggers was installed in June 2010 at the Portage Rd and the UConn Law School sites. These will be calibrated during multiple events to discharge using ISCO® discharge recorders in Summer 2011.

Additional sediment samplers are being installed in June 2011 to collect solids mobilized during events. These will be characterized for OC content as well as for CHNS, trace metals and anthropogenic organic compounds.

Dissolved Organic Carbon Characterization

A column was set up and utilized to separate the humic acid, fulvic acid, hydrophobic acid and hydrophilic acid fractions from 5 water sources: WPCF influent, WPCF effluent, impervious surface runoff, forested stream water and a sample collected at peak discharge at the UConn Law School site in late February 2011. Organic characteristics have been documented to reflect source contributions to the watershed and also to influence contaminant, particularly trace metal, mobilization. The DOC from each sample has been characterized according to SUVA₂₅₄, fluorescence, EEMS, size and characteristic fractionation. We are currently lyophilizing the final runoff sample collected in May 2011. Once finalized, we will analyze each DOC via NMR for basic characteristics (e.g., amino acid fraction) as well as for CHNS with a particular focus on the S content.

A 100 L sample was collected from each site, and filtered through precombusted Whatman GF/C glass fiber 0.45 µm filters into 50 L carboys and were acidified to a pH of 2.0 with hydrochloric acid. These samples were fractionated into hydrophobic (humic) and hydrophilic (non humic) fractions of DOC using analytical-scale column chromatography with DAX-8 Supelite resin (40-60 mesh) and XAD-4 Amberlite resin (20-60 mesh) according to published methods (Thurman and Malcolm, 1981; Aiken et al, 1992; Hood et al, 2003; Wang et al, 2009). The organic matter isolates were desalted, proton saturated, and lyophilized for use in the Hg-DOC sorption experiments. Total dissolved organic carbon was determined with a Tekmar Apollo 900 TOC analyzer. Additional surface water samples were collected in 500 ml trace-clean Teflon® bottles, filtered through precombusted Whatman GF/C glass fiber 0.45 µm filters and analyzed for total dissolved mercury via oxidation, purge, and trap, cold vapor atomic

fluorescence spectroscopy (CVAFS; EPA Method 1631). A spectral analysis of each sample and its isolates was obtained by measuring SUVA₂₅₄ and fluorescence. Fluorescence was determined on a spectrofluorometer equipped with a xenon arc lamp as the excitation source. A Matlab code was developed (M. Quaranta, personal communication) to separated the excitation emission matrix into contour plots using the Ex/Em and intensities of fluorescence maxima for characterization. High performance size exclusion chromatography (HPSEC) measured estimates of the molecular size of the DOC and an elemental analyzer will be used to estimate the percentages of carbon, nitrogen, hydrogen, and sulfur content of the DOC source.

Hg-DOC Sorption Analysis

An equilibrium dialysis ligand exchange (EDLE) experiment will be performed on each sample to observe the complexation potential of ionic mercury (Hg^{2+}) to the hydrophilic and hydrophobic fractions of freshwater DOC isolates (Hintelmann et al, 1997; Haitzer et al, 2002; 2003; Waples et al 2003). Dialysis CE 500 MWCO membranes were cleaned by immersing the membrane in DI water overnight and then rinsing several times with DI water. The membrane was stored at 4°C in DI water. Using about 20 cm length of dialysis tubing as the inner membrane (bag), 1.0 mg/L of the freeze dried organic matter was reconcentrated in 0.1 M KClO_4 and 0.01 M EDTA. This membrane was placed in an outside solution which is spiked with Hg^{2+} in 10% HCl in a 250 ml Teflon bottle. The outside solution was spiked with Hg^{2+} at concentrations from 1.0 to 25 ng/L. The bottles were placed on an end-over-end rotator for 24 hours in a dark room to reduce photo degradation of the organic matter. Sample aliquots were taken from inside and outside of the bag and analyzed for Hg^{2+} by EPA Method 1631 for cold vapor atomic fluorescence spectroscopy (CVAFS) and DOC from a Teledyne Tekmar Apollo 9000 TOC analyzer. Experiments were completed in triplicate for each type of DOM source with a control containing only EDTA and Hg^{2+} . The Hg^{2+} concentration inside the bag indicated the amount of Hg^{2+} bound to the organic matter and the Hg^{2+} outside represents the amount of the total (bound and unbound) Hg.

Laboratory Nitrogen Speciation Shift Impacts

The Park River sites are being assessed for potential shifts in microbial community diversity and function in response to shifting N species contributions. CSOs and impervious

surface runoff contribute significantly to N flux during precipitation events. The overarching objective of Ms. Horrell's project will be to determine potential impacts on microbial nitrogen cycling with urbanization. To address this objective she has developed a microfluidic device to directly assess microbial communities in the natural systems. We propose to deploy the microfluidic devices in the natural environment along the urbanization gradient of the NPR to assess impacts on the microbial community as well as to harvest microbial communities to conduct chemical assays in the laboratory. These will allow us to characterize the impact of chloride loading and to assess potential shifts due to N species shifts. Devices will be deployed for various time intervals to establish how long the device needs to be deployed in order to recruit enough microbes and the chloride gradient stability will be tested. This will be tested at an individual vernal pool location prior to deployment at other locations. Devices will be deployed at three Park River sites.

Nitrogen utilization assays

A technique also has been developed to assess the ability of microbial communities to utilize various N chemical species. The microbial community collected from the upstream Park River location theoretically represents a community that is primarily influenced by forested inputs with sporadic stormwater runoff from impervious surfaces. Downstream locations receive CSO inputs. Batch systems will be prepared using sediments from upstream and downstream locations with N as the limiting nutrient. The solutions will be spiked with various N species, either reduced or oxidized, and monitored for chemical speciation of N. This will provide a measure of N conversion and utilization in the sediments similar to that proposed using the in-stream sediment pore water devices. The sediments can be brought back to the lab and incubated with 40 mL stream water collected from various levels of the urban gradient in Park River. Initial samples of the water will be analyzed for N species (NO_3^- , NO_2^- , NH_4^+ , and N_{org}) and dissolved organic carbon (DOC). The carbon content will be measured and additional carbon added to satisfy the Redfield ratio of 16:1 (C:N) so that N is the limiting nutrient for microbial respiration. The incubations will be carried out in mason jars and lids will be fitted with septa for sampling gas (N_2 , CO_2 , and O_2). Denitrification will be determined by monitoring the production of N_2 . The total duration for the incubations will be 30 days with samples collected at days 0, 10, 20, and 30. This will include water samples for N species and gas samples as described above. On days 0

and 30, the microbial community will be extracted from the sediment samples using commercially available kits and compared to the community structure that is present in the control sample. We will then be able to determine if the change in source impacts community structure and if this influences the N transformations.

Microbial community analysis

Microbial DNA will be extracted using commercially available kits and PCR used to amplify genetic material. The 16s rRNA gene from each genome will be sequenced and a comparison will be made between microbial communities as a function of the chloride gradient. This method will allow us to determine the abundance of the species present in the sample, but not specific species. This is a simple method that allows researchers to make relative comparisons between different communities. In this case, we are interested in the change in community diversity and this method is appropriate.

Future Work

- Collect stream water samples monthly
 - Analyze for Hg speciation, N speciation, metals, DOC characterization and ancillary parameters
- Perform Hg-DOC sorption experiments (June 2011)
- Analyze sediment samples for Hg speciation, metals, POC characterization, organic content and ancillary parameters (Fall 2011)
- Assess changes in microbial diversity due to shifting nitrogen sources (Summer 2011)
- Evaluate potential impact of shifting source on denitrification potential (Summer 2011)