

**D.C. Water Resources Research Center  
Annual Technical Report  
FY 2006**

## Introduction

This report summarizes the activities of the District of Columbia (DC) Water Resources Research Institute (the Institute) for the period of March 1, 2006 through February 28, 2007. This fiscal year was one of hope as we implemented strategic action plans to strengthen the viability of the Institute. More internal collaborations and partnerships were forged among Departments at the University of the District to provide relevant water resources research results and transfer information to assist policy makers and residents in the District of Columbia.

In an effort to assist in ensuring high municipal drinking water quality in the District of Columbia, the Institute has partnered with the Cooperative Extension Service (CES) Water Quality Education Program, the Agriculture Experiment Station (AES), the School of Arts and Sciences, and the School of Engineering and Applied Sciences to establish a Water Quality Testing Laboratory and an Environmental Simulation and Modeling Lab [http://www.udc.edu/docs/WRRIPoster\\_final.pdf](http://www.udc.edu/docs/WRRIPoster_final.pdf). The Water Quality Testing Lab will allow the Institute and the Water Quality Education Program the opportunity to serve as unbiased monitor of DC municipal drinking water quality through random sampling and testing of residential homes and public/private facilities. The Environmental Simulation Lab will develop and evaluate the application of mathematical models as a predictive tool for water resource management. Integrating monitoring and mathematical modeling, both labs will serve the research and training needs of our faculty, students as well as water and wastewater operators in the District.

The Institute collaborated with the School of Engineering and Applied Sciences at the University of the District of Columbia to sponsor the International Conference on Renewable Energy for Developing Countries (ICREDC-06) held April 6-8, 2006 at the OMNI Shoreham Hotel. This was one of the first conferences of this kind, addressing not only the needs and importance for renewable energy sources in the developing world but also what designs are available. Various applications were presented that could literally transform the lives of people, especially in the area of water availability. Mr. David Garman, the Under Secretary of Energy from the U.S. Department of Energy and Congressman Mike Honda (D) of California were guest speakers. The School of Engineering and Applied Sciences Center of Excellence for Renewable Energy (CERE) was inaugurated. A demonstration site, with a combination of a solar photovoltaic panel that can reposition itself to face the direction of maximum sun exposure and a wind powered turbine that can generate energy to pump water from a depth of more than 100 feet, was also highlighted. The Institute and the Cooperative Extension Service also added a solar powered weather station to the site.

In order to ensure consistency and continuity in programs, the Institute has hired a Project Assistant that will assist in coordinating its day to day activities. Ms. Mary Farrah, a former two year student intern with the Institute, is a 2006 summa cum laude graduate from the University of the District of Columbia with a BS in Environmental Science and an Associate degree in Water Quality. Mary will provide regular information for our website update and a bi-annual newsletter. WRRRI will continue to provide the District with inter-disciplinary research support to both identify and contribute to the solution of DC water resources problems.

## Research Program

The DC Water Resources Research Institute will continue to provide the District with inter-disciplinary research support to both identify and contribute to the solution of DC water resources problems. These research and educational projects provide students with essential practical skills required for future job opportunities and also allow faculty members access to new technologies and equipment that develop their expertise in water resource management. Four of the five project funded were completed and a no cost extension was granted on one.

In summary, Dr. Barkatt's project entitled, Silica and Siliceous Surfaces as Hosts for Hazardous Metals in Water indicated that the uptake of Cu and Pb from dilute aqueous solutions showed that the sorption of these ions on silica gel reached constant levels in less than two hours, indicative of the establishment of equilibrium. Also observed was that uptake gradually decreased with increasing temperature. Observed increase in uptake at higher pH was also in agreement with equilibrium constant expressions. Dissolved Pb was sorbed in preference to Cu. The effects of pre-treatment of silica gel on the sorption of Pb and Cu could be summarized by the following sequence:  $\text{HNO}_3 = \text{HCl} = \text{H}_2\text{SO}_4 \ll \text{H}_2\text{O} \ll \text{NH}_4\text{OH}/\text{NaNO}_3 < \text{NH}_4\text{OH}$  The use of silica gel with a larger value of specific surface area associated with narrower pores caused a slight decrease in the uptake of Cu and Pb. Dissolution of silica from the sorbent, unlike the sorption of Cu and Pb, was kinetically controlled. Thus, the extent of silica dissolution was observed to grow with increases in time, temperature, and specific surface area of the silica gel.

Dr. Glass in his project Monitoring the Effectiveness of Best Management Practice in Removing Pollutants from Urban Stormwater Runoff reported that in general, the results imply that the DC Sand filter as a BMP is working properly and is properly maintained. The bioretention BMP at Benning Road was not performing well during the study and it is believed to be undersized for the amount of runoff that results during an average storm in this area. The BaySaver did not perform well for the majority of this investigation; however, once the device was cleaned performance did improve substantially. All of the devices, no matter whether they were maintained or designed properly, did perform better than if there was no device present at all, for at least some parameters of interest.

Dr. Graczyk who published five peer-reviewed articles from his project Assessment of Waterborne Contamination with Human Pathogens in Tributaries of the Anacostia River Using Asiatic Clams (*Corbicula fluminea*) concluded the following: *Corbicula fluminea* collected from the Anacostia River are highly contaminated with human's waterborne pathogens such as *Cryptosporidium parvum*, *Giardia lamblia*, *Encephalitozoon intestinalis*, *Encephalitozoon hellem*, and *Enterocytozoon bieneusi*. Anacostia River water is contaminated with human pathogens. *Corbicula fluminea* clams are able to bioaccumulate waterborne parasites recovered from contaminated water in proportion to ambient concentrations. *Corbicula fluminea* clams can be used as bioindicators for waterborne contamination and for sanitary assessment of water quality. *Corbicula fluminea* clams have an important role in aquatic habitats because of filtering suspended particles, thereby clarifying the water and improving water quality. *Corbicula fluminea* clams are convenient for biomonitoring because they form dense Populations do not have economic value, are easily collected, have a relatively small size, and occur in large numbers that facilitate collection of a large sample.

Dr. Behera in the project Wet-Weather Flow Characterization for the Rock Creek through Monitoring and Modeling showed that Combined Sewer Overflows and stormwater runoff are a major source of water pollution problem for the District of Columbia. In order to address the problem, long-term monitoring of

runoff quality and modeling of drainage system is necessary. As an initial attempt, Dissolved Oxygen was measured at three locations at the Rock Creek during fall 2006 and spring 2007. From the measurement, it is found that there is no evidence of low dissolved oxygen at the measured location of the Rock Creek. As an alternative to continuous simulation and/or to complement continuous simulation, analytical probabilistic models of urban storm water management systems can be developed using derived distribution theory. This is a promising approach to develop analytical expression which can be easily used for solving runoff quantity and quality problems in urban areas.

Dr. MacAvoy was granted a no cost extension and thus provided a progress report. The project Nutrient flow and biological dynamics in the Anacostia River objectives were to evaluate the microbial and macroinvertebrate communities of several sites within the upper reaches of the Anacostia River, upstream and downstream of the combined sewage outflow are in Bladensburg Maryland. Specifically, we wished to 1) establish seasonal changes in biological oxygen demand, developing profiles of demand versus depth, 2) evaluate nutrient sources to bacteria, algae, invertebrates and characterize the origins of particulate organic matter through the use of the stable isotopes of sulfur, carbon and nitrogen, 3) characterize the composition of microbial communities at the different sites by DNA analysis, fatty acid profile and standard microbiological techniques. Pending a full analysis, a final report will be submitted.

Listed below are the five grants awarded to researchers for FY 2007 104B grant.

Title of Award: Decision Support System to Deal with Water Emergencies for Metropolitan DC Principal Investigator: Shivraj Kanungo, Ph.D. Associate Professor, Department of Decision Sciences, George Washington University, Tel: 202-274-3734, Email: kanungo@gwu.edu, Grant Award: \$15,000

Title of Award: Active Biomonitoring for PCB, PAH and Chlordane Pollutants in the Nontidal Sources of the Anacostia Watershed Principal Investigator: Harriette L. Phelps, Ph.D., Professor Emeritus, Dept of Biological and Environmental, Sciences, University of the District of Columbia, Email: hphelps@hers.com, Telephone: (301) 441-2207, Grant Award: \$14,464

Title of Award: Gradual Variation Analysis for Groundwater Flow in the District of Columbia Principal Investigator: Li Chen, Ph.D., Associate Professor, University of the District of Columbia, Email: lchen@udc.edu, (202) 274-6301 Grant Award: \$15,000

Title of Award: Modeling of Integrated Urban Wastewater System in the District of Columbia Principal Investigator: Tolessa Deksissa, Ph.D, Research Associate, University of the District of Columbia, Phone: 202-274-5273, E-mail: tdeksissa@udc.edu, Grant Award: \$14,876

Title of Award: Molecular Signaling by Environmental Arsenicals in Mammalian Cells Principal Investigator: Deepak Kumar, Ph.D. Assistant Professor, University of the District of Columbia, Email: dkumar@udc.edu, Telephone: (202) 274-5937, Grant Award: \$14,960

Our matching requirements were met with non federal in-kind contributions from the indirect cost waived by each university and cash match from the University of the District of Columbia. These research projects are related to DC drinking water quality, water chemistry and bio-monitoring of pollutants in Anacostia River and Rock Creek and will provide water quality training for graduate and undergraduate students in the District of Columbia.

# Silica and Siliceous Surfaces as Host for Hazardous Metals in Water

## Basic Information

<b>Title:</b>	Silica and Siliceous Surfaces as Host for Hazardous Metals in Water
<b>Project Number:</b>	2006DC76B
<b>Start Date:</b>	3/1/2006
<b>End Date:</b>	2/28/2007
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	District of Columbia
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Geochemical Processes, Toxic Substances, Solute Transport
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Aaron Barkatt, April L. Pulvirenti

## **Publication**

# **Silica and Siliceous Surfaces as Hosts for Hazardous Metals in Water**

Aaron Barkatt, April L. Pulvirenti, and Mohamad A. Adel-Hadadi  
Department of Chemistry  
201 Maloney Hall  
The Catholic University of America  
Washington, DC 20064

and

Edward R. Landa  
U.S. Geological Survey  
Reston, VA 20192

A Report

submitted to

DC Water Resources Research Institute  
University of the District of Columbia  
Building 52 Room 416A  
4200 Connecticut Avenue NW  
Washington, DC 2008

June 2007

# **Silica and Siliceous Surfaces as Hosts for Hazardous Metals in Water**

## **Executive Summary**

Systematic studies of the uptake of Cu and Pb from dilute aqueous solutions showed that the sorption of these ions on silica gel reached constant levels in less than two hours, indicative of the establishment of equilibrium. Consistent with this observation, the uptake gradually decreased with increasing temperature. Observed increase in uptake at higher pH was also in agreement with equilibrium constant expressions. Dissolved Pb was sorbed in preference to Cu. The effects of pre-treatment of silica gel on the sorption of Pb and Cu could be summarized by the following sequence:

$\text{HNO}_3 = \text{HCl} = \text{H}_2\text{SO}_4 \ll \text{H}_2\text{O} \ll \text{NH}_4\text{OH}/\text{NaNO}_3 < \text{NH}_4\text{OH}$

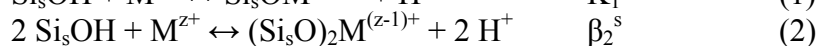
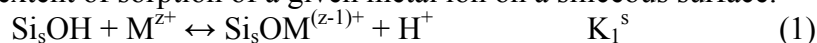
The use of silica gel with a larger value of specific surface area associated with narrower pores caused a slight decrease in the uptake of Cu and Pb. Dissolution of silica from the sorbent, unlike the sorption of Cu and Pb, was kinetically controlled. Thus, the extent of silica dissolution was observed to grow with increases in time, temperature, and specific surface area of the silica gel.



## Introduction

Sorption of polyvalent metal ions on siliceous surfaces is of great importance to water quality. For instance, if such sorption takes place on rocks or soils bordering a contaminated stream, it can facilitate removal of dissolved hazardous species such as Pb, Cr, Cu, Ni, Hg, U, or Ra ions from the water. On the other hand, sorption of such ions on small suspended particles in the water, such as corrosion products in water distribution systems, can facilitate the transport of hazardous species and reduce the efficiency of household filters in removing them from drinking water (Senftle *et al.*, 2007). Many studies of the applied aspects of the sorption of metal ions on the surfaces of siliceous solids (e.g., silica gel) have been performed. However, much work remains to be done in order to provide accurate models of the extent of sorption and its effects on water quality in contaminated environmental streams and water distribution systems.

Sorption of various metal ions on siliceous surfaces as a function of pH was characterized and the relative tendency of various ions to undergo sorption was established. The results were expressed in terms of models that describe the sorption equilibria of metal ions on siliceous surfaces in terms of complex formation between the metal ions and the surface silanol groups. These models assign equilibrium constants to such complex formation processes (Schindler *et al.*, 1976). These models account for the strong pH dependence of the extent of sorption of a given metal ion on a siliceous surface.



$\text{Si}_s\text{OH}$  denotes a surface-bound silanol group, and  $K_1^s$  and  $\beta_2^s$  are equilibrium constants. According to such models, the surface-bound silanol group  $\text{Si}_s\text{OH}$  behaves as a ligand similar to HOH, and the extent of sorption varies between 0% and 100% of the surface capacity (reflecting the number of surface-bound silanol groups) over a narrow pH range. For instance, in the cases of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ , this pH range is between about 4 and about 7, with the extent of sorption reaching 50% of ultimate capacity around pH 6.

However, such simple reaction schemes are not sufficient to account for all aspects of the sorption of metal ions from solutions, especially when such solutions contain constituents that form insoluble precipitates or complexes with the metal ions, or when the siliceous sorbent had been pre-treated with solutions containing such constituents. For instance, in the case of radium ions, very different results were obtained for the extent of sorption on fine quartz grains and also for the extent of desorption of Ra into EDTA solutions depending on whether these grains had been pre-washed with HCl or with  $\text{H}_2\text{SO}_4$  (Nirdosh *et al.*, 1987). Chelating agents such as EDTA, poly(ethylene amine) and N-[-3-(trimethoxysilyl) propyl]-ethylenediamine were found to have large effects on adsorption/desorption equilibria whether such reagents were present in the solution or on the siliceous surface (Nirdosh *et al.*, 1987; Ghoul *et al.*, 2001; Chiron *et al.*, 2003). Other studies on the sorption of radium ions also showed that differences in the nature of the siliceous sorbent were also very important (Ames *et al.*, 1983). In addition to the thermodynamic characteristics of silica-metal system, various system parameters also affect the sorption kinetics. For instance, as metal concentrations are decreased, charge

reversal occurs and a longer period of time is required for the system to reach equilibrium (Vithayaveroj *et al.*, 2003).

The present study was intended to explore in a systematic manner the effects of system parameters, including contact time, temperature, pH, specific surface area, weight-to-volume ratio, and pre-treatment of the sorbent in various environments, on the sorption of Cu and Pb ions on silica surfaces. In order to minimize the effects of uncontrolled impurities, pure silica gel was used as the sorbent.

## **Experimental**

Combined solutions of copper and lead were prepared by dissolving appropriate amounts of copper acetate dihydrate,  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , and of lead acetate trihydrate,  $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ , in de-ionized water. The pH of the combined copper/lead solutions usually did not require adjustment to bring it  $5.0 \pm 0.1$ . Whenever necessary, a slight adjustment with acetic acid was used to bring it to within this range. In several experiments, the pH of the combined solution was brought to  $8.0 \pm 0.1$  using sodium acetate. The reaction vessels consisted of 60-mL polyethylene bottles. The sorbents used in the experiments consisted of two varieties of silica gel. The sorbent most commonly used was silica gel, Merck, grade 10184, 7-230 mesh,  $100 \text{ \AA}$  pore size, Sigma-Aldrich 403601-100G, Batch # 10203AO, surface area  $300 \text{ m}^2/\text{g}$ . The other sorbent was silica gel, Merck, grade 10180, 70-230 mesh,  $40 \text{ \AA}$ , Sigma-Aldrich 403563-100G, Batch # 09018CD, surface area  $750 \text{ m}^2/\text{g}$ , distinguished from the former type of silica gel by having smaller pores and a larger surface area. Samples of the two types of silica gel were dissolved in warm dilute solution of HF and analyzed to determine the concentration of impurities using a Perkin-Elmer Plasma 400 ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometer). The results of the analysis are shown in Table 1.

Table 1  
Impurity Content of Silica Gel Sorbents

Impurity	Concentration, mg/kg	
	Merck grade 10184, 300 m <sup>2</sup> /g	Merck grade 10180, 750 m <sup>2</sup> /g
Ca	782	563
Na	358	558
Al	242	<10
Mg	113	69
Ti	75	5
Pb	<60	<100
K	37	20
Cr	20	20
Fe	11	<10
Ni	5	4
Cu	1	<2
Zn	1	1
Mn	<1	<1

Sorbent powders were used without pre-treatment or following a pre-treatment with de-ionized water, an acidic solution or a basic solution. The pre-treatment consisted of rotating a 5-g sample of the grade 10184 (300 m<sup>2</sup>/g) silica gel at 30 rpm for 50 hours with one of the following aqueous phases: de-ionized water, 2 M H<sub>2</sub>SO<sub>4</sub>, 4 M HCl, 4 M HNO<sub>3</sub>, 4 M NH<sub>4</sub>OH, or 4 M NH<sub>4</sub>OH + 3 M NaNO<sub>3</sub>. Each of the pre-treated samples was filtered using grade 42 Whatman filter paper. The solid accumulated on each filter paper was washed with 500 mL of de-ionized water. The final pH of the wash water was 5 in the cases of the samples pre-treated with H<sub>2</sub>SO<sub>4</sub>, HCl, or HNO<sub>3</sub> and 9 in the cases of the samples pre-treated with ammonia solutions. The last stage of the pre-treatment consisted of air-drying the samples at room temperature.

In each of the sorption experiments, a quantity of 0.5 g or 1.0 g of an as-received or pre-treated sorbent was placed in a polyethylene bottle, together with 50 mL of the combined Cu-Pb solution. Mixing was performed using either a TCLP rotator, operated at 30 rpm, or a magnetic stirrer. Contact times ranged between 2 and 240 hours. Temperatures varied between 1.5 and 40 °C. All experiments at temperatures other than ambient were carried out using a magnetic stirrer/hot plate. Experiments at a low temperature were conducted by placing the beaker containing the sorbent powder and the test solution within a larger beaker filled with ice water. At the end of each experiment, the bottle was removed from the rotator or stirrer. The mixture was filtered through a filter paper with very fine (2.5-µm) pores (Whatman grade 42), and the filtrate was collected. The solid sorbent accumulated on the filter was washed with 100 mL of de-ionized water, and the spent wash solution was collected for analysis. The starting solution, the filtrate and the used wash solution were analyzed for Cu, Pb and Si. The sorbent was then rotated with 10 mL of 0.1 M HCl for 16 hours, and the eluate was filtered through Whatman grade 42

filter paper and collected for analysis. Following the elution, the sorbent was washed with a second volume of 10 mL of 0.1 M HCl. The spent wash solution was then combined with the original eluate, and the combined 20 mL of acidic solution was analyzed. This procedure allowed determination of the amount of the amount of copper and lead adsorbed on the sorbent in two independent ways. One method was based on the subtraction of amounts of these elements in the filtrate and the de-ionized water wash from the corresponding amounts of these elements in the starting solution which was contacted with the silica gel. The other method was based on the determination of the amounts of Cu and Pb in the combined acidic eluate and acidic wash solution. In addition to the amounts of Cu and Pb sorbed on the silica gel, the amount of SiO<sub>2</sub> dissolved during the contact with the copper/lead solution and the subsequent water wash was also determined. The analysis of Cu, Pb and Si in the solutions was performed using a Perkin-Elmer Plasma 400 ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometer). The results of the Cu and Pb analysis were expressed in terms of the percentage of Cu or Pb initially present in the test solution that was taken up by the sorbent during the test period. The results of the Si analysis were expressed in terms of the percentage of the weight of the sorbent that was dissolved during the test period.

Five sets of sorption experiments were performed. The experimental conditions used in the experiments included in each test are summarized in Table 2.

Table 2  
Experimental Conditions

Set	Sorbent			Starting solution				Temperature, °C	Contact time, hours	Mixing method
	Material	Pre-treatment	Weight, g	Cu conc., mg/L	Pb conc., mg/L	pH	Volume, mL			
1	Merck 10184, 300 m <sup>2</sup> /g	DIW	0.5,1	5,10	5,10	5	50	20	2,6,24, 72,240	TCLP rotator
2	Merck 10184, 300 m <sup>2</sup> /g	DIW	0.5	10	10	5,8	50	1.5,20, 40	6,24	Magnetic stirrer
3	Merck 10184, 300 m <sup>2</sup> /g, Merck 10180, 750 m <sup>2</sup> /g	DIW, 2M H <sub>2</sub> SO <sub>4</sub> , 4M HCl, 4M NH <sub>4</sub> OH, 4MNH <sub>4</sub> OH +3M NaNO <sub>3</sub> , 4M HNO <sub>3</sub>	0.5	10	10	5	50	20	6,24	Magnetic stirrer
4	Merck 10184, 300 m <sup>2</sup> /g, Merck 10180, 750 m <sup>2</sup> /g	DIW, 2M H <sub>2</sub> SO <sub>4</sub> , 4M HCl, 4M NH <sub>4</sub> OH, 4MNH <sub>4</sub> OH +3M NaNO <sub>3</sub> , 4M HNO <sub>3</sub>	0.5	10	10	5	50	20	6,24	TCLP rotator
5	Merck 10184, 300 m <sup>2</sup> /g	DIW, 2M H <sub>2</sub> SO <sub>4</sub> , 4M NH <sub>4</sub> OH, 4MNH <sub>4</sub> OH +3M NaNO <sub>3</sub>	0.5	10	10	5	50	20	6,24	TCLP rotator

## Results

The results of the five sets of experiments outlined in Table 2 are shown in Tables 3-7, respectively.

The sorbent used in the first set of experiments (Table 3) was Merck grade 10184 silica gel (300 m<sup>2</sup>/g) without any pre-treatment.

Table 3  
Effects of time, solute concentration, solute concentration, and mass of sorbent on the sorption of Cu and Pb on silica gel

Amount of sorbent, g	Concentration of initial solution, mg·L <sup>-1</sup>		Time, hr	Amount of metal ion sorbed, %				Amount of silica dissolved, %
	Cu	Pb		Based on subtraction		Based on elution		
				Cu	Pb	Cu	Pb	
0.5	5	5	2	75.2	65.6	71.8	92.8	0.225
0.5	5	5	6	74.8	66.8	79.0	99.6	0.411
0.5	5	5	24	75.2	66.4	80.2	91.4	0.627
0.5	5	5	72	74.0	66.0	100.0	100.0	0.753
0.5	5	5	240	77.2	68.0	100.0	78.0	1.162
0.5	10	10	2	59.6	88.0	44.0	57.3	0.201
0.5	10	10	6	48.8	83.4	30.5	33.3	0.394
0.5	10	10	24	49.4	82.8	49.9	61.9	0.614
0.5	10	10	72	49.0	82.4	38.5	42.6	0.674
0.5	10	10	240	57.2	85.6	69.0	90.0	1.068
1.0	5	5	2	77.6	66.4	6.8	6.4	0.225
1.0	5	5	6	78.8	67.6	55.6	40.8	0.291
1.0	5	5	24	78.0	66.8	49.6	44.4	0.413
1.0	5	5	72	78.0	66.8	89.2	86.0	0.428
1.0	5	5	240	78.0	67.2	92.4	88.0	0.287

The type of silica gel used in the second set of experiments (Table 4) was the same as the one used in the first set (Merck grade 10184, 300 m<sup>2</sup>/g).

Table 4  
Effects of temperature, pH, and time on the sorption of Cu and Pb on silica gel

Temperature, °C	pH	Time, hours	Amount of metal ion sorbed, %				Amount of silica, dissolved, %
			Based on subtraction		based on elution		
			Cu	Pb	Cu	Pb	
1.5	5.02	6.0	12.5	56.0	9.4	16.2	0.079
1.5	5.02	6.0	7.7	28.8	9.1	16.6	0.083
1.5	7.98	6.0	54.6	61.7	32.0	41.3	0.563
1.5	7.98	6.0	47.3	56.7	19.2	21.5	0.507
21.0	5.02	6.0	0	0	6.7	11.6	0.165
21.0	5.02	6.0	5.5	10.3	6.2	9.1	0.175
21.0	7.99	6.0	56.2	63.9	25.4	29.4	1.545
21.0	7.99	6.0	53.9	54.6	36.1	40.9	0.766
40.2	5.02	6.0	0	4.2	8.1	11.8	0.449
40.2	5.02	6.0	5.2	13.3	9.0	13.5	0.501
40.2	7.99	6.0	71.5	73.9	45.1	34.2	1.371
40.2	7.99	6.0	68.2	71.2	46.0	37.6	1.363
1.7	5.01	27.7	46.3	75.6	13.5	33.2	0.126
1.7	5.01	27.7	0	55.8	13.2	25.8	0.128
1.7	7.96	27.6	43.4	31.7	5.4	8.2	0.458
1.7	7.96	27.6	30.9	40.5	5.7	8.9	0.528
19.7	5.01	26.2	0	57.0	15.5	27.9	0.058
19.7	5.01	26.2	4.6	48.0	12.4	24.1	0.417
19.7	7.96	27.1	34.1	11.6	5.0	7.0	0.901
19.7	7.96	27.1	27.3	21.7	5.4	7.6	1.020
39.3	5.01	25.1	0	53.1	14.8	27.7	1.262
39.3	5.01	25.1	0	11.8	18.6	90.5	0.881
39.3	7.96	25.4	32.1	9.9	6.2	10.3	1.476
39.3	7.96	25.4	42.8	35.4	5.4	8.4	1.301

The third set of experiments (Table 5) examined the difference in sorption behavior between the two types of silica gel and the effects of various pre-treatments.

Table 5  
Effects of type and pre-treatment of silica gel and of time on the sorption of Cu and Pb

Type of silica gel	Pre-treatment of silica gel	Time, hours	Amount of metal ion sorbed, %				Amount of silica, dissolved, %
			Based on subtraction		Based on elution		
			Cu	Pb	Cu	Pb	
Grade 10184, 300 m <sup>2</sup> /g	De-ionized water	6	71.0	86.5	49.9	77.0	0.415
Grade 10184, 300 m <sup>2</sup> /g	De-ionized water	6	69.9	87.2	33.9	48.3	1.095
Grade 10180, 750 m <sup>2</sup> /g	De-ionized water	6	79.9	90.7	40.9	64.3	0.319
Grade 10180, 750 m <sup>2</sup> /g	De-ionized water	6	65.0	83.7	41.8	65.2	0.717
Grade 10184, 300 m <sup>2</sup> /g	2 M H <sub>2</sub> SO <sub>4</sub>	6	44.3	64.8	21.0	37.5	0.167
Grade 10184, 300 m <sup>2</sup> /g	2 M H <sub>2</sub> SO <sub>4</sub>	6	19.2	36.6	13.5	26.9	0.235
Grade 10184, 300 m <sup>2</sup> /g	4 M HCl	6	29.4	38.6	13.2	24.3	0.116
Grade 10184, 300 m <sup>2</sup> /g	4 M HCl	6	36.9	56.6	11.6	21.1	1.279
Grade 10184, 300 m <sup>2</sup> /g	4 M NH <sub>4</sub> OH	6	99.5	98.7	79.4	82.0	0.627
Grade 10184, 300 m <sup>2</sup> /g	4 M NH <sub>4</sub> OH	6	98.9	98.4	26.9	26.3	2.261
Grade 10184, 300 m <sup>2</sup> /g	4 M NH <sub>4</sub> OH + 3 M NaNO <sub>3</sub>	6	55.3	75.9	42.1	62.6	2.837
Grade 10184, 300 m <sup>2</sup> /g	4 M NH <sub>4</sub> OH + 3 M NaNO <sub>3</sub>	6	87.4	79.4	90.0	84.7	1.393
Grade 10184, 300 m <sup>2</sup> /g	4 M HNO <sub>3</sub>	6	24.0	45.0	14.8	27.5	0.218
Grade 10184, 300 m <sup>2</sup> /g	4 M HNO <sub>3</sub>	6	17.9	26.9	14.6	26.1	0.186
Grade 10184, 300 m <sup>2</sup> /g	De-ionized water	24	64.1	79.5	36.0	50.1	0.920
Grade 10184, 300 m <sup>2</sup> /g	De-ionized water	24	62.0	81.5	49.7	78.6	0.730
Grade 10180, 750 m <sup>2</sup> /g	De-ionized water	24	51.4	77.0	45.5	68.6	0.759
Grade 10180, 750 m <sup>2</sup> /g	De-ionized water	24	84.5	92.8	45.5	68.9	0.911
Grade 10184, 300 m <sup>2</sup> /g	2 M H <sub>2</sub> SO <sub>4</sub>	24	93.5	93.2	15.3	28.5	0.400
Grade 10184, 300 m <sup>2</sup> /g	2 M H <sub>2</sub> SO <sub>4</sub>	24	96.2	94.9	15.5	29.3	0.364
Grade 10184, 300 m <sup>2</sup> /g	4 M HCl	24	15.6	30.4	14.6	25.3	0.285
Grade 10184, 300 m <sup>2</sup> /g	4 M HCl	24	6.9	18.7	9.6	17.9	0.362
Grade 10184, 300 m <sup>2</sup> /g	4 M NH <sub>4</sub> OH	24	98.1	96.8	42.3	42.1	2.520
Grade 10184, 300 m <sup>2</sup> /g	4 M NH <sub>4</sub> OH	24	99.0	97.7	66.4	65.5	1.018
Grade 10184, 300 m <sup>2</sup> /g	4 M NH <sub>4</sub> OH + 3 M NaNO <sub>3</sub>	24	94.3	89.5	83.9	88.9	1.557
Grade 10184, 300 m <sup>2</sup> /g	4 M NH <sub>4</sub> OH + 3 M NaNO <sub>3</sub>	24	84.6	90.8	72.4	76.6	1.281
Grade 10184, 300 m <sup>2</sup> /g	4 M HNO <sub>3</sub>	24	97.6	96.6	15.4	27.0	0.340
Grade 10184, 300 m <sup>2</sup> /g	4 M HNO <sub>3</sub>	24	39.7	58.4	15.5	28.8	0.466



The fourth set of experiments (Table 6) was similar to the third set, except that the mixing of the sorbent with the starting solution was performed using the TCLP rotator instead of a magnetic stirrer.

Table 6  
Effects of type and pre-treatment of silica gel and of time on the sorption of Cu and Pb

Type of silica gel	Pre-treatment of silica gel	Time, hours	Amount of metal ion sorbed, %				Amount of silica, dissolved, %
			Based on subtraction		Based on elution		
			Cu	Pb	Cu	Pb	
Grade 10184, 300 m <sup>2</sup> /g	De-ionized water	6	65.8	89.3			0.451
Grade 10184, 300 m <sup>2</sup> /g	De-ionized water	6	61.1	87.1	61.8	81.3	0.441
Grade 10180, 750 m <sup>2</sup> /g	De-ionized water	6	55.7	83.3	53.3	77.4	0.610
Grade 10180, 750 m <sup>2</sup> /g	De-ionized water	6	54.5	84.4	54.0	79.6	0.640
Grade 10184, 300 m <sup>2</sup> /g	2 M H <sub>2</sub> SO <sub>4</sub>	6	15.1	41.6	17.9	31.1	0.263
Grade 10184, 300 m <sup>2</sup> /g	2 M H <sub>2</sub> SO <sub>4</sub>	6	17.0	38.0	18.3	30.5	0.265
Grade 10184, 300 m <sup>2</sup> /g	4 M HCl	6	19.5	34.3	14.5	24.0	0.242
Grade 10184, 300 m <sup>2</sup> /g	4 M HCl	6	17.4	27.4	14.2	23.1	0.231
Grade 10184, 300 m <sup>2</sup> /g	4 M NH <sub>4</sub> OH	6	99.7	97.6	96.6	92.8	0.798
Grade 10184, 300 m <sup>2</sup> /g	4 M NH <sub>4</sub> OH	6	100.0	98.8	97.6	95.3	0.834
Grade 10184, 300 m <sup>2</sup> /g	4 M NH <sub>4</sub> OH + 3 M NaNO <sub>3</sub>	6	89.3	97.2	87.2	100.0	4.482
Grade 10184, 300 m <sup>2</sup> /g	4 M NH <sub>4</sub> OH + 3 M NaNO <sub>3</sub>	6	90.8	95.8	90.6	102.9	4.383
Grade 10184, 300 m <sup>2</sup> /g	4 M HNO <sub>3</sub>	6	21.6	35.8	17.1	28.1	0.282
Grade 10184, 300 m <sup>2</sup> /g	4 M HNO <sub>3</sub>	6	13.3	25.6	15.4	26.0	0.259
Grade 10184, 300 m <sup>2</sup> /g	De-ionized water	24	62.5	84.4	66.7	90.3	0.721
Grade 10184, 300 m <sup>2</sup> /g	De-ionized water	24	61.2	84.3	67.8	89.8	0.736
Grade 10180, 750 m <sup>2</sup> /g	De-ionized water	24	56.0	81.3	57.3	82.9	0.976
Grade 10180, 750 m <sup>2</sup> /g	De-ionized water	24	56.0	82.2	59.0	84.1	0.937
Grade 10184, 300 m <sup>2</sup> /g	2 M H <sub>2</sub> SO <sub>4</sub>	24	10.3	29.2	18.4	30.5	0.608
Grade 10184, 300 m <sup>2</sup> /g	2 M H <sub>2</sub> SO <sub>4</sub>	24	12.4	27.9	18.9	31.2	0.588
Grade 10184, 300 m <sup>2</sup> /g	4 M HCl	24	8.4	20.0	14.2	24.4	0.454
Grade 10184, 300 m <sup>2</sup> /g	4 M HCl	24	13.5	22.9	13.6	24.0	0.443
Grade 10184, 300 m <sup>2</sup> /g	4 M NH <sub>4</sub> OH	24	100.0	97.3	105.4	106.6	1.001
Grade 10184, 300 m <sup>2</sup> /g	4 M NH <sub>4</sub> OH	24	100.0	97.5	103.3	102.0	0.997
Grade 10184, 300 m <sup>2</sup> /g	4 M NH <sub>4</sub> OH + 3 M NaNO <sub>3</sub>	24	87.2	96.1	86.5	103.7	1.731
Grade 10184, 300 m <sup>2</sup> /g	4 M NH <sub>4</sub> OH + 3 M NaNO <sub>3</sub>	24	89.5	94.8	90.5	107.9	1.788
Grade 10184, 300 m <sup>2</sup> /g	4 M HNO <sub>3</sub>	24	18.8	36.6	19.4	33.9	0.449
Grade 10184, 300 m <sup>2</sup> /g	4 M HNO <sub>3</sub>	24	12.4	25.3	15.9	27.1	0.471
Grade 10184, 300 m <sup>2</sup> /g	2 M H <sub>2</sub> SO <sub>4</sub>	336	67.0	75.7	18.3	31.5	0.875
Grade 10184, 300 m <sup>2</sup> /g	2 M H <sub>2</sub> SO <sub>4</sub>	336	15.3	43.2	20.3	33.7	0.822

The fifth set of experiments (Table 7) was similar to the fourth set, except that Merck grade 10180 silica gel (750 m<sup>2</sup>/g) was used in all experiments.

Table 7  
Effects of type and pre-treatment of silica gel and of time on the sorption of Cu and Pb

Type of silica gel	Pre-treatment of silica gel	Time, hours	Amount of metal ion sorbed, %				Amount of silica, dissolved, %
			Based on subtraction		Based on elution		
			Cu	Pb	Cu	Pb	
Grade 10180, 750 m <sup>2</sup> /g	De-ionized water	6	52.1	70.9	28.6	52.7	1.249
Grade 10180, 750 m <sup>2</sup> /g	De-ionized water	6	42.8	74.9	31.7	56.8	0.963
Grade 10180, 750 m <sup>2</sup> /g	2 M H <sub>2</sub> SO <sub>4</sub>	6	35.0	77.9	26.5	47.4	0.943
Grade 10180, 750 m <sup>2</sup> /g	2 M H <sub>2</sub> SO <sub>4</sub>	6	17.5	51.1	28.9	48.8	0.866
Grade 10180, 750 m <sup>2</sup> /g	4 M NH <sub>4</sub> OH	6	88.1	96.6	73.7	84.0	1.605
Grade 10180, 750 m <sup>2</sup> /g	4 M NH <sub>4</sub> OH	6	85.9	95.8	66.4	82.9	1.658
Grade 10180, 750 m <sup>2</sup> /g	4 M NH <sub>4</sub> OH + 3 M NaNO <sub>3</sub>	6	80.5	92.8	74.8	99.5	5.338
Grade 10180, 750 m <sup>2</sup> /g	4 M NH <sub>4</sub> OH + 3 M NaNO <sub>3</sub>	6	86.6	91.1	76.8	95.3	5.385
Grade 10180, 750 m <sup>2</sup> /g	De-ionized water	24	79.9	83.0	31.2	57.4	0.980
Grade 10180, 750 m <sup>2</sup> /g	De-ionized water	24	36.6	69.4	30.6	53.0	0.830
Grade 10180, 750 m <sup>2</sup> /g	2 M H <sub>2</sub> SO <sub>4</sub>	24	19.5	44.8	26.4	47.4	0.881
Grade 10180, 750 m <sup>2</sup> /g	2 M H <sub>2</sub> SO <sub>4</sub>	24	29.5	59.0	25.4	47.3	0.851
Grade 10180, 750 m <sup>2</sup> /g	4 M NH <sub>4</sub> OH	24	92.5	96.2	83.8	95.4	1.455
Grade 10180, 750 m <sup>2</sup> /g	4 M NH <sub>4</sub> OH	24	93.8	98.2			1.395
Grade 10180, 750 m <sup>2</sup> /g	4 M NH <sub>4</sub> OH + 3 M NaNO <sub>3</sub>	24	86.6	95.3		77.9	4.905
Grade 10180, 750 m <sup>2</sup> /g	4 M NH <sub>4</sub> OH + 3 M NaNO <sub>3</sub>	24	90.8	96.4	36.9	50.4	5.077

## Discussion

The results summarized in Tables 3-7 shed light on the effects of various parameters on the sorption of copper and lead on silica surfaces. The results reported here exhibit considerable inconsistencies with respect to the quantitative determination of the uptake of copper and lead on the silica gel substrates. The results based on subtraction of the concentrations of these dissolved metals in the test solutions after contact with the silica gel from the initial concentrations are, in many cases, considerably different from those obtained by extracting the silica gel with acid following the sorption process. In addition, considerable disagreement has been observed between the two individual results when an experiment was carried out in duplicate. Discrepancies were also observed in some cases between the results of an experiment included in a given set and those of a similar experiment included in another set. Clear trends for the dependence of the uptake of Cu and Pb on specific parameters were difficult to discern, especially in the earlier experiments. Throughout the experimental program, efforts have been made to identify the causes of the discrepancies and eliminate or minimize them. Indications were obtained, for instance, that variation in the time interval between the end of the experiment and the analysis, the material of which the test vessels were made (CPE, LDPE, HDPE), the geometric shape of the vessel (wide mouth, narrow mouth), the number of test vessels placed on a single magnetic stirrer and the size of that stirrer, and the details of the techniques of filtration, washing the precipitate and its elution with acid, and the small number (one or two) of replicate experiments performed under each set of conditions might have contributed to the observed inconsistencies. In general, the results obtained based on subtraction (i.e., on differences in concentration between the original test solution and the same solution following contact with silica gel) appeared to be more consistent and more reliable than those based on elution by acid, especially in the earlier experiments. Standardization of the experimental procedures with respect to these initially overlooked factors was thought to account for the improvement of the consistency of the results observed in the more recent sets of experiments (see Tables 6 and 7). Improved control of these secondary parameters is necessary in order to make it possible to obtain more quantitative trends and conclusions.

Notwithstanding the limitations of the data, it was possible to establish a number of trends and to arrive at useful conclusions.

\* At room temperature, a contact time as short as 2 hours between the silica gel and the solution is sufficient to remove most of the Cu and Pb from the solution under the conditions employed in the first set (Table 3) of the experiments (pH 5, 0.5 or 1 g of silica gel, 5 or 10 mg/L of Cu and Pb). Upon extending the contact time to periods as long as 240 hours, a statistically significant increase in the extent of sorption was not observed. Comparison between data obtained in 6-hour experiments and in 24-hour experiments included in the other sets has led to a similar conclusion. Of course, the uptake or sorption process is expected to take a certain amount of time, but the results of the present experiments indicate that the time required for this process to reach its maximum extent is smaller than 2 hours.

\* Trends observed upon measuring the uptake of  $\text{Cu}^{2+}$  and of  $\text{Pb}^{2+}$ , respectively, on silica gel as a function of time, temperature, pH, etc., are generally similar, but, under the same conditions, the absolute extent of sorption of  $\text{Pb}^{2+}$  is usually larger than the extent of  $\text{Cu}^{2+}$  sorption. This observation is consistent with previous findings regarding the relative magnitudes of the equilibrium constants of sorption of these metal ions on siliceous surfaces (Saeki, 2006).

\* According to the data (in particular, the more reliable data based on subtraction rather than elution) of the second set (Table 4), using a higher temperature within the range between 2 °C and 40 °C decreases the extent of Cu and Pb sorption. The temperature effect appears to be more noticeable at pH 5 than at pH 8.

\* The decrease in Cu and Pb uptake upon increasing the temperature is consistent with the absence of an increase in uptake upon extending the contact time beyond 2 hours. Both observations indicate that the values obtained for the uptake of Cu and Pb under the conditions of the experiments reported here reflect sorption capacities under equilibrium conditions, which are expected to decrease with increasing temperature, rather than sorption rates, which are expected to increase with increasing temperature.

\* Raising the pH of the solution enhances the uptake of Cu from the solution in 6-hour experiments as well as in 24-hour experiments (Table 4), as expected on the basis of equations (1) and (2). The same trend is observed in the 6-hour experiments on the sorption of Pb, but not in the corresponding 24-hour experiments. Upon prolonged immersion at pH 8, some Pb appears to de-sorb from the silica gel surface.

\* According to the data of the fourth set (Table 6), the use of silica gel with a small pore size (40 Å) and a correspondingly high surface area (750 m<sup>2</sup>/g) is not more effective, and may actually be slightly less effective, in removing Cu and Pb from solution compared with the use of silica gel with a larger pore size (100 Å) and a smaller surface area (300 m<sup>2</sup>/g). The same trend is observed upon comparing the results given in Table 6 with those shown in Table 7. This observation may be attributed to limited penetration of the solution containing the Cu or Pb ions into narrow pores, especially as regards the deep regions of such pores. The small diameter of such pores retards effective transport and replacement of solution depleted with respect to Cu and Pb within the pores by fresh test solution.

\* The effects of pre-treatment of the silica gel sorbent by contacting it with various aqueous media have been explored in the experiments of the third, fourth and fifth sets (Tables 4, 5 and 6, respectively). Discounting a few obvious outliers (in particular, the subtraction-based data for 2 M H<sub>2</sub>SO<sub>4</sub> in Table 5), the data show that the uptake of Cu and Pb is smallest in the cases of silica gel pre-treated with acids (HNO<sub>3</sub>, HCl, or H<sub>2</sub>SO<sub>4</sub>), larger in the case of silica gel pre-treated with de-ionized water, and largest in the case of silica gel pre-treated with NH<sub>4</sub>OH. These results generally agree with the model of Schindler *et al.* (1976) described above, which represents the sorption equilibria in terms of equations (1) and (2) above. Since the pre-treatment with acids generates a local low-pH environment around the surface, while pre-treatment with ammonia gives rise to a

high local pH, sorption on the ammonia-treated silica gel is much greater than on the acid-treated silica gel. Consistent differences among silica gel powders pre-treated with HNO<sub>3</sub>, HCl, and H<sub>2</sub>SO<sub>4</sub>, respectively, were not observed. Silica gel pre-treated with de-ionized water exhibits an intermediate extent of Cu and Pb sorption because the local environment is near-neutral. Of course, the effective pH of the surface is not solely determined by the pre-treatment but is also influenced by the pH (originally 5) of the test solution. However, the acetate concentration in that solution (10 mg/L Cu introduced as copper acetate and 10 mg/L Pb introduced as lead acetate) is only  $4.1 \cdot 10^{-4}$  M. This accounts for the observation that some Cu and Pb are sorbed even on the silica gel pre-treated in acid solutions, but the low concentration of acetate is insufficient to overwhelm the local pH resulting from the introduction of H<sup>+</sup> or OH<sup>-</sup> ions into the surface sites during the preceding pre-treatment. It should be emphasized that following pre-treatment, the silica gel powders (5 g each) were washed with several portions of de-ionized water, and the total volume of wash water was 500 mL water. The final portion of wash water was near-neutral (pH = 5) in the cases of the powders pre-treated with acids, but was still basic (pH = 9) in the cases of those pre-treated with ammonia.

\* High uptake of Cu and Pb is observed with silica gel samples pretreated with 4 M NH<sub>4</sub>OH alone or with 4 M NH<sub>4</sub>OH + 3 M NaNO<sub>3</sub>, but the extent of sorption in the case of the combined solution is slightly smaller. It was noted (Patrick and Barclay, 1925; Simmons, 1981) that polyvalent metal ions such as Cu<sup>2+</sup> can be effectively incorporated into the surfaces of silica gel or porous high-silica, either through a single treatment with a solution of the ion of interest, or through a two-step process consisting of ion-exchange with an alkali ion such as Na<sup>+</sup> followed by immersion in a solution of the polyvalent ion. The two-step process was found to result in more effective sorption only when the polyvalent ion was loaded onto the siliceous surface from a neutral or acidic solution; the amount of Cu<sup>2+</sup> taken up directly from an ammoniacal solution was similar to, or even slightly larger than, the uptake of Cu<sup>2+</sup> in the two-step process. The present findings are in agreement with the reported observations. The slight reduction in uptake observed in the present studies upon using silica gel pre-treated with NH<sub>4</sub>OH + NaNO<sub>3</sub> rather than with NH<sub>4</sub>OH alone may be attributed to a greater reduction in the effective surface area of the silica gel due to corrosion when it is exposed to the former solution. Such enhanced corrosion is reflected in the larger concentrations of dissolved silica observed in the NH<sub>4</sub>OH + NaNO<sub>3</sub> solutions following contact with silica gel compared with the corresponding concentrations in the NH<sub>4</sub>OH solutions. In addition, -Si-NH<sub>2</sub> groupings may form a hydrogen-bonded ammoniacal layer on the siliceous surface. [A similar structure is formed with -Si-OH groups (Dove and Crerar, 1990; Dove and Elston, 1992)] Such a layer would tend to complex polyvalent ions such as Cu<sup>2+</sup> and Pb<sup>2+</sup>. In contrast, Na<sup>+</sup> ions bound to -Si-O<sup>-</sup> sites would compete against, and even repel, Cu<sup>2+</sup> and Pb<sup>2+</sup> ions.

\* The extent of silica dissolution in the experiments exhibits consistent increase with increasing time, temperature, amount of silica gel, pH, and Na<sup>+</sup> concentration. The use of silica gel with a larger surface area also appears to result in a higher concentration of dissolved silica (Table 6). These findings indicate that under the conditions of the present experiments the dissolution of the silica gel, unlike the sorption of Cu and Pb, is

largely controlled by kinetics rather than by equilibrium solubility. As in the case of Cu and Pb sorption, within the uncertainty of the experiments performed here no consistent differences were observed among the silica dissolution data obtained in HNO<sub>3</sub>, HCl, and H<sub>2</sub>SO<sub>4</sub> solutions, respectively. As noted above, the extent of silica dissolution is larger in NH<sub>4</sub>OH + NaNO<sub>3</sub> solution than in a solution of NH<sub>4</sub>OH. This finding can again be interpreted according to the model of Dove et al. (Dove and Crerar, 1990; Dove and Elston, 1992). According to this interpretation, ammonia, like water, forms a hydrogen-bonded layer which covers the siliceous surface and protects it against hydrolysis, while Si-O-Na<sup>+</sup> groups are perpendicular to the surface and allow water to penetrate, hydrolyze the siliceous surface, release dissolved silica, and transport this silica to the bulk solution (Wickert *et al.*, 1999; Pulvirenti *et al.*, 2006).

\* The low content of impurities in the silica gel used in the study (Table 1) indicates that the findings truly reflect the properties of siliceous surfaces rather than the effects of minor components.

The study described above has led to the identification of a number of experimental issues involved in the characterization of the sorption of metal ions in silica gel and to the resolution of the majority of these issues. Further work is necessary in order to obtain an accurate and fully quantitative picture of all aspects of the sorption process so as to give proper consideration to such sorption in the analysis of issues of water quality in environmental streams and in drinking water systems.

## References

- Ames, L.L.; McGarrah, J.E.; Walker, B.A. (1983) Sorption of trace constituents from aqueous solutions onto secondary minerals. II. Radium. *Clays and Clay Minerals* **31**, 335-342.
- Chiron, N.; Guilet, R.; Deydier, E. (2003) Adsorption of Cu(II) and Pb(II) onto a grafted silica: isotherms and kinetic models, *Water Research* **37**, 3079-3086.
- Dove, P.M. and Crerar, D.A. (1990) Kinetics of quartz dissolution in electrolyte solutions using a hydrothermal mixed flow reactor. *Geochimica et Cosmochimica Acta* **54**, 955-969.
- Dove, P.M. and Elston, S.F. (1992) Kinetics of quartz dissolution in electrolyte solutions using a hydrothermal mixed flow reactor. *Geochimica et Cosmochimica Acta* **56**, 4147-4156.
- Ghoul, M.; Bacquel, M.; Morcellet, M. (2003) Uptake of heavy metals from synthetic aqueous solutions using modified PEI-silica gels. *Water Research* **37**, 729-734.

Nirdosh, I.; Trembley, W.B.; Muthuswami, S.V.; Johnson, C.R. (1987) Adsorption-desorption on the radium-silica system. *Canadian Journal of Chemical Engineering* **65**, 928-934.

Patrick, W.A.; Barclay, E.M. (1925) The behavior of silica gel towards certain alkalis and salts in aqueous solutions. *Journal of Physical Chemistry* **29**, 1400-1405.

Pulvirenti, A.L.; Eddy, S.J.; Calabrese, T.M.; Adel-Hadadi, M.A.; Barkatt, A.; Morgenstein, M.E. (2006) Interaction of iron containing silicate glasses with aqueous salt solutions. *Physics and Chemistry of Glasses: European Journal of Glass Science and Technology A* **47**, 47-57.

Schindler, P.W.; Fürst, B.; Dick, R.; Wolf, P. (1976) Ligand properties of surface silanol groups. I. Surface complex formation with  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$ . *Journal of Colloid and Interface Science* **55**, 467-475.

Saeki, K. (2006) Adsorption sequence of heavy metal divalent ions on silica. *Nendu Kagaku* **45**, 90-94.

Senftle, F.E.; Thorpe, A.N.; Grant, J.R.; Barkatt, A. (2007) Superparamagnetic particles in tap water. *Water Research* **41**, 3005-3011.

Simmons, C.J. (1981) Ion-exchange method for fabricating high-silica glasses. *Journal of the American Ceramic Society* **64**, 200-205.

Vithayaveroj, V.; Yiacoumi, S.; Tsouris, C. (2003) Modification of surface forces by metal ion adsorption. *Journal of Dispersion Science and Technology* **24**, 517-525.

Wickert, C.L.; Vieira, A.E.; Dehne, J.A.; Wang, X.; Wilder, D.M.; Barkatt, A. (1999) Effects of salts on silicate glass dissolution in water: kinetics and mechanisms of dissolution and surface cracking. *Physics and Chemistry of Glasses* **40**, 157-170.

# Nutrient flow and biological dynamics in the Anacostia River

## Basic Information

<b>Title:</b>	Nutrient flow and biological dynamics in the Anacostia River
<b>Project Number:</b>	2006DC77B
<b>Start Date:</b>	3/1/2006
<b>End Date:</b>	2/28/2007
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	District of columbia
<b>Research Category:</b>	Biological Sciences
<b>Focus Category:</b>	Nutrients, Solute Transport, Water Quality
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Stephen E. MacAvoy, Karen L. Bushaw-Newton



## **Publication**

Nutrient flow and biological dynamics in the Anacostia River  
Progress Report  
June 18, 2007

Prepared by Drs. Stephen MacAvoy and Karen Bushaw-Newton for Water Resources  
Institute

Table on Contents

I. Problem and Research Objectives	1
II. Fatty acid Community Profiling	2
III. Nutrient Source Assessment: isotope characterization/season and site	3
IV. Biological and Chemical Studies:	4
V. Chemical Analyses-Sediment	5
VI. Chemical Analyses-Water	5
VII. Biological Analyses-Water	7
VIII. Microbial Community Analyses: Sediment and Water:	8
Literature cited	8
Appendix A: Fatty acid profile data	11
Appendix B: Stable Isotope data	36

Nutrient flow and biological dynamics in the Anacostia River  
Progress Report  
June 18, 2007

**I. Problem and Research Objectives:**

Rivers are longitudinally linked systems with processes occurring in the upper reaches impacting downstream reaches and processes occurring in downstream reaches impacting upstream reaches through biological migration. The Anacostia River is an important link between the terrestrial and aquatic regions of the Potomac watershed and the larger Chesapeake Bay system. Although the health of the Potomac Estuary has been improving in recent years (Walker et al. 2004; Carter and Rybioki 1986), the Anacostia River, which runs into the estuary, remains a seriously stressed system with high levels of PAHs, PCBs, pesticides, and heavy metals (Phelps 2004). Researchers have also observed elevated concentrations of *Aeromonas* spp. during the summer months in Anacostia waters relative to concentrations observed in most natural waters (Cavari 1981). The effects of the degraded condition have been far reaching on the biological communities with high mortality rates of filter feeding bivalves (Phelps 1993, 2004); high tumor incidence among resident bullhead catfish (Sakaris et al. 2005, Pinkney et al. 2004), and adverse impacts on the populations of invertebrate macrofauna (Phelps 1985). These effects may impact the microbial community as well. Microbial DNA isolated from sediment from several locations on the Anacostia River reflecting a pollution gradient of heavy metals and organics (see Velinsky et al. 1994 and Wade et al. 1994 for sites), was found to have unique signatures in different regions of the river (Bushaw-Newton, Adams, and Velinsky, unpublished data). Despite increased attention on the Anacostia's environmental degradation, improvements have been marginal (Hall et al. 2002). Benthic organisms remain rare; Asiatic clams experience extremely low survival and have not established resident populations; fish remain unsafe to eat; and over 100 million gallons of raw waste entered the river in the past two years (Washington Post 2005). While studies have concentrated on the larger, macrofauna, little attention has been paid to the microbial and the macroinvertebrate communities. Yet, the structure and function of these two communities often plays a key role in dictating the structure and function of the larger biological community as well as the chemical components of the system. Therefore in order to best improve and protect the ecological function of the rivers, it is imperative to understand the role of the microbial community within that system.

Our objectives were to evaluate the microbial and macroinvertebrate communities of several sites within the upper reaches of the Anacostia River, upstream and downstream of the combined sewage outflow are in Bladensburg Maryland. Specifically we wished to 1) establish seasonal changes in biological oxygen demand, developing profiles of demand versus depth, 2) evaluate nutrient sources to bacteria, algae, invertebrates and characterize the origins of particulate organic matter through the use of the stable isotopes of sulfur, carbon and nitrogen, 3) characterize the composition of microbial communities at the different sites by DNA analysis, fatty acid profile and standard microbiological techniques.

The following is a progress report on our progress thus far and is being submitted to WRRRI pending a full analysis, which will be provided at a later date (a 6 month co-cost extension was granted 2/28/2007).

## **II. Fatty acid Community Profiling:**

## Background

Fatty acid profiling was used to determine the dominant sources of carbon in the sediment and water column at our research sites. Freshwater algae and bacteria both synthesize 18:1 fatty acids however the dominant isomer is different for each, algae have a greater abundance of 18:1D9 and bacteria have a greater abundance of 18:1D7. Bacteria also have odd and branched fatty acids, which algae do not (Lechevalier 1982). Bacteria do not have fatty acids larger than 18 carbon atoms long, which is sharply different from fatty acid profiles of the eukaryotic freshwater algae (DeLong and Yayanos 1986). These and other characteristics make fatty acid analysis a robust tool for differentiating carbon sources in freshwater. Several studies have effectively shown that specific fatty acids are diagnostic of certain carbon sources. 18:1D7 is diagnostic of freshwater cyanobacteria (Fredrickson et al. 1986), 18:1D15 is diagnostic of green algae (Napolitano et al. 1994) 20:5D17 is diagnostic of freshwater diatoms and 17:1D11 and iso17:0 are diagnostic of sulfate reducing bacteria (Boon et al. 1996).

### Fatty acid results and analysis.

#### July 2006 sediment and water column FAME profiles

Soils at Bladensburg (7/20/06) show a number of both odd-number and branched fatty acids, indicating bacterial origins. These unusual fatty acids made up approximately 9% of all the fatty acids. 16:0, 16:1 and 18:1 were the dominant fatty acids in the Bladensburg sediments and these are probably derived from photosynthesis. The soil samples also showed Filtered material from the water column for this date and site showed several short chain fatty acids and the sample was dominated by trans-4,4-dimethyl-2-pentenoic acid, which may indicate bacteria (the cis was also present, but a much lower amount).

#### November 2006 sediment and water column FAME profiles

Soils at the Navy Yard and site Waterpark (11/16/06) did not show a wide range of fatty acids, mostly 16:0, 18:0, 18:1 and 18:2 (navy yard only), which are not characteristic of bacteria. Interestingly, the dominant fatty at the Navy Yard (5x greater than any other fatty acid) was 2-oxo-hexadecanoic acid, a fatty acid metabolite (Appendix A, Tables 9 and 11). This acid was absent from the Aquatic Garden. Sediment at the Waterpark 11/16/06 didn't show a diverse group of FAs, and the dominant groups were 16 and 18 carbon saturated and single unsaturated species. Fatty acids were not obtained in sufficient quantity for analysis in filtered water from the Aquatic Gardens, probably because of lower productivity in the water column in November relative to the summer. Sediment and GFF from the Navy Yard on 11/16/07 also failed to show any distinctive bacterial FAs (Appendix A, Tables 11 and 12). Sediment FA profiles were similar to those at the Waterpark and only a single relatively short chain FA was detected within the water column filtrate (Appendix A, Table 12).

### **III. Nutrient Source Assessment: isotope characterization with season and site:**

#### Background.

Stable isotope analyses of carbon, nitrogen and sulfur have become important tools for determining the relative contributions of different nutrient sources in aquatic ecosystems. While it is expected that a stream such as the Anacostia will derive most of its organic carbon from allochthonous sources, which, will be fairly depleted in  $^{13}\text{C}$  relative to autochthonous streams, nitrogen and sulfur isotopes have the potential to yield interesting information at the Bladensburg sites. Enriched  $^{15}\text{N}$  in organic matter is often associated with human sewage impact (Aravena et al. 1993; Wayland and Hobson 2001) and sulfur isotopes have recently been shown to be a very effective tracer of nutrients from different geographical areas (Krouse and Tabatabai, 1986, MacAvoy et al. 1998, 2000). Unlike carbon and nitrogen isotopes, sulfur isotope signature is derived from sulfur in local minerals and atmospheric deposition (Krouse and Tabatabai, 1986). This has allowed researchers to use sulfur to trace sewage into estuarine ecosystems (Sweeney et al. 1980a;b).

#### Source assessment.

In July 2006 very negative  $\delta^{13}\text{C}$  values for water column filtrate suggest that a pulse of terrestrial (allochthonous) production not bacterial or autochthonous processes dominate (particularly at the downstream site) (Appendix B). Within the sediment there appears to be a draw down of nitrogen (lower C/N ratios, Appendix B) than other sites resulting in lower  $\delta^{15}\text{N}$  although higher  $\delta^{15}\text{N}$  values appear within the well mixed water column organic matter. The same sediments at the waterpark (middle) site show negative  $\delta^{34}\text{S}$  values, suggesting sulfate reduction in the sediments. This is consistent with lower oxygen at this site during the summer.

During the November 2006, uniform water column filtrate  $\delta^{15}\text{N}$  values reflect a low level of microbiological activity. Soils show a distinct clustering of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ . The Navy Yard and waterpark overlap in  $\delta^{13}\text{C}$  but are approximately 3‰ apart in  $\delta^{15}\text{N}$ . The elevated  $\delta^{15}\text{N}$  at the Navy Yard is unusually high for autotrophic production (whether autochthonous or allochthonous). This suggests that heterotrophs may have excreted  $^{15}\text{N}$ -enriched material, which accumulated as the river continued downstream (there is a sediment  $\delta^{15}\text{N}$  increase as one progresses downstream) (Appendix B). The waterpark has substantially more  $^{13}\text{C}$ -enriched sediments, possibly indicating that benthic production is more important at this site during November than the others.

#### **IV. Biological and Chemical Studies:**

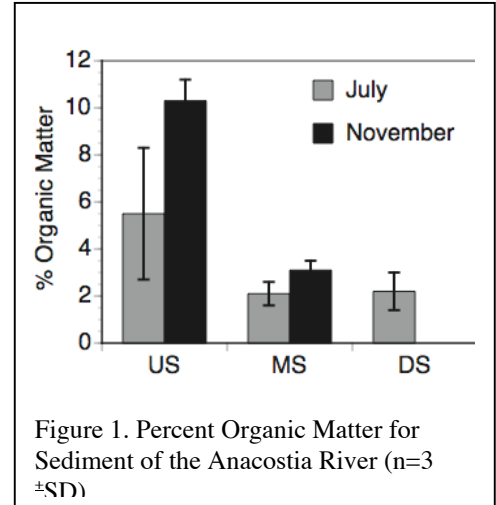
In July and November, replicate water and sediment samples were taken from three sites representing an upstream to downstream gradient in the Anacostia River. The upstream site (US) is located at Bladensburg, MD, while the middle stream site (MS) is located by Kenilworth Marsh, and the downstream site (DS) is located underneath the 11<sup>th</sup> street bridge. For the water samples, water was collected in acid-washed HDPE bottles and placed on ice for transport. Triplicate sediment samples were collected using a Stainless steel Petit Ponar, which was rinsed between samples. Surface sediment was collected from the ponar in whirl pak bags and placed on ice for transport. Several biological and

chemical analyses have been conducted on the collected samples to determine the linkages between microorganisms, their activities, and their environment.

**V. Chemical Analyses-Sediment:**

Microbes rely heavily upon the organic matter to provide the carbon and nutrients necessary to carryout reactions. Triplicate sediment samples were taken at all sites, except the DS site in November, for organic matter content analysis. At the DS site, main channel sediment samples were not obtainable due to the high concentration of rocks and gravel in the sediment. To determine organic matter content, sediment samples were analyzed for ash free dry mass. Sediment samples were weighed, dried, and re-weighed before muffling at 500°C for 2 h.

Preliminary results demonstrate that the sediment for the Anacostia River has low organic matter content ranging from 2% at the MS site in July to 10% at the US site in November (Figure 1). Overall concentrations are higher at the US site most likely reflecting higher inputs of leaf litter.



**VI. Chemical Analyses-Water:**

*in situ Measurements*

At each site, *in situ* measurements were conducted to provide information on several parameters. Using a YSI environmental probe, temperature, conductivity, dissolved oxygen concentrations and pH (Table 1). As expected temperature decreased from July to November at all sites from 30°C to 13°C. Conductivity also decreased though the reasons for this are not clear as concentrations of nutrients such as nitrate which can influence conductivity were higher in November than July (Table 2). Dissolved oxygen levels were similar at all sites in July but highly varied in the November samples. Given the lower temperatures in November, one would expect oxygen saturation. The lower levels in the MS and DS sites compared with the US site may be reflective of biological activity or potentially, chemical oxygen consumption in those areas. For July vs November, pH was elevated. November samples probably have increased acidity due to leaf litter leachates (e.g., humic acids) and lower activities of algae and plants which drawdown carbon dioxide levels in water.

Table 1. Measurement of temperature, conductivity, oxygen concentrations and pH for three areas of the Anacostia River using a YSI Environmental Probe

Station	Temperature (°C)	Conductivity (mS cm <sup>-1</sup> )	% Dissolved Oxygen	Dissolved Oxygen (mg L <sup>-1</sup> )	pH
---------	------------------	-------------------------------------	--------------------	--	----

<u>July</u>					
US	27.4	0.376	69.2	5.46	6.85
MS	30.27	0.326	62.5	4.7	6.79
DS	30.21	0.317	67.2	5.06	7.1
<u>November</u>					
US	12.85	0.272	94.1	9.9	5.06
MS	13.32	0.312	72.9	7.6	6.19
DS	12.81	0.215	38.9	4.08	6.17

### Nutrient concentrations

Within a few hours of collection, triplicate (July) or duplicate (November) water samples were filtered through muffled glass fiber filters and frozen at -20°C. Ammonium and Soluble Reactive Phosphate (SRP) measurements were done spectrophotometrically using standard methods. All other nitrogen components ( $\text{NO}_3^- + \text{NO}_2^-$ , and Dissolved Organic nitrogen (DON) were analyzed using an Alpkem autoanalyzer by the Academy of Natural Sciences Philadelphia using standard methods. Dissolved organic carbon (DOC) was measured using a total organic carbon analyzer (Shimadzu Corp) by the Academy of Natural Sciences Philadelphia using standard methods.

In both July and November, nitrate and ammonium levels increase with downstream movement (Table 2). These concentrations are less than 1 mg L nitrate which means that for classification purposes this system is not seen as very anthropogenically influenced. Ammonium levels are much lower than nitrate levels at all sites. This is expected as nitrate is readily absorbed in the watershed and nitrate is highly soluble in soil systems. Nitrate and ammonium levels are higher in November than July which is most likely represents lower biological uptake and higher concentrations in the water column. DON concentrations represent half of the nitrogen pool in these system though its biological availability is not determined in these studies. As will all freshwater systems, SRP levels are 20 to 60x lower than nitrogen concentrations. Phosphorus is most likely limiting in these systems. DOC concentrations range from 8.6 mg C L<sup>-1</sup> at the US site in July to 16.8 mg C L<sup>-1</sup> at the DS site in November. DOC measures all organic carbon in these system and while a portion of this organic carbon comes from natural sources, it is not clear if other pollutants are contributing to the carbon pool. In November, the leaching of leaf litter may be responsible for the overall increases in DOC concentrations compared with July.

Table 2. Nutrient concentrations for three areas of the Anacostia River, for July n=3 ( $\pm$ SD), for November n=2(  $\pm$ SD)

Station	$\text{NO}_3^- + \text{NO}_2^-$ (mg L <sup>-1</sup> )	$\text{NH}_4$ (mg L <sup>-1</sup> )	DON (mg L <sup>-1</sup> )	SRP (mg L <sup>-1</sup> )	DOC (mg L <sup>-1</sup> )
---------	--	--	------------------------------	------------------------------	------------------------------

July

US	0.320 (0.228)	0.029 (0.004)	0.205 (0.071)	0.014 (0.001)	8.6 (2.8)
MS	0.447 (0.011)	0.066 (0.016)	0.481 (0.053)	0.015 (0.002)	13.7 (0.32)
DS	0.556 (0.094)	0.140 (0.002)	0.391 (0.038)	0.021 (0)	12.2 (1.0)

November

US	0.434 (0.124)	0.085 (0.003)	0.319 (0.042)	0.008 (0)	10 (1.0)
MS	0.532 (0.003)	0.186 (0.001)	0.411 (0.033)	0.010 (0.001)	11.9 (1.1)
DS	0.606 (0.006)	0.195 (0.008)	0.420 (0.02)	0.011 (0.001)	16.8 (0.71)

**VII. Biological Analyses-Water:**

Oxygen Consumption Rates

Microbes represent an important component of the total biological community in aquatic environments. For the July samples, biological oxygen demand was measured in both whole water and filtered (3  $\mu\text{m}$  nominal pore size) water samples to determine the relative contributions of the microbial communities to overall metabolic activities. Triplicate 60 ml BOD bottles were filled with either whole or filtered water samples and incubated in

the dark. To determine oxygen demand, triplicate samples were sacrificed over a period of 5 days and oxygen concentrations were calculated using the Winkler method. Distilled water was used as a control. To determine relative rates of oxygen consumption, linear regression analyses were done for each data set and correlations calculated ( $r^2$ , Table 3).

	Oxygen Consumption Rate ( $\text{mg O}_2 \text{ L}^{-1} \text{ h}^{-1}$ )	$r^2$
US	0.0203	0.90
US-Filtered	0.0134	0.99
MS	0.0307	0.96
MS-Filtered	0.0133	0.98
DS	0.0355	0.95
DS-Filtered	0.0184	0.97
Distilled Water	0.0007	0.08

Microbial respiration in the water column (Filtered samples) was shown to be an important component of total community respiration at all sites (Table 3). Similar to nutrient concentrations, respiration rates increased in a downstream direction from 0.0203  $\text{mg O}_2 \text{ L}^{-1} \text{ h}^{-1}$  for the US site to 0.0355  $\text{mg O}_2 \text{ L}^{-1} \text{ h}^{-1}$  for the DS site. This increase may be attributed to higher availability of nutrients and carbon in the water column.

Bacterial utilization of different carbon sources

Biolog plates-These analyses are ongoing.



### Concentrations of Bacteria

Enumeration of bacteria using direct count method-These analyses are ongoing.

### **VIII. Microbial Community Analyses-Sediment and Water:**

The diversity of the microbial community can be determined using molecular techniques. For both water and sediment samples, microbial DNA was extracted using ~100-200 ml of water or ~0.25 g of sediment. Extracted DNA is currently being amplified using primers for total community (16S rRNA) or specific communities of PCB or PAH degraders (TMOA gene) (see Figure 2 for a representative example).

Our results, thus far demonstrate that while

some strains are found throughout the river system, other strains are unique to one area of the system versus another area.

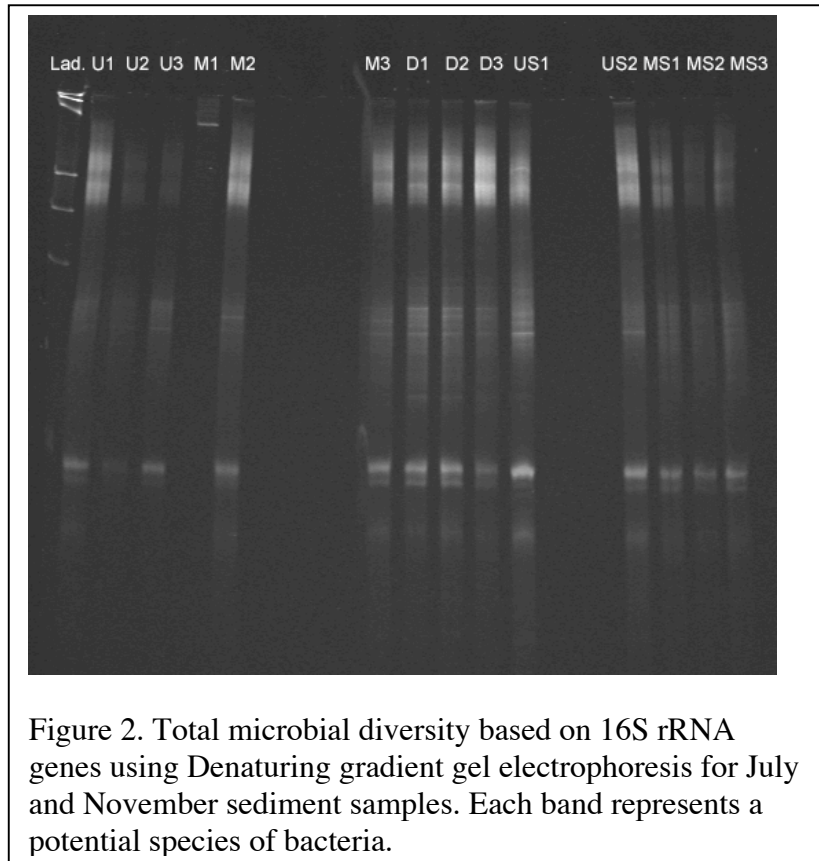


Figure 2. Total microbial diversity based on 16S rRNA genes using Denaturing gradient gel electrophoresis for July and November sediment samples. Each band represents a potential species of bacteria.

Literature cited:

Aravena, R., Evans, M.L., Cherry, J.A. 1993. Stable isotopes of oxygen and nitrogen in source identification of nitrate from septic systems. *Ground Water* 31(2):180-186.

Boon PI, Virtue P, Nichols PD. 1996. Microbial consortia in wetland sediments: a biomarker analysis of the effects of hydrological regime, vegetation and season on benthic microbes. *Mar. Freshwat. Res.* 47:27-41.

Carter V, Rybicki N. 1986. Resurgence of submersed aquatic macrophytes in the Tidal Potomac River, Maryland, Virginia, and the District of Columbia. *Estuaries* 9(4b): 368-375.

Cavari, BZ, Allen DA, Colwell RR. 1981. Effect of temperature on growth activity of *Aeromonas* spp. mixed bacterial populations in the Anacostia River. *Applied and Environmental Microbiology* 41(4):1052-1054.

Delong EF, Yayanos AA. 1986. Biochemical function and ecological significance of novel bacterial lipids in deep-sea procaryotes. *Applied Environmental Microbiology* 51:730-737.

Fredrickson HL, Cappenberg TE, Leeuw JW. 1986. Polar lipid ester-linked fatty acids composition of Lake Vechten seston: an ecological application of lipid analysis. *FEMS Microbiological Ecology* 38:381-396.

Hall LW, Anderson RD, Alden RW. 2002. A ten year summary of concurrent ambient water column and sediment toxicity tests in the Chesapeake Bay watershed: 1990-1999. *Environmental Monitoring and Assessment* 76:311-352.

Krouse HR and MA Tabatai. 1986. Stable Sulfur Isotopes. In *Sulfur in Agriculture*; 27th in the series *Agronomy* ed MA Tabatai.

Lechevalier H, Lechevalier MP. 1982. Lipids in bacterial taxonomy. In: Laskin AI and Lechevalier HA eds. *CRC Handbook of Microbiology*. Boca Raton FL. CRC Press Inc. p. 435-541.

Napolitano GE, Hill WR, Guckert JB, Stewart AJ, Nold SC, White DC. 1994. Changes in periphyton fatty acids composition in chlorine polluted streams. *Journal of the North American Benthological Association* 13:237-249.

Phelps HL. 1993. Sediment toxicity of the Anacostia River estuary, Washington DC. *Bull. Environmental Contaminant Toxicology* 51:582-587.

Phelps HL. 2004. Sources of Bioavailable Toxic Pollutants in the Anacostia Watershed. Part III, DC Water Resources Research Center Report 2003DC34B, Washington DC. 12p.

Pinkney, AE, Harshbarger JC, May EB, Reichert WL. 2004. Tumor prevalence and biomarkers of exposure and response in brown bullheads (*Ameiurus nebulosus*) from the Anacostia River, Washington, DC and Tuckahoe River, Maryland, USA.

Sakaris PC, Jensien RV, Pinkney AE. 2005. Brown Bullhead as an indicator species: seasonal movement patterns and home ranges within the Anacostia River, Washington, D.C. *Transactions of the American Fisheries Society* 134:1262-1270.

Sweeney, R.E., E.K. Kalil, I.R. Kaplan. 1980. Characterization of domestic and industrial sewage in Southern California coastal sediments using nitrogen, carbon, sulfur and uranium tracers. *Marine Environmental Research* 3:225-243.

Sweeney, R.E. and I.R. Kaplan. 1980. Tracing flocculent industrial and domestic sewage transport on San Pedro Shelf, Southern California, by nitrogen and sulphur isotope ratios. *Marine Environmental Research* 3:215-224.

Velinsky, D. J., T. L. Wade, C. E. Schlekat, B. L. McGee, and B. J. Presley. 1994. Tidal river sediments in the Washington, D.C. area. I. distribution and sources of trace metals. *Estuaries* 17: 305-320.

Wade, T. L. , D. J. Velinsky, E. Reinharz, and C.E. Schlekat. 1994. Tidal river sediments in the Washington, D.C. area. II. distribution and sources of organic contaminants. *Estuaries* 17: 321-333.

Walker SE, Dickhut RM, Chisholm-Brause C. 2004. Polycyclic aromatic hydrocarbons in a highly industrialized urban estuary: inventories and trends. *Environmental toxicology and chemistry* 23(11):2655-2664.

Wayland, M., K.A. Hobson. 2001. Stable carbon, nitrogen and sulfur isotope ratios in riparian food webs on rivers receiving sewage and pulp-mill effluents. *Canadian Journal of Zoology* 79:5-15.

Washington Post. 2005. WSSC Agrees to Pay Fines, Make Repairs. 7/27 by David Fahrenthold.

Appendix A, Fatty Acid methyl esters (FAMES) and related compounds  
 Drs. MacAvoy and Bushaw-Newton  
 June 18, Progress Report

**Table 1: 6/8/06 Sediment Navy Yard**

MS Data File = FM36475.dat;1

MS Scan #	Area	Integrat Peak Assignment	M.W.	FAMES Area %
181	80994	methyl isobutyl ketone (MIBK)	100	12.96659
186	24941	methyl ester of 3-methylbutanoic acid	116	3.992885
196	2301	toluene	92	0.368375
206	375	2-methyl-3-pentanone	100	0.060035
225	928	2-hexanone	100	0.148567
275	1520	n-nonane	128	0.243342
291	6819	4-methyl-2-pentanol	102	1.091676
300	328	methyl hexanoate	130 6:0	0.052511
311	1151	3-hexanol	102	0.184267
316	269	methyl ester of 4,4-dimethyl-2-pentenoic acid (cis)	142	0.043065
328	1400	2-hexanol	102	0.224131
332	1029	1-methylcyclopentanol	100	0.164736
341	1304	methyl ester of 4,4-dimethyl-2-pentenoic acid (trans)	142	0.208762
346	693			0.110945
353	120			0.019211
357	30			0.004803
363	8599	? methyl ester possibly a cyclopropane carboxylic acid derivativ	156	1.376642
367	639			0.1023
371	876	methyl ester of 3-methyl-2-heptenoic acid	156	0.140242
379	89			0.014248
386	4211	2-propenyl ester of 2-methyl, 2-butenic acid	140	0.674153
391	2188	2-propenyl ester of 3-methyl butanoic acid	142	0.350284
398	640	?		0.10246
404	2752	?	130	0.440577
411	1816	?	130	0.290729
417	7345	dimethyl ester of 2-oxo-pentanedioic acid (dimethyl ketoglutarat	174	1.175885
429	11187	possibly methyl ester of 4-butoxybutyric acid	174	1.790963
437	531	methyl octanoate	158 8:0	0.08501
444	114984	?	172	18.40816
456	10774	possibly methyl ester of 4-butoxybutyric acid	174	1.724845
461	1850	?	182	0.296172
467	2829	?	182	0.452904
472	5024	?		0.804308

478	510 ?		0.081648
485	10184 3-butyl-3-octen-2-one	182	1.63039
490	181		0.028977
498	2078 methyl nonanoate	172 9:00	0.332674
507	27489 ?	182	4.400803
524	1736 ?	152	0.277922
545	1482 ?		0.237258
558	2802 methyl decanoate	186 10:0	0.448581
563	70		0.011207
567	731 methyl benzoate	136	0.117028
571	4532 ?	144	0.725543
584	775 ?		0.124072
588	3718 ?		0.595227
595	129		0.020652
601	1698 2,4,4-trimethylbut-2-enolide	126	0.271838
607	6938 ?		1.110727
613	6635 ?		1.062219
627	644 ? lactone		0.1031
632	2752 ? cyclohexenone derivative	180	0.440577
646	12726 ?	208	2.037347
651	327 ? cyclohexenone derivative	180	0.05235
656	321 ?	194	0.05139
662	2325 methyl dodecanoate	214 12:0	0.372217
674	955 artifact		0.152889
679	13709 dodecadione	198	2.194718
707	1140 ?	192	0.182506
711	2439 methyl tridecanoate	228 13:0	0.390467
716	3465 ?	208	0.554723
722	9894 ? cyclohexenone derivative	194	1.583962
732	26278 ?	226	4.20693
735	1886 ?		0.301936
738	1296 ?		0.207481
743	4914 ?	166	0.786698
753	17318 tridecadione	212	2.772495
758	3480 methyl tetradecanoate	242 14:0	0.557124
772	1920 ?		0.307379
782	937 methyl pentadecanoate (branched)	256 15:0	0.150007
788	1045 methyl pentadecanoate (branched)	256 15:0	0.167297
802	2053 methyl pentadecanoate	256 15:0	0.328671
816	19705 ?	168	3.154637
825	7736 methyl hexadecanoate (branched)	270 16:0	1.238481
828	6065		0.970965
835	211 methyl hexadecanoate (branched)	270 16:0	0.03378
842	2684 ?	222	0.42969
846	14063 methyl hexadecanoate	270 16:0	2.251391
857	8863 methyl hexadecanoate	268 16:1	1.418906
869	2691 methyl octadecanoate (branched)	298 18:0	0.430811
877	1126 ?	192	0.180265
880	2159 ?		0.345641

886	1472	methyl octadecanoate (branched)	298	18:0	0.235657
896	4193	?	192		0.671271
927	9806	methyl octadecanoate	298	18:0	1.569874
935	14531	methyl oleate	296	18:1	2.326315
952	4442	methyl linoleate	294	18:2	0.711134
972	3610	methyl linolenate	292	18:2	0.577937
1006	6244	methyl eicosanoate	326	20:0	0.999622
1015	8280	methyl eicosenoate	324	20:1	1.325572
1104	8467	methyl eicosanoate	326	20:0	1.355509
1117	11987	methyl eicosenoate	324	20:1	1.919038

**Table 2: 7/20/06 Sediment Bladensburg**

MS Data File = FM36470.dat;1

MS Scan #	Area	Integrat Peak Assignment	M.W.	Area %
178	4390	methyl isobutyl ketone (MIBK)	100	0.622577
186	12472	methyl ester of 3-methylbutanoic acid	116	1.768742
300	324	methyl hexanoate	130 6:0	0.045949
311	217	3-hexanol	102	0.030774
328	360	2-hexanol	102	0.051054
333	269	1-methylcyclopentanol	100	0.038149
341	139	methyl ester of 4,4-dimethyl-2-pentenoic acid	142	0.019713
363	6684	? methyl ester possibly a cyclopropane carboxylic acid derivativ	156	0.947905
371	219	methyl heptanoate	144 7:0	0.031058
378	187	2-propenyl ester of 2-butenoic acid	126	0.02652
386	235	?		0.033327
416	343	methyl ester of 3-methyl-2-heptenoic acid	156	0.048643
428	1099	possibly methyl ester of 4-butoxybutyric acid	174	0.155857
437	470	methyl octanoate	158 8:0	0.066654
442	20215	?	172	2.866831
451	15			0.002127
455	779	?	158	0.110475
484	624	?	182	0.088494
497	1359	2-ethylhexyl alcohol	130	0.192729
505	1549	?	182	0.219675
516	338	methyl ester of 2-hydroxy-4-methylpentanoic acid	146	0.047934
556	1481	methyl decanoate	186 10:0	0.210031
567	305	methyl benzoate	136	0.043254
571	1356	?	144	0.192304
589	3091	?	144	0.438356
607	3820	?	144	0.541741
613	5136	?	144	0.728372
627	624	methyl-4-oxooctanonate	174	0.088494
633	4853	?	180	0.688238
646	7855	?	208	1.113973
662	4331	methyl dodecanoate	214 12:0	0.614209
678	4695	dodecadione	198	0.665831
688	467	methyl tridecanoate (branched isomer)	228 13:0	0.066229
695	455	methyl tridecanoate (branched isomer)	228 13:0	0.064527
707	498	?	192	0.070625
711	1379	methyl tridecanoate	228 13:0	0.195566
722	705	? cyclohexenone derivative	194	0.099981
731	4827	?	226	0.684551
736	2462	methyl tetradecanoate (branched isomer)	242 14:0	0.349153
752	4381	tridecadione	212	0.6213

759	26805	methyl tetradecanoate	242	14:0	3.801405
762	963	methyl hexadecanoate (branched isomer)	270	16:0	0.13657
769	1608	methyl tetradecenoate	240	14:1	0.228042
782	9081	methyl pentadecanoate (branched isomer)	256	15:0	1.28784
789	7541	methyl pentadecanoate (branched isomer)	256	15:0	1.069442
803	7996	methyl pentadecanoate	256	15:0	1.133969
809	1040	?	250		0.14749
813	3877	methyl pentadecenoate	254	15:1	0.549825
816	2662	?			0.377517
826	4399	methyl hexadecanoate (branched isomer)	270	16:0	0.623853
850	122891	methyl hexadecanoate	270	16:0	17.42803
858	29857	methyl hexadecenoate	268	16:1	4.234231
863	6363	methyl heptadecanoate (branched isomer)	284	17:0	0.902382
868	6123	methyl heptadecanoate (branched isomer)	284	17:0	0.868346
874	3736	methyl heptadecanoate (branched isomer)	284	17:0	0.529828
887	7632	methyl heptadecanoate	284	17:0	1.082347
896	5240	methyl heptadecenoate	282	17:1	0.743121
908	6714	methyl octadecanoate (branched isomer)	298	18:0	0.952159
923	4703	?	278		0.666965
929	44217	methyl octadecanoate	298	18:0	6.270723
937	87867	methyl oleate	296	18:1	12.46104
953	29575	methyl linoleate	294	18:2	4.194238
957	3735	methyl nonadecanoate	312	19:0	0.529687
978	8117	methyl linolenate	292	18:3	1.151129
1007	14571	methyl eicosanoate	326	20:0	2.066416
1016	17261	methyl eicosenoate	324	20:1	2.447904
1051	5664	methyl heneicosanoate	340	21:0	0.803252
1106	23782	methyl docosanoate	354	22:0	3.372692
1119	23180	methyl docosenoate	352	22:1	3.287318
1167	6621	methyl tricosanoate	368	23:0	0.93897
1230	20219	methyl ester of 10-hydroxyoctadecanoic acid	314		2.867398
1236	5293	glyceryl monopalmitate	330		0.750637
1245	21594	methyl tetradocosanoate	382	24:0	3.062397
1256	4748	methyl abietate (wood rosin ester)	314		0.673347
1264	4313	methyl tetracosenoate	380	24:1	0.611657
1331	5089	methyl pentadocosanoate	396	25:0	0.721707
1368	11130	?	330		1.578423
1395	3919	?	336		0.555781
	705134	Total			100



**Table 3, 7/20/06 GFF Bladensburg**

MS Data File = FM36471.dat;1

MS	Area		M.W.	Area %
Scan #	Integrat	Peak Assignment		
186	23468	methyl ester of 3-methylbutanoic acid	116	1.901672
253	570	methyl 4-methyl-2-pentenoate	128	0.046189
270	863	methyl hexanoate	130 6:0	0.069931
290	28067	methyl methacrylate	100	2.274341
304	1307	methyl cyclohexanecarboxylate	142	0.10591
311	1171	3-hexanol	102	0.094889
325	5734	methyl ester of 4,4-dimethyl-2-pentenoic acid (cis)	142	0.464641
328	1656	2-hexanol	102	0.13419
333	1358	1-methylcyclopentanol	100	0.110042
345	51025	methyl ester of 4,4-dimethyl-2-pentenoic acid (trans)	142	4.134686
365	40017	? methyl ester possibly a cyclopropane carboxylic acid derivativ	156	3.24268
385	896	methyl ester of 3-methyl-2-heptenoic acid	156	0.072605
406	1348	2-methylcyclopentanol	100	0.109232
418	22602	dimethyl ester of 2-oxo-pentanedioic acid (dimethyl ketoglutarat	174	1.831498
429	1333	methyl ester 3-hydroxybutanoic acid	118	0.108016
436	1510	n-undecane	156	0.122359
442	19678	?	172	1.594559
456	30047	possibly methyl ester of 4-butoxybutyric acid	174	2.434785
492	2569	?	166	0.208173
505	12576	methyl, 3-hydroxy-3-methylbutyrate	132	1.019065
514	2660	methyl, 2-hydroxy-4-methylpentanoate	146	0.215547
531	19620	methyl, 6-oxo-octanoate	174	1.589859
547	2528	methyl, 10-oxooctanoate	174	0.20485
609	27175	?		2.20206
615	34313	?		2.78047
626	31131	some type of lactone		2.522624
633	4235	?	180	0.343173
640	4915	?	180	0.398275
645	8443	?	194	0.684158
667	31136	?		2.523029
674	60392	?		4.893718
679	9915	dodecadione	198	0.803438
711	5280	?	192	0.427852
725	58456	? cyclohexenone derivative	194	4.736839
734	15762	?	226	1.277235
739	15732	?	206	1.274804
755	53887	tridecadione	212	4.366601
758	3100	methyl tetradecanoate	242 14:0	0.251201
769	5085	?	252	0.412051
779	4755	?		0.38531

786	17015 ?	182	1.378769
789	6059 dimethyl nonanedioate	216	0.490976
809	5343 ?	236	0.432957
813	6192 ?	176	0.501754
818	6088 ?	252	0.493326
830	4459 ?	252	0.361324
847	19444 methyl hexadecanoate	270 16:0	1.575597
855	18788 methyl hexadecenoate	268 16:1	1.52244
858	13526 ?	224	1.096046
870	36652 ?	224	2.970005
878	6106 ?		0.494785
882	6763 ?		0.548023
897	9576 ?	192	0.775968
900	3118 ?		0.252659
906	7376 ?		0.597696
912	63030 ?	252	5.107482
921	16554 methyl octadecanoate	298 18:0	1.341413
938	23640 methyl oleate	296 18:1	1.915609
946	26257 ?	278	2.127672
953	10073 ?	278	0.816241
960	13910 ?	278	1.127163
964	11648 ?	328	0.943867
1003	64130 ?	310	5.196617
1009	19288 ?	306	1.562956
1056	16580 ?		1.34352
1071	29274 ?		2.372147
1097	5514 ?	330	0.446813
1196	38161 ?	330	3.092283
1228	17094 ?		1.38517
1259	9691 ?	364	0.785286
1270	26556 ?	330	2.1519
1308	11809 ?	336	0.956913
1320	18043 ?	336	1.46207
	1E+06 Total		100

**Table 4, 7/20/06 sediment Waterpark**

MS Data File = FM36473.dat;1

MS	Area		M.W.	Area %
Scan #	Integrat	Peak Assignment		
178	61072	methyl isobutyl ketone (MIBK)	100	10.20222
185	10298	methyl ester of 3-methylbutanoic acid	116	1.720304
193	5418	toluene	92	0.905089
204	4873	2-methyl-3-pentanone	100	0.814046
223	4279	2-hexanone	100	0.714817
236	2049	?		0.34229
274	532	n-nonane	128	0.088872
289	3073	methyl methacrylate	100	0.513352
299	244	methyl hexanoate	130	6:0 0.040761
309	1546	3-hexanol	102	0.258263
315	701	methyl ester of 4,4-dimethyl-2-pentenoic acid (cis)	142	0.117104
327	2209	2-hexanol	102	0.369018
331	1921	1-methylcyclopentanol	100	0.320907
341	2398	methyl ester of 4,4-dimethyl-2-pentenoic acid (trans)	142	0.400591
361	4922	? methyl ester possibly a cyclopropane carboxylic acid derivative	156	0.822231
367	1705	2-propenyl ester of 2-butenoic acid	126	0.284824
372	3604	methyl ester of 3-methyl-2-heptenoic acid	156	0.602056
385	1911	2-propenyl ester of 2-methyl, 2-butenoic acid	140	0.319237
390	3533	2-propenyl ester of 3-methyl butanoic acid	142	0.590196
397	3753	?		0.626947
404	1686	2-methylcyclopentanol	100	0.28165
417	48608	dimethyl ester of 2-oxo-pentanedioic acid (dimethyl ketoglutarat	174	8.120077
428	5324	possibly methyl ester of 4-butoxybutyric acid	174	0.889386
435	5593	n-undecane	156	0.934323
442	86202	?	172	14.40024
456	73379	possibly methyl ester of 4-butoxybutyric acid	174	12.25813
466	1320	?	182	0.220509
472	7540	?	182	1.259574
484	4232	3-butyl-3-octen-2-one	182	0.706965
491	650	dihydrojasmane	166	0.108584
496	4626	2-ethylhexyl alcohol	130	0.772784
505	13504	?	182	2.255874
543	1029	? cyclohexenone derivative	138	0.171897
556	1346	? cyclohexenone derivative	138	0.224852
570	4840	?	144	0.808533
582	2806	?		0.468749
587	3515	?		0.587189
590	3561	?		0.594873
601	16942	2,4,4-trimethylbut-2-enolide	126	2.8302
606	2822	?		0.471422

611	4991 ?		0.833758
623	2650 ? lactone		0.442689
631	3345 ? cyclohexenone derivative	180	0.55879
637	894 ? cyclohexenone derivative	180	0.149345
643	6487 ?	194	1.083668
664	2112 methyl dodecanoate	214 12:0	0.352814
670	6388 artifact		1.06713
677	14263 dodecadione	198	2.382667
705	496 ?	192	0.082858
722	36457 ? cyclohexenone derivative	194	6.090225
729	4313 ?	226	0.720496
736	4710 ?	206	0.786816
752	41825 tridecadione	212	6.986962
787	2193 dimethyl nonanedioate	216	0.366346
814	6915 ?	168	1.155167
818	3129 ?	238	0.522707
828	1289 ?	238	0.21533
843	1386 methyl hexadecanoate (branched)	270 16:0	0.231534
853	5635 ?	224	0.94134
867	10106 ?	224	1.68823
894	2057 ?	192	0.343627
906	1249 ?	252	0.208648
918	926 ?	252	0.15469
921	1077 ?	192	0.179915
929	314 methyl octadecanoate	298 18:0	0.052454
932	1264 methyl oleate	296 18:1	0.211154
957	535 methyl linoleate	294 18:2	0.089373
984	2901 methyl linolenate	292 18:2	0.484619
1006	1947 ?	306	0.325251
1046	2489 phenanthrene or anthracene	178	0.415793
1067	3987 ?	306	0.666037
1192	3008 ?	330	0.502493
1254	1529 methyl abietate (wood rosin)	314	0.255423
1285	2024 ?	336	0.338114
1315	2008 ?	336	0.335441
1354	2150 pyrene or fluoranthene	202	0.359162
	598615 Total		100

**Table 5, 7/20/06 GFF Waterpark**

MS Data File = FM36474.dat;1

MS	Area		
Scan #	Integrat	Peak Assignment	M.W. Area %
477	843	?	3.462012
520	761	artifact	3.125257
557	1272	artifact	5.223819
632	148	?	180 0.607803
645	220	?	208 0.903491
661	187	methyl dodecanoate	214 12:0 0.767967
677	368	dodecadione	198 1.511294
699	1739	artifact	7.141684
715	223	?	192 0.915811
721	583	? cyclohexenone derivative	194 2.394251
730	1504	?	226 6.176591
752	942	tridecadione	212 3.868583
757	2235	methyl tetradecanoate	242 14:0 9.178645
781	251	methyl hexadecanoate (branched)	270 16:0 1.030801
802	517	methyl hexadecanoate (branched)	270 16:0 2.123203
826	1440	artifact	5.913758
845	7398	methyl hexadecanoate	270 16:0 30.38193
857	1082	?	196 4.443532
886	288	methyl octadecanoate (branched)	298 18:0 1.182752
925	2137	methyl octadecanoate	298 8.776181
933	212	methyl oleate	296 18:1 0.870637
	24350	Total	100

**Table 6, 7/20/06 Sediment Navy Yard**

MS Data File = FM36472.dat;1

MS Scan #	Area	Integrat Peak Assignment	M.W.	Area %
179	27923	methyl isobutyl ketone (MIBK)	100	3.474341
186	33001	methyl ester of 3-methylbutanoic acid	116	4.106175
224	5645	3-heptanone	114	0.702384
269	401	methyl hexanoate	130 6:0	0.049895
290	6867	methyl methacrylate	100	0.854432
310	1090	3-hexanol	102	0.135624
324	616	methyl ester of 4,4-dimethyl-2-pentenoic acid (cis)	142	0.076646
328	1266	2-hexanol	102	0.157523
332	1533	1-methylcyclopentanol	100	0.190745
342	5477	methyl ester of 4,4-dimethyl-2-pentenoic acid (trans)	142	0.68148
363	19985	? methyl ester possibly a cyclopropane carboxylic acid derivativ	156	2.486649
373	802	methyl heptanoate	144 7:0	0.099789
385	2116	2-propenyl ester of 2-butenic acid	126	0.263285
398	1162	?		0.144583
403	1931	methyl ester of 3-methyl-2-heptenoic acid	156	0.240266
411	831	2-methylcyclopentanol	100	0.103398
417	18187	dimethyl ester of 2-oxo-pentanedioic acid (dimethyl ketoglutarat	174	2.262932
428	7302	possibly methyl ester of 4-butoxybutyric acid	174	0.908557
436	5978	n-undecane	156	0.743817
443	76230	?	172	9.484977
456	26575	possibly methyl ester of 4-butoxybutyric acid	174	3.306615
460	850	?	182	0.105762
466	599	?	182	0.074531
471	1960	?	142	0.243875
484	3207	3-butyl-3-octen-2-one	182	0.399033
491	1369	dihydrojasmane	166	0.170339
497	2235	2-ethylhexyl alcohol	130	0.278092
505	10553	?	182	1.313065
512	278	? cyclohexenone derivative	138	0.03459
515	1229	methyl, 2-hydroxy-4-methylpentanoate	146	0.152919
523	948	methyl ester of 3,4,4-trimethyl-5-oxo-2-hexenoic acid	152	0.117956
543	732	? cyclohexenone derivative	138	0.09108
555	1515	methyl decanoate	186	0.188505
567	517	methyl benzoate	136	0.064328
571	2272	?	144	0.282695
583	1244	methyl ester of 2-ethyl, 2-propyl hexanoic acid	200	0.154786
601	5098	2,4,4-trimethylbut-2-enolide	126	0.634323
607	7857	?		0.977613
613	10607	?		1.319784
624	3768	? lactone		0.468836
632	9631	? cyclohexenone derivative	180	1.198345

646	28621	?	194	3.56119
661	4482	methyl dodecanoate	214 12:0	0.557676
672	3162	artifact		0.393434
678	14604	dodecadiene	198	1.817114
683	1790	methyl tridecanoate (branched isomer)	228 13:0	0.222722
707	1271	?	192	0.158145
710	2655	methyl tridecanoate	228 13:0	0.33035
717	5174	? cyclohexenone derivative	194	0.643779
722	33389	? cyclohexenone derivative	194	4.154452
731	12839	?	226	1.597503
737	3686	?	206	0.458633
741	2556	?	226	0.318032
754	51508	tridecadiene	212	6.408923
757	5411	methyl tetradecanoate	242 14:0	0.673268
762	650	?	252	0.080877
768	1357	methyl pentadecanoate (branched)	256 15:0	0.168846
776	2505	?	214	0.311687
781	2023	methyl pentadecanoate (branched)	256 15:0	0.251713
784	724	?	182	0.090084
788	5382	dimethyl nonanedioate	216	0.66966
796	1989	2-isopropylphenol	136	0.247483
802	3033	methyl pentadecanoate	256 15:0	0.377383
808	637	?	236	0.079259
812	4782	?	176	0.595004
815	2571	?	168	0.319899
824	1950	methyl hexadecanoate (branched)	270 16:0	0.24263
829	3704	?	238	0.460873
836	1074	?		0.133633
846	31518	methyl hexadecanoate	270 16:0	3.921652
854	24286	methyl hexadecanoate	268 16:1	3.021804
869	21845	methyl heptadecanoate (branched)	284 17:0	2.718081
873	1258	methyl heptadecanoate (branched)	284 17:0	0.156528
876	3018	?	192	0.375517
879	3673	?	238	0.457016
886	2688	methyl heptadecanoate	284 17:0	0.334456
896	17661	?	192	2.197484
909	6705	methyl octadecanoate (branched)	298 18:0	0.834275
919	3177	?		0.395301
922	1601	?	252	0.199206
926	13708	methyl octadecanoate	298 18:0	1.705629
934	22026	methyl oleate	296 18:1	2.740602
942	3151	?	304	0.392066
951	4304	methyl linoleate	294 18:2	0.535529
963	2720	?	312	0.338438
973	2777	?	310	0.34553
977	2198	?	306	0.273488
985	5195	methyl linolenate	292 18:2	0.646392
1000	6481	?		0.806403
1007	11559	methyl eicosanoate	326 20:0	1.438238

1018	10258	?	306	1.27636
1019	11391	methyl eicosenoate	324 20:1	1.417334
1103	7395	methyl docosanoate	354 22:0	0.920129
1111	3757	?	276	0.467468
1117	11758	methyl docosenoate	352 22:1	1.462998
1166	5264	methyl tricosanoate	368 23:0	0.654977
1193	11807	?	330	1.469095
1242	6319	methyl tetradocosanoate	382 24:0	0.786246
1255	7553	methyl abietate (wood rosin)	314	0.939788
1266	3391	?	330	0.421928
1277	3487	?	330	0.433873
1305	5590	?	336	0.69554
1317	7099	?	336	0.883299
1336	2158	methyl pentacosanoate	396 25:0	0.268511
	803692	Total		100



**Table 7, 11/16/06 sediment Bladensburg**

MS Data File = FM36477.dat;1

MS Scan #	Area	Integrat Peak Assignment	M.W.	Area %
180	110747	methyl isobutyl ketone (MIBK)	100	3.634973
187	2964	methyl ester of 3-methylbutanoic acid	116	0.097285
206	539	2-methyl-3-pentanone	100	0.017691
225	3258	2-hexanone	100	0.106935
238	2449	?		0.080382
275	1734	n-nonane	128	0.056914
290	4866	4-methyl-2-pentanol	102	0.159713
311	5775	3-hexanol	102	0.189549
317	1239	methyl ester of 4,4-dimethyl-2-pentenoic acid (cis)	142	0.040667
329	8375	2-hexanol	102	0.274887
333	8213	1-methylcyclopentanol	100	0.26957
341	1597	methyl ester of 4,4-dimethyl-2-pentenoic acid (trans)	142	0.052417
346	556			0.018249
357	2555	? methyl ester possibly a cyclopropane carboxylic acid derivativ	156	0.083861
363	2950	methyl ester of 3-methyl-2-heptenoic acid	156	0.096826
369	2223	3-ethyl-4-methyl-3-penten-2-one	126	0.072964
374	10855	?	156	0.356286
387	6244	2-propenyl ester of 2-methyl, 2-butenic acid	140	0.204943
393	8252	2-propenyl ester of 3-methyl butanoic acid	142	0.27085
406	7947	?	130	0.260839
421	185133	dimethyl ester of 2-oxo-pentanedioic acid (dimethyl ketoglutarat	174	6.076493
451	305808	?	172	10.03733
460	176473	possibly methyl ester of 4-butoxybutyric acid	174	5.792252
470	6099	?	182	0.200183
476	61492	?	182	2.01831
487	22931	3-butyl-3-octen-2-one	182	0.752648
494	5211	dihydrojasmane	166	0.171037
499	3448	2-ethylhexyl alcohol	130	0.113171
509	74082	?	182	2.431543
514	4232	?	138	0.138904
521	2801	?	156	0.091935
525	4360	?	152	0.143105
533	3383	?	144	0.111038
544	8738	?	138	0.286801
558	2117	?	150	0.069485
568	3558	?		0.116782
573	1786	?		0.058621
585	14842	?		0.487149
589	5489	?		0.180162
592	12077	?	170	0.396395
603	52078	2,4,4-trimethylbut-2-enolide	126	1.70932
607	15874	?		0.521021

614	15001 ?		0.492367
621	814 ? lactone		0.026717
626	11863 ? cyclohexenone derivative	180	0.389371
636	83849 ? cyclohexenone derivative	180	2.752118
641	5637 ?		0.185019
649	81670 ?	194	2.680598
653	6427 possibly methyl ester of 2-propylheptanoic acid	170	0.210949
664	4503 ?	184	0.147799
668	1732 ?	180	0.056848
675	40717 artifact		1.336426
682	98638 dodecadione	198	3.237527
685	7954 ?	224	0.261069
694	709 ?	180	0.023271
699	737 ?	192	0.02419
728	206862 ? cyclohexenone derivative	194	6.789689
735	107315 ?	226	3.522326
742	39592 ?	206	1.299501
757	162126 tridecadione	212	5.32135
761	43779 ?	196	1.436928
773	10889 ?	206	0.357402
781	5433 ?	238	0.178324
791	42016 dimethyl nonanedioate	216	1.379062
796	7012 ?		0.23015
817	58844 ?	168	1.931396
821	37364 ?	238	1.226373
832	33833 ?	238	1.110477
842	17290 ?	238	0.567498
847	20895 ?	238	0.685822
857	82482 ?	224	2.70725
873	121087 ?	224	3.974355
878	15655 ?	206	0.513833
882	16357 ?	238	0.536875
896	11835 ?	192	0.388452
925	32599 ?	278	1.069975
936	9500 ?	238	0.311812
944	22781 ?	304	0.747725
967	18531 ?	304	0.60823
980	19189 ?	292	0.629827
1010	42774 ?	306	1.403942
1017	24743 ?	306	0.812122
1047	11585 ?	306	0.380246
1053	13985 ?	306	0.45902
1072	72548 ?	324	2.381193
1122	14974 ?	314	0.491481
1144	10817 ?	408	0.355039
1195	26438 ?	330	0.867756
1232	17145 ?	336	0.562739
1254	29904 ?	388	0.981518
1268	11168 ?	330	0.36656

1289	26091 ?	336	0.856367
1309	17484 ?	336	0.573865
1322	36792 ?	336	1.207598
1333	11750 ?	336	0.385662
1361	9643 ?	402	0.316506
	3E+06 Total		100

**Table 8, 11/16/06 GFF Bladensburg**

MS Data File = FM36476.dat;1

MS	Area		M.W.	Area %
Scan #	Integrat	Peak Assignment		
178	10182	methyl isobutyl ketone (MIBK)	100	1.398761
185	10380	methyl ester of 3-methylbutanoic acid	116	1.425961
224	2232	2-hexanone	100	0.306623
290	480	methyl methacrylate	100	0.06594
310	248	3-hexanol	102	0.034069
328	271	2-hexanol	102	0.037229
332	309	1-methylcyclopentanol	100	0.042449
342	384	methyl ester of 4,4-dimethyl-2-pentenoic acid (trans)	142	0.052752
362	689	? methyl ester possibly a cyclopropane carboxylic acid derivativ	156	0.094652
373	367	methyl ester of 3-methyl-2-heptenoic acid	156	0.050417
386	409	2-propenyl ester of 2-methyl, 2-butenic acid	140	0.056187
391	625	2-propenyl ester of 3-methyl butanoic acid	142	0.08586
397	138	?		0.018958
404	270	?	130	0.037091
411	228	?	130	0.031322
418	21569	dimethyl ester of 2-oxo-pentanedioic acid (dimethyl ketoglutarat	174	2.96306
436	2250	n-undecane	156	0.309096
443	36065	?	172	4.95446
457	34054	possibly methyl ester of 4-butoxybutyric acid	174	4.678197
460	1158	?	182	0.159081
466	2035	?	182	0.27956
472	1957	?		0.268845
485	6157	3-butyl-3-octen-2-one	182	0.845823
491	695	dihydrojasmone	166	0.095476
506	19115	?	182	2.625939
513	788	?	138	0.108252
524	390	?	152	0.053577
571	2409	?	144	0.330938
583	1301	?		0.178726
588	795	?		0.109214
591	1412	?	170	0.193975
601	1197	2,4,4-trimethylbut-2-enolide	126	0.164439
606	1694	?		0.232715
616	893	?		0.122677
625	1557	? lactone		0.213894
633	8646	? cyclohexenone derivative	180	1.187752
639	2265	? cyclohexenone derivative	180	0.311156
645	25112	?	194	3.449782
652	651	possibly methyl ester of 2-propylheptanoic acid	170	0.089432
659	623	?	184	0.085585
663	741	?	180	0.101796

672	6483	artifact		0.890608
678	8786	dodecadione	198	1.206984
688	728	?	224	0.10001
701	1003	?	180	0.137788
707	1678	?	192	0.230517
725	114211	? cyclohexenone derivative	194	15.68983
733	31202	?	226	4.286401
739	8426	?	206	1.157529
744	1513	?		0.20785
750	812	?	166	0.111549
756	113987	tridecadione	212	15.65906
772	2186	?	196	0.300304
779	1767	?	206	0.242743
785	1194	?	238	0.164027
790	9327	dimethyl nonanedioate	216	1.281305
813	5328	?	218	0.731939
820	6996	?	294	0.961081
825	1188	?		0.163203
830	5217	?	238	0.71669
837	1924	?	294	0.264311
840	1468	?	238	0.201668
845	2763	?	238	0.379569
856	24566	?	224	3.374775
860	5916	?		0.812716
871	46584	?	224	6.399516
877	5165	?	206	0.709546
880	3637	?	238	0.499636
896	4132	?	192	0.567637
931	2525	?	238	0.346874
964	4736	?	304	0.650612
986	4507	?	306	0.619153
1009	21539	?	306	2.958938
1016	5954	?	306	0.817936
1033	1565	?	306	0.214993
1071	24186	?	324	3.322572
1121	2481	?	314	0.340829
1193	7304	?	330	1.003393
1230	4894	?	336	0.672317
1252	4109	?	336	0.564477
1266	2322	?	336	0.318987
1288	3770	?	336	0.517907
1306	5281	?	336	0.725482
1319	11829	?	336	1.625019
	727930	Total		100

**Table 9, 11/16/06 sediment waterpark**

MS Data File = FM36469.dat;1

MS Scan #	Area	Integrat Peak Assignment	M.W.	Area %
187	421468	methyl isobutyl ketone (MIBK)	100	14.15267
190	26173	methyl ester of 3-methylbutanoic acid	116	0.878875
223	5859	3-heptanone	114	0.196742
242	9930	5-methyl-3-hexen-2-one	112	0.333444
248	793	2,4,4-trimethylbut-2-enolide	126	0.026629
270	563	methyl hexanoate	130	0.018905
275	935	n-nonane	128	0.031397
290	38138	propylene glycol, monomethacrylate	144	1.280653
301	442			0.014842
304	1417	?	142	0.047582
311	2514	3-hexanol	102	0.084419
316	2354	3-methyl-3-hepten-2-one	126	0.079046
325	3887	methyl ester of 4,4-dimethyl-2-pentenoic acid (cis isomer)	142	0.130523
328	3015	2-hexanol	102	0.101242
333	2254	1-methylcyclopentanol	100	0.075688
344	36986	methyl ester of 4,4-dimethyl-2-pentenoic acid (trans isomer)	142	1.24197
356	2182	?	156	0.07327
365	49957	? methyl ester possibly a cyclopropane carboxylic acid derivativ	156	1.677529
369	5478	?	126	0.183948
374	10587	methyl ester of 3-methyl-2-heptenoic acid	156	0.355506
379	10933	2-propenyl ester of 2-butenic acid	126	0.367124
386	7462	dimethyl ester of 3,3-dimethylpentadioate	188	0.25057
392	7763	2-propenyl ester of 3-methylbutanoic acid	142	0.260677
406	4159	?		0.139657
422	166497	dimethyl ester of 2-oxo-pentanedioic acid (dimethyl ketoglutarat	174	5.590879
429	580			0.019476
438	29335	n-undecane	156	0.985053
448	212572	?	172	7.138053
461	168045	possibly methyl ester of 4-butoxybutyric acid	174	5.64286
468	3391	?	182	0.113868
474	15259	2,6-dimethyl-4-heptanone	142	0.512389
486	12048	3-butyl-3-octen-2-one	182	0.404565
492	5472	dihydrojasmane	166	0.183747
498	1467	?	170	0.049261
507	44115	?	182	1.481358
516	7054	? cyclohexenone derivative	138	0.23687
520	3101	?	156	0.10413
523	2492	?	156	0.08368
526	1570			0.05272
531	10114	methyl ester of a C11 branched fatty acid	200	0.339623
546	10124	methyl ester of a C12 branched fatty acid	214	0.339958

559	9692 ?		0.325452
572	16564 ?	144	0.55621
585	8501 ?	184	0.285459
589	32480 ?	154	1.090661
604	70029 2,4,4-trimethylbut-2-enolide	126	2.351536
609	17999 ?		0.604397
614	27430 methyl ester of 4-oxooctanoate	174	0.921085
620	969		0.032538
625	21229 ?		0.712858
634	29214 methyl ester of butanoic acid, 4-(2-methoxy-1-methyl-2-oxoetho	188	0.98099
640	7315 ? cyclohexenone derivative	180	0.245634
645	35158 ?	194	1.180587
674	45434 artifact		1.525649
680	48846 dodecadione	198	1.640222
728	194232 ? cyclohexenone derivative	194	6.522206
733	41466 ?	226	1.392406
740	47112 ?	206	1.581995
759	211010 tridecadione	212	7.085602
777	22535 ?	242	0.756713
790	18442 dimethyl nonanedioate	216	0.619272
795	5500 ?	210	0.184687
813	16530 ?	176	0.555068
816	16870 ?	168	0.566485
820	21020 ?	294	0.70584
830	14761 ?	238	0.495666
847	20616 methyl hexadecanoate	270 16:0	0.692274
856	58796 ?	224	1.974338
871	89900 ?	224	3.018793
878	23049 ?	306	0.773973
897	15108 ?	192	0.507318
911	35838 ?	252	1.203421
921	40858 ?		1.37199
926	8220 methyl stearate	298 18:0	0.276023
931	5340 ?		0.179314
937	15029 ?		0.504666
943	19110 methyl oleate	296 18:1	0.641703
986	17489 ?		0.587271
1001	28577 ?	310	0.9596
1009	41963 ?	306	1.409095
1071	70356 ?	324	2.362516
1195	34509 ?	330	1.158794
1231	7917 ?	336	0.265849
1254	16680 ?	336	0.560105
1269	15162 ?	330	0.509132
1289	11479 ?	336	0.385459
1308	17723 ?	336	0.595129
1323	46648 ?	336	1.566415
1334	8821 ?	336	0.296204
	3E+06 Total		100

**Table 10, 11/16/06 GFF waterpark**

MS Data File = FM36466.dat;1

MS	Area		M.W.	Area %
Scan #	Integrat	Peak Assignment		
179	151552	methyl isobutyl ketone (MIBK)	100	13.50322
221	2058	3-heptanone	114	0.183367
236	1072	artifact		0.095515
241	11307	5-methyl-3-hexen-2-one	112	1.007449
256	179	artifact		0.015949
274	360	n-nonane	128	0.032076
290	2830	2-hexanol	102	0.252152
317	415	methyl butanedioic acid (monomethyl succinate)	132	0.036976
328	652	2-heptanol	116	0.058093
332	616	1-methylcyclopentanol	100	0.054885
340	422	3-methyl-3-hepten-2-one	126	0.0376
355	1251	methyl ester of 4,4-dimethyl-2-pentenoic acid	142	0.111464
373	4517	methyl ester of 3-methyl-2-heptenoic acid	156	0.402463
377	3110	2-propenyl ester of 2-butenic acid	126	0.2771
384	2471	dimethyl ester of 3,3-dimethylpentadioate	188	0.220165
390	1334	2-propenyl ester of 3-methylbutanoic acid	142	0.118859
418	79101	dimethyl ester of 2-oxo-pentanedioic acid (dimethyl ketoglutarat	174	7.047864
436	9759	n-undecane	156	0.869523
442	58760	?	172	5.23549
457	109364	possibly methyl ester of 4-butoxybutyric acid	174	9.744284
465	1736	?	182	0.154677
471	4251	2,6-dimethyl-4-heptanone	142	0.378762
484	5067	3-butyl-3-octen-2-one	182	0.451467
491	1262	dihydrojasmone	166	0.112444
504	16416	?	182	1.462658
511	2173	? cyclohexenone derivative	138	0.193613
568	2289	?	144	0.203949
580	3237	?		0.288415
588	8002		170	0.712975
599	19226	2,4,4-trimethylbut-2-enolide	126	1.713028
603	321			0.028601
608	2477	possibly a methyl ester of 4-oxooctanoate		0.2207
613	1690	?		0.150578
622	1166	?	194	0.10389
627	7521	methyl ester of butanoic acid, 4-(2-methoxy-1-methyl-2-oxoethc	188	0.670118
636	2041	? cyclohexenone derivative	180	0.181852
642	12213	?	194	1.088173
669	9830	artifact		0.875849
675	3372	dodecadione	198	0.300444



722	137369	? cyclohexenone derivative	194	12.23952
728	10259	?	226	0.914072
736	23847	?	206	2.124757
739	1156	?		0.102999
752	131465	tridecadione	212	11.71347
776	3644	?	206	0.324679
786	4400	dimethyl nonanedioate	216	0.392038
803	1527	?	252	0.136055
809	3309	?	178	0.29483
817	7197	?	294	0.64125
827	3761	?	238	0.335103
852	31857	?	224	2.838445
867	60553	?	224	5.395246
1005	24216	?	306	2.157635
1067	26976	?	324	2.40355
1192	15304	?	330	1.36358
1228	6970	?	336	0.621024
1249	11139	?	336	0.99248
1264	10275	?	330	0.915498
1283	11489	?	336	1.023665
1303	13365	?	336	1.190816
1316	30010	?	336	2.673878
1328	6832	?	336	0.608728
	1E+06	Total		100

**Table 11, 11/16/06 sediment Navy Yard**

MS Data File = FM36468.dat;1

MS	Area		M.W.	Area %
Scan #	Integrat	Peak Assignment		
596	815	methyl 3-methylbutyrate	116	0.17469
631	454	?	180	0.097312
645	1858	?	208	0.398251
661	203	methyl-2-methylhexanoate	130	0.043512
671	1031	artifact		0.220989
677	2883	dodecadione	198	0.617953
721	22045	? cyclohexenone derivative	194	4.725211
730	12492	?	226	2.677584
737	1709	?	206	0.366314
753	56392	tridecadione	212	12.08728
775	3101	?	242	0.66468
784	3707	?	182	0.794573
788	7392	dimethyl nonanedioate	216	1.58443
812	5153	?	176	1.104514
818	3622	?	238	0.776354
829	5099	?	238	1.09294
835	1432	?	294	0.30694
844	8023	methyl hexadecanoate (methyl palmitate)	270 16:0	1.719681
853	8238	?	224	1.765765
858	8131	?	238	1.74283
868	30698	?	238	6.579929
877	12321	?	206	2.640931
888	4135	?		0.886312
896	6886	?	192	1.475972
904	2974			0.637459
909	28680	?	252	6.147383
919	13359	?	270	2.86342
922	12818	?	278	2.74746
925	3611	methyl stearate	298 18:0	0.773996
929	2394	?	318	0.513139
935	8456	?	318	1.812492
941	7959	methyl oleate	296 18:1	1.705963
951	8506	methyl linoleate	294 18:2	1.823209
985	11131	?		2.385862
999	12401	?	320	2.658079
1006	16540	?	306	3.545248
1015	16856	?	306	3.612981
1068	53958	methyl ester of 2-oxo-hexadecanoic acid	286	11.56557
1194	24459	?	330	5.242637
1226	5722	dimethyl ester of bicyclo 2.2.2 oct-2-ene-2,3-dicarboxylic acid, 1	324	1.226476

1278	10669 ?	288	2.286835
1305	8178 ?	336	1.752904
1316	10049 ?	336	2.153942
	466540 Total		100

**Table 12, 11/16/06 GFF Navy Yard**

MS Data File = FM36478.dat;1

MS Scan #	Area Integ.	Peak Assignment	M.W.	Area %
185	10885	methyl ester of 3-methylbutanoic acid	116	2.52761
205	4092	2-methyl-3-pentanone	100	0.950205
224	4435	2-hexanone	100	1.029853
288	2845	methyl methacrylate	100	0.660638
310	307	3-hexanol	102	0.071289
315	214	cyclohexanone	98	0.049693
324	340	methyl ester of 4,4-dimethyl-2-pentenoic acid (cis)	142	0.078952
327	522	2-hexanol	102	0.121214
332	493	1-methylcyclopentanol	100	0.11448
342	4311	methyl ester of 4,4-dimethyl-2-pentenoic acid (trans)	142	1.001059
363	15234	? methyl ester possibly a cyclopropane carboxylic acid derivativ	156	3.537493
370	182	methyl ester of 3-methyl-2-heptenoic acid	156	0.042262
384	298	2-propenyl ester of 2-methyl, 2-butenic acid	140	0.069199
391	144	2-propenyl ester of 3-methyl butanoic acid	142	0.033438
405	582	?	130	0.135146
417	15575	dimethyl ester of 2-oxo-pentanedioic acid (dimethyl ketoglutarat	174	3.616676
436	955	n-undecane	156	0.221761
442	26080	?	172	6.056046
456	28465	possibly methyl ester of 4-butoxybutyric acid	174	6.609868
460	207	?	182	0.048068
465	239			0.055498
471	469	?	182	0.108907
484	1461	3-butyl-3-octen-2-one	182	0.339259
491	314	dihydrojasmone	166	0.072914
498	142	2-ethylhexyl alcohol	130	0.032974
505	5243	?	182	1.217479
512	389	?	138	0.09033
515	1802	methyl, 2-hydroxy-4-methylpentanoate	146	0.418443
519	139	?	156	0.032277
525	636	?	152	0.147686
530	857	?		0.199004
544	2223	?	138	0.516204
557	2244	methyl decanoate	186 10:0	0.52108
571	3969		144	0.921643
583	1047			0.243124
588	5417	?	116	1.257884
591	1570	?	170	0.36457
607	6990	?	144	1.62315
613	10296	?	144	2.390838
624	4129	lactone		0.958797
633	10335	? cyclohexenone derivative	180	2.399894

639	869 ? cyclohexenone derivative	180	0.201791
644	6047 ?	194	1.404176
655	714 ?	214	0.165798
661	438 ?	184	0.101708
663	445 ?	180	0.103334
672	7130 artifact		1.65566
678	8889 dodecadione	198	2.064118
683	618 ?	224	0.143506
701	691 ?	180	0.160457
707	291 ?	192	0.067573
710	672 ? cyclohexenone derivative	194	0.156045
716	1932 ?	208	0.44863
723	43478 ? cyclohexenone derivative	194	10.09604
731	7236 ?	226	1.680274
738	4579 ?	206	1.063291
754	47701 tridecadione	212	11.07667
771	392 ?	196	0.091026
776	2546 ?	214	0.591208
784	523 ?	238	0.121446
788	1832 dimethyl nonanedioate	216	0.425409
794	719 ?	210	0.166959
812	2076 ?	218	0.482069
819	3254 ?	238	0.755613
830	2612 ?	238	0.606533
836	546 ?	238	0.126787
844	3412 ?	238	0.792302
854	7369 ?	224	1.711158
869	19462 ?	224	4.519278
877	3843 ?	206	0.892384
889	361 ?	238	0.083828
895	4438 ?	192	1.03055
910	4065 ?	252	0.943935
920	8572 ?	252	1.990507
923	2310 ?	278	0.536406
1007	10902 ?	306	2.531557
1069	11728 ?	324	2.723363
1098	12191 ?	364	2.830877
1193	6632 ?	330	1.540019
1326	13052 ?	426	3.03081
	430644 Total		100

Appendix B. Stable isotope data, micrograms carbon, nitrogen and C/N ratios. Means and standard deviations included where possible for each site and time point

Anacostia Samples

Macavoy, biology dept. American University

Date	item	number	mg sample	Micro g N	<b>d15N</b>	Micro g C	<b>d13C</b>	C/N	<b>d34S</b>
6/8/06	sed 1	navy yard	113.8	10.3	<b>5.27</b>	182.5	<b>-19.53</b>	17.7	<b>10.90</b>
6/8/06	sed 2	navy yard	103.6	9.5	<b>5.62</b>	171.4	<b>-18.02</b>	18.0	<b>1.93</b>
7/20/06	sed 1	bladensburg	23.4	16.3	<b>1.83</b>	268.2	<b>-26.23</b>	16.5	<b>-3.54</b>
7/20/06	sed2	bladensburg	28.4	21.0	<b>2.07</b>	320.4	<b>-27.04</b>	15.2	<b>-5.65</b>
7/20/06	sed 3	bladensburg	33	18.5	<b>2.35</b>	279.4	<b>-26.35</b>	15.1	
		<b>means</b>			2.08		-26.54	15.61	-4.60
		<b>s.d.</b>			0.26		0.44	0.76	1.49
7/20/06	GFF	bladensburg 1	6.1	26.2	<b>3.38</b>	198.7	<b>-27.71</b>	7.6	<b>3.92</b>
7/20/06	GFF	bladensburg 2	7.4	26.4	<b>3.44</b>	202.4	<b>-27.98</b>	7.7	
7/20/06	sed	1 water park	13.3	9.1	<b>3.79</b>	159.3	<b>-26.04</b>	17.5	<b>-3.18</b>
7/20/06	sed	2 water park	14.7	4.8	<b>-2.68</b>	58.6	<b>-26.27</b>	12.1	<b>-5.45</b>
7/20/06	sed	3 water park	14.4	2.7	<b>-5.45</b>	25.0	<b>-23.81</b>	9.4	<b>-2.28</b>
		<b>means</b>			-1.45		-25.37	13.01	-3.64
		<b>s.d.</b>			4.74		1.36	4.08	1.63
7/20/06	GFF	water park 1	10.7	38.2	<b>4.10</b>	250.8	<b>-31.16</b>	6.6	
7/20/06	GFF	water park 2	?	55.5	<b>4.05</b>	352.7	<b>-31.08</b>	6.4	<b>2.59</b>
7/20/06	GFF	water park 3	6.3	39.6	<b>3.72</b>	249.6	<b>-31.11</b>	6.3	<b>2.85</b>
		<b>means</b>			3.96		-31.12	6.41	2.72
		<b>s.d.</b>			0.21		0.04	0.14	0.18
7/20/06	sed 1	Navy Yard 1	27.4	9.3	<b>3.24</b>	155.9	<b>-24.67</b>	16.8	
7/20/06	sed 2	Navy Yard 2	26.9	8.8	<b>1.95</b>	157.0	<b>-24.49</b>	17.9	
7/20/06	sed 3	Navy Yard 3	30.3	8.7	<b>3.86</b>	180.5	<b>-26.46</b>	20.7	<b>-0.68</b>
		<b>means</b>			3.02		-25.21	18.43	
		<b>s.d.</b>			0.97		1.09	2.00	
7/20/06	GFF 1	Navy Yard 1	7.2	24.5	<b>4.70</b>	196.3	<b>-31.69</b>	8.0	<b>3.21</b>
7/20/06	GFF 2	Navy Yard 2	12.6	35.6	<b>4.83</b>	294.7	<b>-31.74</b>	8.3	
		<b>means</b>			4.77		-31.71	8.15	
		<b>s.d.</b>			0.09		0.04	0.19	
11/16/06	soil	bladensburg 1	31.9	19.6	<b>3.24</b>	347.7	<b>-26.17</b>	17.7	<b>2.24</b>
11/16/06	soil	bladensburg 2	36.8	28.7	<b>3.21</b>	429.7	<b>-26.45</b>	15.0	<b>0.67</b>
11/16/06	soil	bladensburg 3	35	30.1	<b>3.77</b>	522.8	<b>-26.04</b>	17.4	
		<b>means</b>			3.41		-26.22	16.69	1.46
		<b>s.d.</b>			0.32		0.21	1.49	1.11
11/16/06	GFF	bladensburg 1	0.0052	11.4	<b>4.55</b>	134.1	<b>-26.94</b>	11.8	
11/16/06	GFF	bladensburg 2	0.0037	19.3	<b>4.74</b>	260.8	<b>-24.79</b>	13.5	
		<b>means</b>			4.65		-25.86	12.63	
		<b>s.d.</b>			0.14		1.52	1.23	
11/16/06	sed	waterpark 1	58.3	49.2	<b>4.90</b>	687.9	<b>-23.31</b>	14.0	<b>0.55</b>
11/16/06	sed	waterpark 2	46.2	42.4	<b>5.04</b>	617.2	<b>-23.36</b>	14.6	<b>0.23</b>
11/16/06	sed	waterpark 3	40.9	41.3	<b>4.59</b>	581.2	<b>-24.30</b>	14.1	
		<b>means</b>			4.84		-23.66	14.20	0.39
		<b>s.d.</b>			0.23		0.56	0.32	0.23
11/16/06	GFF extr	waterpark 1	0.0073	11.9	<b>3.59</b>	229.7	<b>-18.37</b>	19.3	
11/16/06	GFF not extr	waterpark 2	0.0101	24.9	<b>5.23</b>	720.2	<b>-14.79</b>	28.9	
		<b>means</b>			4.41		-16.58	24.09	
		<b>s.d.</b>			1.15		2.53	6.77	
11/16/06	sed	navy yard 1	76.7	42.4	<b>5.69</b>	901.5	<b>-26.14</b>	21.3	<b>3.47</b>
11/16/06	sed	navy yard 2	63.9	17.3	<b>5.07</b>	407.3	<b>-26.36</b>	23.5	
11/16/06	sed	navy yard 3	63.5	18.9	<b>5.23</b>	336.5	<b>-25.96</b>	17.8	
		<b>means</b>			5.33		-26.15	20.86	3.47
		<b>s.d.</b>			0.32		0.20	2.86	
11/16/06	GFF	navy yard 1	0.015	71.7	<b>3.87</b>	953.7	<b>-24.80</b>	13.3	



# Wet-Weather Flow Characterization for the Rock Creek through Monitoring and Modeling

## Basic Information

<b>Title:</b>	Wet-Weather Flow Characterization for the Rock Creek through Monitoring and Modeling
<b>Project Number:</b>	2006DC78B
<b>Start Date:</b>	3/1/2006
<b>End Date:</b>	2/28/2007
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	District of Columbia
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Surface Water, Non Point Pollution, Solute Transport
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Pradeep K. Behera, Abiose Adebayo, Wellela Hirpassa



## **Publication**

# Wet-Weather Flow Characterization for the Rock Creek through Monitoring and Modeling



## Progress Report

Prepared for  
DC Water Resources Research Institute  
University of the District of Columbia  
Washington DC

Prepared by  
Pradeep K Behera, Ph.D., P.E. and Segun Adebayo, Ph.D.  
Department of Engineering, Architecture, & Aerospace Technology  
School of Engineering and Applied Sciences  
University of the District of Columbia

June 2007

## **Acknowledgement**

This research study would not have possible without the generous support of the following organizations:

- DC Water Resources Research Institute
- U.S. Geological Survey through US Department of Interior
- School of Engineering and Applied Sciences, UDC

## Table of Contents

Introduction .....	4
District of Columbia Drainage System .....	5
Characterization of Urban Runoff Quality .....	6
Sources of Pollutants .....	7
Urban Runoff Quality Constituents.....	10
Monitoring Runoff Quality at the Rock Creek.....	16
Modeling of Urban Stormwater Management .....	21
Analytical Probabilistic Stormwater Models .....	24
Modeling Approach.....	28
Example - Development of an Analytical Probabilistic Model .....	29
Conclusions.....	33
References.....	34

## Introduction

In spite of massive public investments in sewage and drainage infrastructure, pollution loading from wet-weather flows continues to have significant impacts on receiving waters. Trends in urbanizations, increased quantities of urban wet-weather flows and corresponding increase in pollution loadings discharged to receiving waters demand that wet-weather flow control systems be planned and engineered to effect higher levels of water quality control. For future investments in drainage infrastructure to be cost-effective, decisions in wet-weather flow control systems planning must be made within a rigorous, comprehensive and systematic framework.

Similar to many older cities in the nation, the sewer system in the District of Columbia is comprised of both combined and separate sewer systems. It has recognized that these systems contribute significant pollution to the Anacostia and Potomac Rivers and Rock Creek through Combined Sewer Overflows (CSOs) and Storm Sewer discharges during wet-weather (i.e., rainfall and snowmelt) events. These overflows and associated pollutant loads can adversely impact the quality of the receiving waters. As per the District of Columbia water quality standards, the designated use of the Anacostia River, Potomac River and Rock Creek is Class A or suitable for primary contact recreation. Because the water quality in the receiving waters currently does not meet these standards much of the time, the actual use of the water body is Class B or suitable for secondary contact recreation and aquatic enjoyment. As a result, the District law prohibits primary contact recreation such as swimming in each of the receiving waters (DC WASA, 2002). To address these problems, the District of Columbia Water and Sewer Authority (WASA) has developed a Long Term Control Plan (LTCP) that provides the alternative solutions and their implementation costs.

In order to support LTCP a continuous monitoring and modeling of the watershed and drainage system is necessary not only to provide technical assessment but also to develop a cost-effective solution. In this regard, a long-term research program has been proposed at the University of the District of Columbia. The research program include capacity building for environmental research such as development of environmental simulation and modeling laboratory and water quality testing laboratory and student training in the field of environmental science and engineering. As a part of this program, it is envisioned that a number of water quality parameters that include suspended solids, nutrients, heavy metals and other toxins, will be monitored and monitored data will be used for the development of models which ultimately support in developing effective solutions. The purpose of the proposed study is to collect information on the District drainage system, characterize runoff quality constituents, and field monitoring of runoff quality parameters and development of urban stormwater modeling systems. The modeling of urban stormwater system is developed using analytical probabilistic approach.

## **District of Columbia Drainage System**

The sewerage system of the District of Columbia is the result of both random growth and planned development. Starting about 1810, sewer and culverts were built to drain streets and these scattered sewers gradually become linked together to form a system intended to carry storm and ground water (ASCE, 1982). Currently, the District of Columbia sewer system comprised of both combined and separate sanitary sewers. A combined sewer carries both sanitary sewage and runoff from wet weather events (i.e., rainfall and snowmelt). The combined system was built early 1900's exists in the oldest part of the city and modern practice is to build separate sewers for sewage and stormwater. Approximately one-third of the District (12,478 acres) is served by combined sewers (DCWASA, 2002).

In the combined sewer system, sewage from residential, institutional and commercial areas during dry weather conditions is conveyed to the District of Columbia Wastewater Treatment Plant at the Blue Plains, which is located in the southwestern part of the District on the east bank of Potomac River. The Blue Plain treatment plant was put into operation in 1938. At the treatment plant, the wastewater is treated to removed harmful pollutants before being discharged to the Potomac River. During wet weather events, when the capacity of combined sewer is exceeded, the excess flow, which is mixture of runoff and sewage, is discharged to the Anacostia and Potomac Rivers, Rock Creek and tributary waters through the sewer outfalls. The excess flow is called as Combined Sewer Overflow (CSOs). There are a total of 60 CSO outfalls in the combined sewer system listed in the National Pollutant Discharge Elimination System (NPDES) permit issued by the Environmental Protection Agency to WASA. The discharges from the separated storm sewer system generally directs to the river systems without any treatments. The CSOs and stormwater discharges known as urban wet weather flow or urban runoff can adversely impact the quality of the receiving waters. The pollutants in urban runoff include visible matter, suspended solids, oxygen demanding materials, nutrients, pathogenic microorganisms and toxicants such as heavy metals, pesticides and hydrocarbons. These pollutants impose considerable physical, chemical and biological stresses on the receiving waters that affect aquatic life and human health [Field et al., 1998] and impair the designated uses of water resources. Typical urban stormwater-related receiving water quality problems include the degradation of aquatic habitats, degradation in water quality during and after wet weather events, beach closures, and accelerated rates of eutrophication in lakes and estuaries, and thermal pollution [WEF, 1998].

The primary purpose of the LTCP is to control CSOs such that water quality standards are met. In order to assess the existing condition, WASA conducted study that developed the computer model of combined sewer systems, separate storm water

systems. The computer models were calibrated based on the historical data and 9 to 12 months of monitored data collected in the receiving waters, combined and separated sewer systems. Table 1 presents annual CSO overflow predictions for existing conditions (WASA, 2002).

**Table 1: Existing Condition Annual Average CSO Overflow Volume and Overflows**

Description	<i>Anacostia River</i>	<i>Potomac River</i>	<i>Rock Creek</i>	<i>Total System</i>
<b>CSO Overflow Volume (million gallons/yr)</b>	2,142	1,063	48	3,254
No Phase I Controls (prior to 1991)	1,485	953	52	2,490
With Phase I Control (after 1991)				
<b>Number of Overflow/yr</b>	82	74	30	
No Phase I Controls (prior to 1991)	75	74	30	
With Phase I Control (after 1991)				

## Characterization of Urban Runoff Quality

Assessments of urban runoff pollution problems are rarely well prescribed. Stormwater runoff from urban watersheds contains constituents that can, in some cases, occur with damaging pollutant levels. These situations and the urban areas that produce such runoff quality levels need to be identified. While information from the literature might be adequate to understand certain general issues, site-related data are often collected and analyzed to characterize the runoff pollution problem.

Urban stormwater management from a runoff quality perspective is generally related to the magnitude and frequency of pollutant mass discharges from combined sewer overflows (CSOs), stormwater discharges and runoff-induced sanitary sewer overflows to receiving waters. These discharges are intermittent in nature and often difficult to quantify. Nonetheless, documentation and characterization of site-specific runoff quality are important in developing effective stormwater management programs for the urban areas. Such a characterization includes assessment of the existing runoff pollution condition and its contribution to local water quality problems, and is followed by an analysis of future pollution conditions and the development of management options. In addition, characterization is required by many jurisdictions in the U.S. for compliance of new regulatory requirements (WEF, 1998). Therefore, most North American cities are investing significant resources in assembling and analyzing information on urban runoff in an effort to develop plans to meet the new regulatory requirements.

Runoff quality data collection and analysis are the most expensive component of an urban stormwater management study. Thus, there is a need to maximize the use of existing data so that the need for new runoff quality data can be minimized. In such cases, the information derived from the existing data is relatively more important. In many instances, the availability of continuous runoff quality data (e.g., on an event basis) is not long enough to perform reasonable statistical evaluations. Therefore, whenever a continuous data set of longer period is available, the statistical characteristics should be obtained which is useful for modeling and management of urban runoff pollution.

To assess and address urban runoff pollution problems, the characterization of runoff quality is necessary. The term characterization refers to the evaluation of statistical characteristics of measurable pollution causing variables (i.e., pollutant concentrations). From the quality perspective, urban runoff pollution is primarily influenced by the type of sewer system (i.e., separated stormwater and combined sewer systems). Accordingly, the characterization of runoff quality developed in this chapter is based on types of catchments, separated and combined systems.

## **Sources of Pollutants**

Numerous studies on urban runoff quality conducted in different parts of the world over recent decades have proved that runoff carries relatively high concentrations of a variety of pollutants. These pollutants originate from diverse sources, both natural and anthropogenic, categorized by various boundary inputs, pollution processes and human activities that occur on the urban catchment. In addition, pollutant-generating activities are considered to be more prevalent on impervious areas than on pervious areas. The understanding of pollution sources is important for both the prediction and the control of pollutant loads. Common sources of urban runoff pollution include dry and wet atmospheric deposition; accumulation of street refuse including litter, street dirt, and organic residues, vehicular traffic emissions; vegetation; accidental spills; urban area erosion; and road deicing chemicals. One of the principal sources of pollutant accumulation in urban areas is dry and wet atmospheric deposition, which is considered as a boundary input caused by local or distant air pollution sources. In most cities, the deposition rate of atmospheric particulate matter is higher in the congested downtown core and industrial areas than rates in residential and suburban areas. Wet and dry fallout rates range from 7 to more than 30 tonnes/km<sup>2</sup>-month (Novotny and Olem, 1994).

Dry deposition results from the turbulent and gravitational transfer of pollutants from the air to the underlying surface, unaccompanied by atmospheric precipitation (Hicks, 1997). A study of the chemical composition of particulate matter and aerosols over Edmonton, Alberta (Klemm and Grey, 1982) concluded that industrial emissions and transport are the major sources of dry deposition from the atmosphere. Atmospheric particulate



matter is composed of aerosols and larger particles in the form of dust, soot, ash, fiber and pollen. The Edmonton study reported that the water soluble portion of collected urban air samples of total suspended particulates contained pollutants such as lead, nickel, chromium, cadmium, zinc, sulfate, nitrate and ammonium. The origin of atmospheric pollutants is attributed to sources such as construction sites, paved and unpaved areas, roads, landfills, tailing piles, industrial sources, fuel combustion from stationary and transportation sources, waste incineration, etc. A study (Hilborn and Still, 1990) of U.S. data indicated that the amounts and sources of toxic air pollutants can vary geographically from city to city and from neighborhood to neighborhood. Moreover, toxic air pollution is strongly influenced by local widespread sources, such as motor vehicles, wood stoves, combustion of oil and gas, metallurgical industries, chemical production and manufacturing, gasoline marketing, solvent use and waste oil disposal.

Wet deposition is a result of cloud processes that scavenge pollutants from the air at cloud altitudes and deposit them in falling rain, snow, and so on (Hicks, 1997). Studies on pollutant mass loading in precipitation and runoff have concluded that most of the atmospheric contaminants are washed out during the early stages of a rainfall event (Randall et al., 1982). Furthermore, the washout of atmospheric pollutants by rainfall droplets is effective and may contribute to a first-flush effect, indicating that pollutant concentrations in the earlier part of a precipitation event are higher than in the latter rainfall (Novotny et al., 1985). Urban rainfall is generally acidic in nature with pH values less than 5, which can cause damage to structures such as pavements, sewers and buildings. The atmospheric deposition of nitrogen compounds, trace metals, and organic compounds has caused substantial effects on water quality in the Chesapeake Bay area (Hicks, 1997). An example of typical atmospheric loadings in urban catchments is presented in Table 1 in the form of reported mean values.

**Table 1: Atmospheric loading in urban catchments**

Pollutant	Total Deposition Rate (g / m <sup>2</sup> -yr)	Wet Deposition Concentration (mg/L)	Snowmelt Concentration (mg/L)	Contribution to Runoff (%)
Total suspended solids	8.4 - 36.2	5 - 70	263 - 690	10 - 25
Chemical oxygen demand	0.44 - 31.6	8 - 27	15 - 25	15 - 30
Sulfates	6 - 15	4.8 - 46.1		31 - 100
Phosphorus	0.021 - 0.20	0.02 - 0.37		17 - 140 (sic)
Nitrate-nitrogen	1.8 - 8.2	0.5 - 4.4	4.1 - 5.7	30 - 94
Lead	0.04 - 4.0	0.03 - 0.12	0.3 - 0.12	15 - 54
Zinc	0.1 - 1.3	0.05 - 0.38	0.35 - 0.41	20 - 62

*Source: After Ellis (1986)*

Street refuse accumulation is characterized by locally generated particles of various sizes on the street surfaces. Typically, the fraction of street refuse passing a 3mm (1/8-inch) sieve is referred as 'dust and dirt'. In general, most of the accumulation of street refuse occurs within one meter of the curb, and hence the accumulation is often expressed as mass per unit of curb length. Particle sizes greater than dust and dirt are considered as litter deposits. The general litter deposits in urban areas include debris, solid wastes deposited on surfaces, paper and plastic products, building materials, vegetation, dead animals, and animal excreta, so on. The street dirt particles include disintegrated parts of larger litter particles, pavement deterioration particles, soil particles and small organisms.

Vegetation inputs including fallen leaves, seeds, grass clippings, and other vegetation residues contribute significant quantities of dust and dirt in urban areas. The rate of vegetation input increases substantially during the fall season depending on the density of vegetation. A study conducted in Etobicoke, in the Greater Toronto Area (GTA), showed that a significant amount of organic load originates from autumn leaves in an urban area (James and Boregowda, 1986). The presence of phosphorus in runoff is commonly attributed to its leaching from vegetation in addition to plant fertilizers. For example, the potential phosphorus content of tree leaves and seeds is reported to range from 1.6 to 11 mg/g (Waller and Hart, 1986).

Vehicular traffic constitutes a major source of pollutants in urban areas. It contributes to solids (including fine particles) and many chemicals including heavy metals, polycyclic aromatic hydrocarbons (PAHs) and deicing salts (Thomson et al., 1997). These pollutants originate from vehicle exhaust pipe emissions, vehicle operation, tire wear, solids carried on tires and vehicle bodies, and the abrasion and corrosion of highway structures. The more important sources of PAHs are from oil leakage of vehicle crankcases and exhaust pipe emissions. Furthermore, pavement conditions also have an effect on pollutant loads. Sartor et al. (1974), reported that streets paved with asphalt could have a loading about 80% higher than streets paved with concrete. A study (Berbee et al., 1999) on the characterization of highway runoff in the Netherlands indicated that the concentration of pollutants in runoff from impervious asphalt is significantly higher than in runoff from pervious asphalt.

In snow-belt areas, deicing salts and sand are applied to road surfaces and side walks to provide safe driving and walking conditions during the winter season. The applied salt potentially increases the chloride content of the runoff. As an example, the citywide salt application rates in Halifax, Nova Scotia contribute to an annual average chloride loading in runoff at the order of 3,000 kg/ha-yr. The median chloride concentration in winter grab samples of runoff increased to as much as 786 mg/L, while the mean summer concentration in runoff is reported at 14 mg/L, which is higher than the concentration of 4.6 mg/L recorded in total atmospheric deposition at Halifax (Waller and Hart, 1986).

Pervious urban areas are generally considered to be well protected by vegetation and they contribute pollutants such as pesticides and herbicides during larger rainfall events. However, erosion of soil from construction sites, vacant lands and suburban agricultural lands may contribute significant amount of solids and sediments, which further degrade the runoff quality.

## **Urban Runoff Quality Constituents**

The quality constituents of typical concern in urban runoff are visible matter, suspended solids, oxygen-demanding materials, nutrients, pathogenic microorganisms, and toxicants such as heavy metals, pesticides, and petroleum hydrocarbons (Field et al., 1998). These constituents can cause substantial impacts in terms of physical, chemical and biological stresses on receiving waters, resulting in ecological and environmental imbalance (Ellis and Hvitved-Jacobsen, 1996; Field et al., 1998; and Marsalek, 1998). Moreover, these impacts depend on the characteristics of both the catchment producing such discharges (in terms of runoff quantity and quality) and those of receiving waters. Hence, to protect the receiving water, the actual impacts should be evaluated in terms of specific characteristics of each site, including physical habitat alternation (e.g., change in morphology), water quality changes (e.g., dissolved oxygen depletion, and eutrophication), sediment and toxic pollutant impacts, impacts on biological communities, and ground water impacts (Ellis and Hvitved-Jacobsen, 1996).

To assess these impacts of stormwater discharges on receiving water quality, it is necessary to understand the effects of classes of pollutants independently as well as the combined effects of various pollutants. In the former case, the effects are understood to a reasonable extent; however, in the latter case, the combined effect of the entire range of different classes of pollutants is not well understood. To restore, maintain and enhance the physical, chemical and biological quality of receiving waters, the premise of urban runoff quality control analysis should focus on understanding the sources, types of pollutants from stormwater discharges and combined sewer overflows, their potential effects on receiving water bodies, and their control alternatives. The sources or origins of various pollutants found in urban runoff are described in the previous section, while the following section focuses on the types of pollutants and their effect on receiving water bodies.

### **Solids**

The most common pollutants in stormwater are organic and inorganic solids in the form of particulate or colloidal matter. These solids are either eroded from pervious surfaces or washed off the paved surfaces by stormwater. In addition, drainage systems supply a significant amount of solids, which are accumulated on the bottom of sewers, and from

the slime growth on the walls of the sewers during dry periods (Novotny and Olem, 1994). The solids content in runoff is measured as total solids, suspended solids, dissolved solids, and volatile solids as well as by turbidity [definitions of which may be found in Standard Methods, (Clesceri, et al., 1998)].

Suspended solids cause a number of direct and indirect environmental impacts such as increased turbidity, abrasion of fish gills and other sensitive tissues, reduction of visibility, transport of pollutants, loss of riparian vegetation with the concomitant loss of shade and refuge, decrease in sunlight penetration (interference with photosynthesis), and degradation of spawning areas. Suspended solids usually carry considerable quantities of other pollutants sorbed to their surfaces (Randall et al., 1986). Pollutants that are believed to have a particularly high affinity of adsorption on suspended solids include phosphorus, metals, and petroleum based organics. The effective means of removing suspended solids from stormwater are sedimentation and other forms of physical separation. In addition, the removal of suspended solids from stormwater may significantly improve the water quality because of simultaneous removal of the other pollutants with suspended solids. Typically, combined sewer overflows contain a higher suspended solids concentration than stormwater discharges (Moffa, 1990).

### **Nutrients**

Urban runoff may contain significant concentrations of nitrogen, phosphorus and carbon compounds which accelerate the nutrient enrichment and eutrophication of receiving waters. These substances are essential for the growth of aquatic plants and are regarded as biostimulants. The source of nutrients is attributed to leaching of vegetation, agricultural fertilizers in runoff and municipal wastewater discharges. Nitrogen in the form of ammonia and nitrates and phosphorus occurring as orthophosphates are readily available for plant growth, possibly leading to algal blooms and excessive macrophytic growth and causing depletion of dissolved oxygen upon death and decay. Common measures of nutrients are total nitrogen, nitrates, ammonia, total Kjeldahl nitrogen (TKN), total phosphorus, total organic carbon, and indirectly, alga mass and chlorophyll a. (Wanielista and Yousef, 1993).

### **Oxygen Demanding Matter**

Sufficient levels of dissolved oxygen (DO) in the water column are necessary to maintain aerobic conditions to support aquatic life. The influx of stormwater containing organic and other oxidizable matter may exert substantial oxygen demand on the water column impairing the water quality by depleting DO level. These impacts are estimated either by direct measurement of DO or by the indirect measures of biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC). Typically CSOs contain higher levels of oxygen demanding substances relative to storm discharges.

### **Microbiological Pollutants**

Both CSOs and stormwater discharges can be significant sources of microbiological pollution in receiving waters. Microbiological pollutants are typically described by organism counts per unit volume of water and include indicator bacteria, such as *Escherichia coli*, fecal coliforms, fecal streptococci and specific pathogens such as *Shigella*, *Salmonella* and *Clostridium*. These pollutants enter the drainage system from the washoff of animal feces and organic matter from catchment surfaces. Bacteria may also enter the drainage system through illegal sanitary sewer connections. Concentrations of indicator bacteria, such as *E. coli* and fecal coliforms, in CSOs and stormwater are often found in magnitudes well exceeding recreational water quality guidelines. Thus, recreational beaches in urban areas are frequently closed during and immediately after rainfall events because of fecal bacteria contamination caused by stormwater and CSOs. By definition, pathogenic bacteria and viruses may seriously affect human health. The removal of such microbiological pollutants is achieved primarily through the processes of biological decay, ultraviolet radiation and artificial disinfection where practiced.

### **Toxic Constituents and Priority Pollutants**

Studies in the United States, Canada and Europe indicate that heavy metals are the most prevalent toxic contaminant found in urban runoff (U.S. EPA, 1983a, Marsalek et al., 1997). Commonly found heavy metals are arsenic, cadmium, copper, iron, mercury, lead, selenium and zinc. The primary sources of heavy metals are traffic-related activities and atmospheric fall out. Unlike some organic compounds, heavy metals are not degraded in the environment and are toxic when present beyond a threshold concentration.

Deterioration of receiving water quality is also caused by the presence of elevated levels of toxic constituents in urban runoff commonly known as priority pollutants. The priority pollutants are a group of 129 toxic chemicals or classes of chemicals identified as substances of serious concern in the Clean Water Act of U.S. (Terstriep et al., 1986). The pollutants fall into ten groups: pesticides, metals and inorganic, PCBs (polychlorinated biphenyls), halogenated aliphatics, ethers, monocyclic aromatics, phenols and creosols, phthalate esters, PAHs, nitrosamines and nitrogen-containing compounds. Comprehensive investigations of toxic constituents and priority pollutants were conducted under the U.S. Nationwide Urban Runoff Program (NURP) (U.S. EPA, 1983a). Further studies conducted in the U.S. and Canada indicate that these priority pollutants are frequently detected in highway runoff (Sansalone and Buchberger, 1997; Marsalek et al., 1997).

The impacts of priority pollutants are evaluated on the basis of toxicity effects. Toxic pollutants have been characterized by acute or chronic effects on the environment (U.S. EPA, 1983b; Harremoes, 1988). Acute effects are characterized by relatively high

concentrations of pollutants within a relatively short time causing immediate physiological impacts such as in the ingestion of heavy metal laden water, while chronic effects are characterized by the cumulative impact of gradual exposure to relatively low concentrations of pollutants that accumulate in the tissues of organisms over long periods of time.

To evaluate the ecological impacts of these constituents in stormwater, water quality standards are defined in terms of their degree of toxicity. The permissible frequency and duration of exposure to conventional and priority pollutants (water quality standards) as suggested by the U.S. EPA are (Novotny, 1997):

- Acute toxicity criteria: 1-h average concentration (essentially a daily grab sample) not to be exceeded more than once in three years on an average.
- Chronic toxicity criteria: 4-day average concentration, not to be exceeded more than once in three years on an average.

It is generally recognized that a large percentage of heavy metals and toxic contaminants have a high affinity for the suspended sediments present in runoff. This association is fortuitous in terms of control and treatment of runoff since it is relatively easy to separate suspended solids and the pollutants attached to them.

### **Other Parameters**

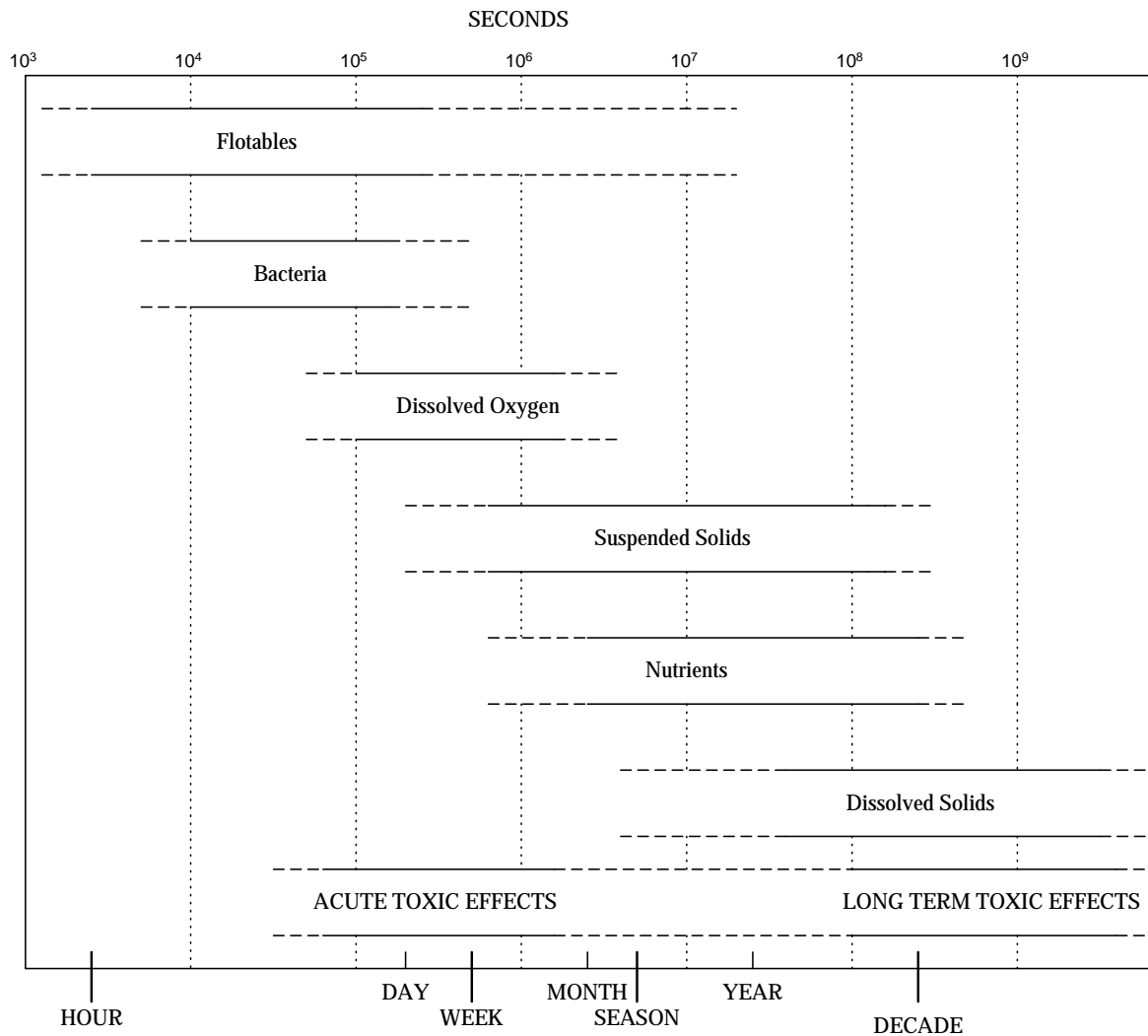
In listing the runoff quality parameters of concern, physical parameters such as gross solids, turbidity, temperature, pH and electrical conductivity are also considered. The presence of dispersed and floatable materials along the shores of beaches or embankments deteriorates the aesthetic value of water bodies.

Temperature is an important parameter because urban surfaces may increase the temperature of runoff by as much as 100C compared to runoff from undeveloped areas (Marsalek, 1998). This thermal enrichment can influence the physiological processes of aquatic organisms such that original cold-water fisheries may become warm-water fisheries over time. The increase in temperature also decreases the water's capacity to dissolve oxygen. In addition, the rise in temperature increases the rate at which nutrients attached to solid particles are converted into readily available soluble forms (Hall, 1984). Urban runoff also conveys large amounts of chlorides originating from road salting during winter. The primary physical environmental effects of elevated chlorides are high discharges of dissolved solids and the establishment of density gradients in receiving waters, especially lakes (Waller and Hart, 1986). The presence and amount of chloride ions is measured by the electrical conductivity of the sample.

## Characteristics of Runoff Quality Constituents

The analysis of urban stormwater quality problems requires an understanding of the characteristics of runoff pollutants and the nature of receiving waters. As described in the previous section, different types of pollutants have different types of impacts on receiving waters, and they operate on different temporal and spatial scales. The time scale of the pollutant effects on the receiving water is influenced by the characteristics of various pollutants.

The time scale of concern ranges from a few hours to a few years. Figure 1 illustrates the time scale of different categories of runoff pollutants. For example, water-borne pathogens may die away relatively quickly in receiving waters; thus, the time scale of interest in this case is relatively short (e.g., on the order of several hours or days). In this case, interest would lie in the low frequency overflow events, causing high concentrations of pathogens. Short-term effects are associated with bacteria, biodegradable organic matter and hydraulic effects. In contrast, plant nutrients such as phosphorus influence long-term effects related to eutrophication, causing interest in relatively long time scales (e.g., on the order of several years). Interest would lie more in the average annual mass discharges to the receiver. Long-term effects tend to be associated with suspended solids, nutrients and heavy metals. In still other cases, such as certain type of hazardous contaminants, both the long and short time scales would be of concern. Typically, the short time scale problem of acute toxicity and long time scale problem of toxic contaminant accumulation and chronic toxicity would cause interest in both the low frequency, high concentration overflow events and the average annual mass discharges to the receiving waters.



**Figure 1: Time scale effects of runoff quality constituents (after U.S. EPA, 1979)**

The spatial scale ranges from the localized receiving water to waters that are hundreds of kilometers from the sources. For instance, bacterial contamination generally occurs in a localized area (e.g., beach closures), while some toxic substances such as pesticides, persistent organics and heavy metals, which are viewed on the longer time scale, tend to be persistent (i.e., they do not readily decay in environment) over hundred of miles (U.S. EPA, 1979). The relevancy of characteristics of pollutants found in urban runoff is an important consideration in receiving water analysis.

To effectively address the water quality problems arising from urban runoff, the quantitative aspects of runoff quality, in particular the acquisition of data and analysis of



data is important. Recent advances in water quantity and quality monitoring technologies gradually provide cost-effective means of collecting large amounts of information for complex water quality problems. Technological advances in water quality data analysis, however, have lagged, particularly for converting raw data into information, which can support decision-making on a regular basis (Hughes and Kummeler, 1998). Therefore, intelligent decisions about the runoff quality management can be made easier when the appropriate data analysis methodologies are developed to derive information in suitable forms that would be useful.

## **Monitoring Runoff Quality at the Rock Creek**

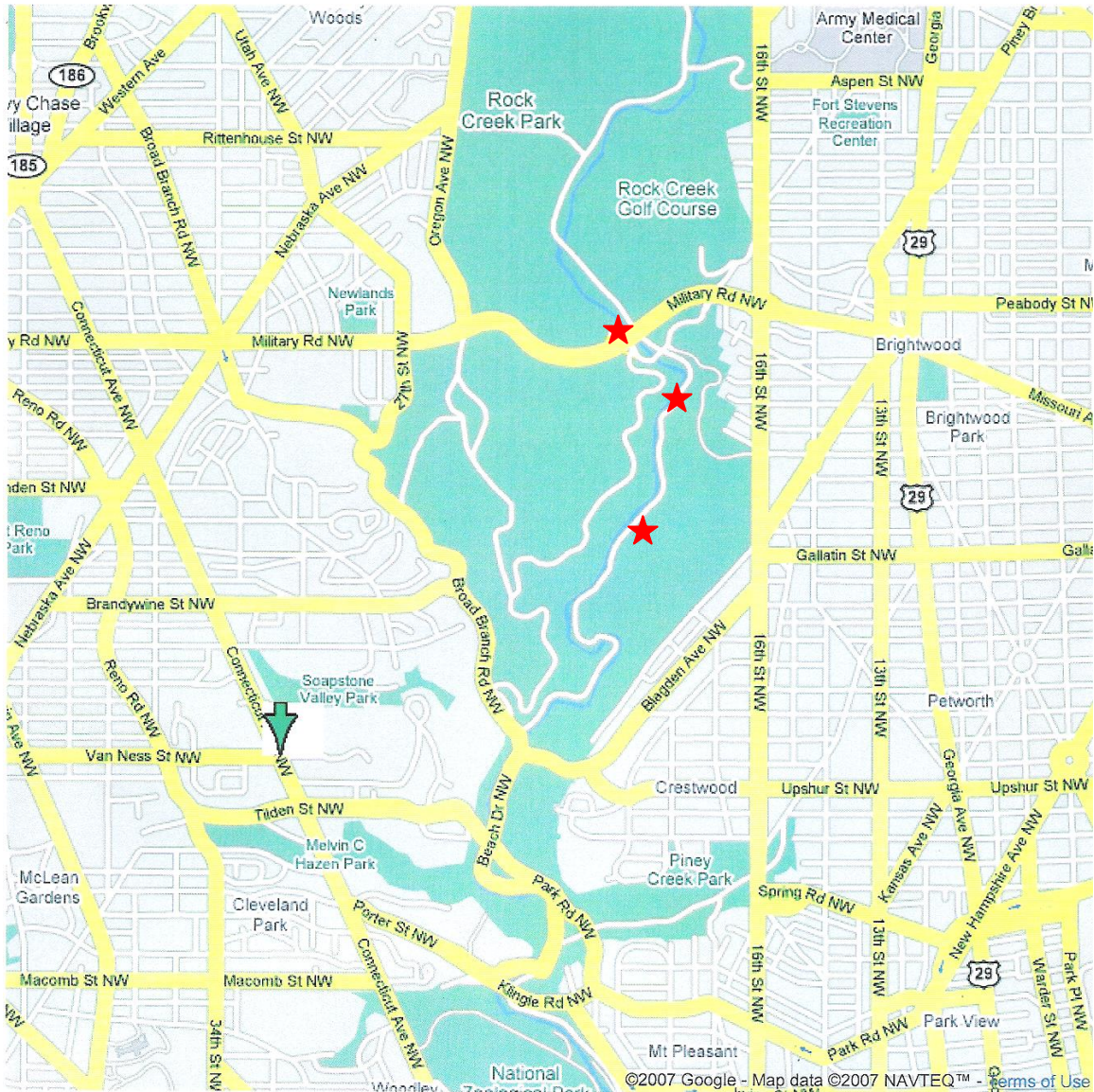
Monitoring and modeling are two essential components of implementing CSO Control policy (EPA, 1999). A planned development and implementation of a monitoring and modeling effort will support the selection and implementation of cost-effective CSO controls and an assessment of their improvements on receiving water quality.

Rock Creek, a tributary of the Potomac River is primarily an urban stream. The watershed for the creek covers part of Montgomery County (approximately 60 mi<sup>2</sup>) and part of the District of Columbia (approximately 16 mi<sup>2</sup>). The total length of the Rock Creek (in Maryland and Washington DC) is approximately 33 mi of meandering stream. The Creek flows from its source near Laytonsville, Maryland to the Potomac River in Washington DC. Water quality in Rock Creek is important to biotic life in and near the creek, and in the Potomac River Basin and the Chesapeake Bay (USGS, 2000). The water quality of the Rock Creek has been affected by urbanization and agricultural growth in the watershed.

In the long-term monitoring program, it is envisioned that a number of water quality parameters that include suspended solids, nutrients, heavy metals and other toxins, will be monitored. Total Suspended Solids (TSS) has been considered as an indicator pollutant and typically used for stormwater modeling. It is also envisioned that TSS will be continuously monitored at various representative sites of Anacostia and Potomac Rivers and Rock Creek and the monitored data will be used for the development of integrated drainage system and receiving water system models. The monitored data will be analyzed in the environmental laboratory of the University.

The scope of this present research is limited to field monitoring of Dissolved Oxygen at several locations within the Rock Creek nearer to University of the District of Columbia. The data presented in this report were collected from three locations along the Rock Creek in the fall and spring season of 2006-2007. The monitoring was conducted in November 2006 to represent fall season and in March 2007 to represent spring season.

Figure 2 presents the location of three sampling stations along the Rock Creek within the Washington DC.



**Figure 2: Locations of DO sampling stations**

Dissolved Oxygen was measured at the three locations using a calibrated Oakton RS232 Dissolved Oxygen meter. Two undergraduate engineering student interns were trained to take the field measurements. The three locations include at the upstream of Military Road bridge crossing, nearer to police head quarter and third location is 0.5 miles south of Military Road bridge crossing.

Figures 2 to 4 presents the location of three sampling stations.



**Figure 2: Station 1 – Located near to Police Head Quarter**



**Figure 3: Station 2 – Located upstream of a Military Road bridge crossing**



**Figure 4: Station 3 – Located south of Military Road bridge crossing**

Table 2 through 4 present the measured DO data for three locations for fall and spring seasons.

**Table 2 - Station 1: Near Police Head Quarter**

Season	Date	Temperature (°C)	Dissolved Oxygen (mg/L)
Fall	11/1/2006	13.7	16.2
	11/13/2006	14.5	9.8
	11/15/2006	12.8	11.2
	11/20/2006	7.8	13.1
	11/27/2006	11.5	11.6
Spring	3/1/2007	5.9	16.2
	3/5/2007	9.2	13.7
	3/6/2007	3.3	17.2
	3/9/2007	9.9	14.0
	3/12/2007	11.8	14.1
	3/13/2007	12.6	14.8
	3/15/2007	16.0	13.4
	3/19/2007	12.4	13.0
	3/20/2007	15.4	12.8
	3/23/2007	18.5	13.6
	3/26/2007	15.5	16.3
	3/27/2007	19.1	16.0
	3/29/2007	15.8	16.9

**Table 2 - Station 2: Upstream of a Military Road bridge crossing**

Season	Date	Temperature (°C)	Dissolved Oxygen (mg/L)
Fall	11/1/2006	18.2	11.4
	11/13/2006	10.9	10.3
	11/20/2006	8.3	12.7
	11/27/2006	8.2	13.2
Spring	3/1/2007	5.2	15.8
	3/5/2007	7.4	14.8
	3/6/2007	4.7	16.5
	3/9/2007	4.7	14.0
	3/12/2007	9.6	15.2
	3/13/2007	12.4	15.2
	3/15/2007	14.2	14.3
	3/19/2007	8.6	14.9
	3/20/2007	12.8	14.1
	3/23/2007	17.1	13.5
	3/26/2007	14.4	17.0
	3/27/2007	19.1	16.0
	3/29/2007	16.0	17.6

**Table 3 - Station 1: 0.5 mile south of Military Road bridge crossing**

Season	Date	Temperature (°C)	Dissolved Oxygen (mg/L)
Fall	11/1/2006	10.7	12.4
	11/13/2006	14.3	10.6
	11/20/2006	7.9	14.2
	11/27/2006	9.7	13.3
Spring	3/1/2007	5.2	16.4
	3/5/2007	7.8	14.9
	3/6/2007	3.1	17.8
	3/9/2007	9.9	14.0
	3/12/2007	10.7	15.4
	3/13/2007	13.1	14.7
	3/15/2007	14.4	14.6
	3/19/2007	7.9	15.6
	3/20/2007	12.9	14.1
	3/23/2007	16.8	13.3
	3/26/2007	13.9	15.9
	3/27/2007	19.6	14.6
	3/29/2007	15.8	16.9

The average temperature for the fall 2006 was 11.4 °C and for the spring 2007 was 12 °C. Table 5 presents the mean and standard deviation of DO at the three locations.

**Table 5: Mean and Standard Deviation of DO at three locations**

Season	Station 1		Station 2		Station 3	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.
Fall 2006	12.4	2.43	11.9	1.31	12.6	1.54
Spring 2007	14.6	1.55	15.3	1.24	15.2	1.26

The measurement of Dissolved Oxygen at the Rock Creek reveals that there is no evidence of low dissolved oxygen problems around the measured locations. The stream is naturally aerated by turbulence as it flows over the irregular channel bottom. It is free-flowing stream which provides relatively short residence time to wet weather pollution.

## Modeling of Urban Stormwater Management

The analysis of urban catchment systems is prerequisite to the planning and design of stormwater management, which not only allows the assessment of existing conditions but also helps to understand the behavior of the system under various design conditions. In addition, the analysis with economic functions assists in determining appropriate cost-effective control measures.

Urban catchment systems are subjected to rainfall input - a random phenomenon. Therefore, the hydrologic, hydraulic and pollutant processes that govern the system are complex in nature. The system variables and process parameters also vary temporally and spatially and, as a result, the analysis of such systems is generally performed on simplified representations based on various assumptions that may or may not sufficiently represent the underlying processes for planning purposes. Often these representations use mathematical relationships intended to imitate the pertinent processes. Because these representations are not perfect, verification and validation is required for their regular use in similar situations. Verification is the adjustment of model parameters to replicate the measured condition and validation is confirmation of verification for a wide range of conditions. The model can be used to understand the system behavior (i.e., how the model output changes realistically as input to the model is varied).

A range of stormwater models, from simple to comprehensive, exists for the analysis of urban catchment systems. Models that provide greater levels of accuracy are complex, comprehensive models and include a heavy computational burden. Therefore, while selecting a model for the analysis, a balance must be struck between the accuracy and simplicity of the model, wherein this balance is dependent on the analysis objectives of the required model (Adams and Papa, 2000).

As is noted, the models are based on simplifications, and cannot provide a precise representation of physical reality under all conditions; however, they should provide reasonable solutions for the intended problems. Therefore, the system analyst should be aware of the assumptions on which the model is formulated and the limitations of the modeling exercise. Beyond these limitations, models provide the analyst an economical advantage over their prototypes because models render performance analysis of the system for the full range of conditions to which the prototype might be subjected.

In urban stormwater quantity and quality analysis, only monitoring theoretically can provide the ideal long-term information required for planning and design of systems (Nix et al., 1983). But, being cost prohibitive, monitoring over a realistic limited time frame cannot directly provide, a priori, the information needed to characterize the long-term behavior of a wide range of future designs. Therefore, it is essential to have properly formulated and validated models which can predict system behavior for analysis and design.

Urban stormwater models are developed in a mathematically descriptive mode to simulate the system or in a predictive mode to evaluate control performance before implementing the expensive measures in the field. These models and their mathematical equations - are defined by:

- System input such as rainfall and temperature;
- System output such as runoff volume, infiltration, runoff rate and pollutant load;
- System parameters of the urban catchment system such as runoff coefficient, depression storage, pollutant buildup and washoff coefficients;
- The control or decision variables such as design storage volumes and outflow rates.

Models describing stormwater management systems are classified in many ways, including the level of detail they provide, the type of approach they adopt and the time frame of analysis. Generally, based on their analysis timeframe, models fall into two categories: (i) event-based models and (ii) continuous simulation models. Each type of model has advantages and disadvantages.

Traditionally, runoff quantity control problems have been dominant in the urban stormwater management, and the design of quantity control systems was accomplished with event-based models. In this approach, an analysis is performed to select a design storm of a specified duration and frequency from a historical rainfall record or from synthetically generated rainfall patterns, and used to estimate runoff peaks and volumes. A commonly used event-based model is, for instance, the "rational method". This approach ignores the effects of successive events on the analysis; therefore, it is not

suitable for estimating the average long-term performance of the system. This approach is not suitable for runoff quality analysis, which is strongly influenced by more frequent and smaller rainfall events and which requires long-term analysis. In addition, a fundamental assumption of assigning a unique frequency to a natural hydrologic event and assigning this same frequency to both input and system output are questionable (Adams and Papa, 2000). Although event-based approaches have been employed in urban runoff control planning for many years, the current direction is towards the application of continuous simulation and probabilistic models for the long-term performance analysis of urban systems.

Continuous simulation modeling is currently considered to be the most sophisticated approach to stormwater modeling. It is a form of deterministic modeling of the physical system that not only considers the properties of a storm but also evaluates the impacts of closely-spaced successive storms. This approach is considered continuous because it uses long-term rainfall records as inputs to produce a continuous time series of output variables and continuously updates soil moisture etc. The statistics of the time series of output variables are then used for predicting the performance of the system. Continuous simulation can provide additional information such as the quality of runoff and pollutant loads as they can track the antecedent conditions, preceding pollutant buildup and storage conditions. However, these models are both data computation, and resource intensive and require elaborate calibrations. They are usually preferred in the detailed design analysis phase of engineering studies. In terms of rigor of the modeling approach, some are less intensive, such as STORM (U.S. Army Corps of Engineers, 1974) and the HSPF (Hydrologic Simulation Program- FORTRAN) (Johanson et al., 1984). The more rigorous and comprehensive continuous simulation models include the U.S. EPA's Storm Water Management Model, SWMM (Huber and Dickinson, 1988), and the Quantity-Quality Simulator, or QQS, (Geiger and Dorsch, 1980).

An alternative to continuous simulation is to model the system by the analytical probabilistic modeling approach. The basic premise for both the continuous simulation and analytical modeling approach remains same - long-term meteorology is the input to the model. Continuous simulation attempts to predict the system response of the output variable (i.e., dependent variable) time series in the sequence that would occur from the input time series (historical or synthetically derived rainfall), and post-processed statistical analysis provides the average, and/or long-term performance of an output variable. The analytical probabilistic approach fits probability distributions to the rainfall characteristics (e.g., rainfall event volume, durations, intensity and interevent times) determined from the same rainfall record otherwise used for continuous simulation. These fitted probability distribution functions (PDFs) are used to represent the independent variables and the parameters of the PDFs constitute the input to the model. The deterministic functional relationships (e.g., hydrologic and hydraulic processes) between the independent and dependent variables of continuous simulation models



constitute the transformation function of the analytical probabilistic models, albeit, in a simplified manner. Using derived probability distribution theory (Benjamin and Cornell, 1970), the PDFs of the dependent variables are derived from those of the independent variables and the transformation functions. Often closed-form solutions of the dependent variable PDFs, which depict the system performance measures in terms of the independent variables, are obtained. The relative modeling agreement between the analytical and the continuous simulation approaches may be attributed to how well the PDFs of the input variables are hypothesized and the transformation functions are simplified and other things.

Since the PDFs of meteorological inputs are derived from the statistical analysis of long-term rainfall records, the mathematically derived PDFs of system outputs reflect the long-term performance of the drainage system under analysis (Papa et al., 1998). This method is intended to approximate continuous simulation modeling and is recommended for preliminary planning and design because of its computational efficiency. Furthermore, the closed-form mathematical equations can be easily incorporated into an optimization framework for system analysis. A recognized limitation of this approach is the simplified representation of urban drainage systems.

In the last decade, researchers have been developing a family of analytical probabilistic models and planning methodologies for analyzing the various aspects of urban stormwater management planning. These models are based on different hydrological representations, which range from simple such as STORM-type hydrology to complex such as SWMM-type hydrology. As an added contribution, analytical probabilistic models and planning methodologies developed in this thesis are intended for analyzing and controlling runoff pollution in urban catchments. The models proposed in this research are intended to be used for screening and planning level analysis to provide immediate insight into the magnitude of stormwater quality problems and to provide preliminary cost-effective designs of quality control alternatives. In the following section, a brief review of existing analytical probabilistic urban stormwater models is presented.

## **Analytical Probabilistic Stormwater Models**

Benjamin and Cornell (1970) outlined the derived distribution theory and its applications to civil engineering problems in their classic textbook *Probability, Statistics and Decisions for Civil Engineers*. The theory permits the derivation of the probabilistic characteristics of a system output from the probabilistic characteristics of system input(s) and the knowledge of relationship between system input and output. As described in the previous section, the application of this theory to hydrological and urban water resources problems has culminated with the development of a set of analytical probabilistic models for urban stormwater management planning which can be used either as a parallel

approach to continuous simulation modeling, or as a complementary aid to continuous simulation. In this research, the models developed on the basis of the derived probability distribution approach are referred as analytical probabilistic models, or analytical models, or derived probability models. The remainder of this section briefly reviews the development and application of analytical models in urban stormwater analyses.

Eagleson (1972) first applied the derived probability distribution theory to water resources engineering through hydrological problems. Eagleson (1972) derived the frequency of peak streamflow rates from a catchment from the exponential PDFs of climatic variables that included rainfall event average intensity, event duration and interevent time. The derived relationship between dependent and independent variables established the theoretical basis for estimating peak flood flow frequency in the absence of streamflow records and provided the insight of the effects of land use and climatic changes on flood frequency.

Howard (1976) applied the derived probability distribution theory to analyze the control performance of storage-treatment systems; which not only introduced the theory of storage in the analysis of urban drainage systems but also paved the way for further research. The probability distribution of spill volumes from a storage reservoir was derived from the joint PDFs of rainfall event volume and interevent time assuming that the reservoir is full at the end of the previous rainfall event. In the derivation, it is assumed that the rainfall events occur instantaneously. Following the pioneering work of Howard, a number of research studies were conducted at the University of Toronto, which improved substantially on the initial development.

Smith (1980) improved the Howard model by incorporating the steady-state probability distribution of reservoir contents at the end of the last storm. The derivation was based on the joint PDFs of three rainfall characteristics - event volume, duration and interevent time. The PDFs of rainfall characteristics were assumed to be independent and exponentially distributed and the joint PDFs were formulated as a product of their marginal distributions. The probability distribution of storage level after a storm event was determined numerically using a transitional matrix. The analysis of a single catchment with a storage reservoir by Howard's and Smith's method was extended to a series of catchments in cascade by Schwarz (1980) and Schwarz and Adams (1981). Each catchment was described by a catchment area, hydrological and meteorological parameters, a reservoir storage volume and a controlled outflow rate. Models were developed for both conditions of spill routed to downstream catchments and spills routed out of the system to a receiving water.

Adams and Bontje (1984) simplified Howard's single catchment model by considering the two extremities of reservoir conditions such as reservoir full and reservoir empty at

the end of the last rainfall event and also derived many other performance characteristics which include annual number of spills and average annual runoff volume control. These theoretical developments were incorporated into a software package called the Statistical Urban Drainage Simulator (SUDS) by Bontje et al. (1984).

In order to relax and/or verify the assumption of statistical independence of rainfall characteristics, Seto (1984) explored several alternative derivations of Howard's model incorporating the statistical dependence between rainfall characteristics. The derived models were compared to that of Howard (1976) and to STORM simulations. The closed-form analytical probabilistic models that were developed on the basis of statistical independence of rainfall characteristics compared favorably with continuous simulation models; however, the Howard model maintained the closest agreement to the simulation model.

Water quality aspects of stormwater drainage were addressed by Flatt and Howard (1978). They initiated the investigation of pollution control effectiveness of storage-treatment systems assuming constant, uniform pollutant concentrations in runoff and uniform treatment efficiencies. Zukovs (1983) developed a methodology to predict the quality behavior of urban runoff. The models were developed to predict runoff volume and pollutant loads from urban catchments, to evaluate the effectiveness of source control measures and to evaluate the pollution control effectiveness of downstream storage-treatment systems. Derivation of analytical models was based on linear pollutant buildup and washoff processes. Storage analysis considered both batch and detention mode operation and pollutant removal was described by either first order decay or sedimentation. Although the mathematical formulations of the above were developed, their closed-form solutions were not obtained. In addition, the models were compared neither with simulation models nor with field data.

DiToro and Small (1979) derived probability distributions of stormwater overflows to evaluate the performance analysis of storage-interceptor treatment devices. They assumed a gamma distribution of runoff characteristics such as runoff flow, duration, and interevent time as opposed to rainfall characteristics, and the flow was assumed to be uniform over the duration. Several of the derived expressions did not have analytical solutions and required numerical evaluation. The analytical control isoquants, which could achieve the same fraction of runoff load control by different combinations of storage-interceptor devices, were compared with those predicted by continuous simulation STORM model. It was found that these control isoquants were in good agreement with those simulated by STORM model. Employing log-normal probability distributions of stormwater overflows and those of upstream flow rates and pollutant concentration, DiToro (1984) derived the probability distribution of in-stream pollutant concentration. This methodology was successfully applied to several water pollutants for several rivers in the U.S. Loganathan and Delleur (1984) and Loganathan et al.

(1985) employed an exponential probability distribution of runoff characteristics such as volume, duration, and interevent time to derive probability distributions for overflow volume from a runoff control reservoir. The overflow volume and pollutant concentrations were used to calculate the in-stream water quality concentration after mixing during critical periods.

The application of derived analytical probabilistic models to various practical problems have been demonstrated through real-world problems and hypothesized examples. Adams and Zukovs (1986, 1987) applied the models of Adams and Bontje (1984) to evaluate several rehabilitation alternatives for combined sewer systems including source controls, downstream storage, interceptor capacity, outfall treatment and sewer separation. The methodology was applied to a single combined sewer catchment in the City of York, Ontario. Zourntos (1987) extended the work of Adams and Zukovs (1986, 1987) by applying the models of Schwarz (1980) to combined sewer overflow analysis for a series of catchments in the City of York, Ontario.

Furthermore, analytical probabilistic models have been compared to both simulation model results and field measurements in many of the above studies. A very comprehensive comparison between analytical and simulation model results was undertaken by Kauffman (1987). In general, the agreement between the two modeling approaches is favorable, which is surprisingly considering the reduced level of effort required to produce the analytical model results.

As the analytical modeling approaches primarily depends on the input of meteorological statistics, extensive studies have been performed on long-term meteorological data to establish the functional forms and parameters of PDFs of rainfall characteristics. These studies include Adams et al. (1986), Walkovich and Adams, (1991).

In order to cater to the current emphasis on runoff quality control of urban drainage systems, many developments have been made, especially with respect to the long-term pollution control performance of stormwater management practices (SWMPs) or best management practices (BMPs). Research efforts include Li (1991), Segarra-Garcia and Loganathan (1992), Guo and Adams (1994), and Papa and Adams (1996).

Many analytical system performance models of urban drainage systems are closed-form expressions. Therefore, they offer two major advantages compared to continuous simulation counterparts in the screening and planning level analysis. First, not only is it easy to generate the results for obtaining runoff control tradeoffs among available alternatives, but it is also possible to perform sensitivity analysis, an approach that helps to gain an understanding of the system behavior. Second, various techniques of system analysis can easily be applied to formulate methodologies, which incorporate economic and performance functions for developing cost-effective design alternatives.

In summary, as an alternative approach to continuous simulations the above analytical models provide not only a computational competitive method but also provide enhanced insight into system behavior for screening and planning level analysis of urban drainage systems. The theoretical developments and the models developed at the University of Toronto are presented in Adams and Papa (2000). As urban runoff quality problems are emerging as major issues of urban stormwater management, models of runoff quality and methodologies that incorporate quality and quantity control simultaneously are warranted.

## **Modeling Approach**

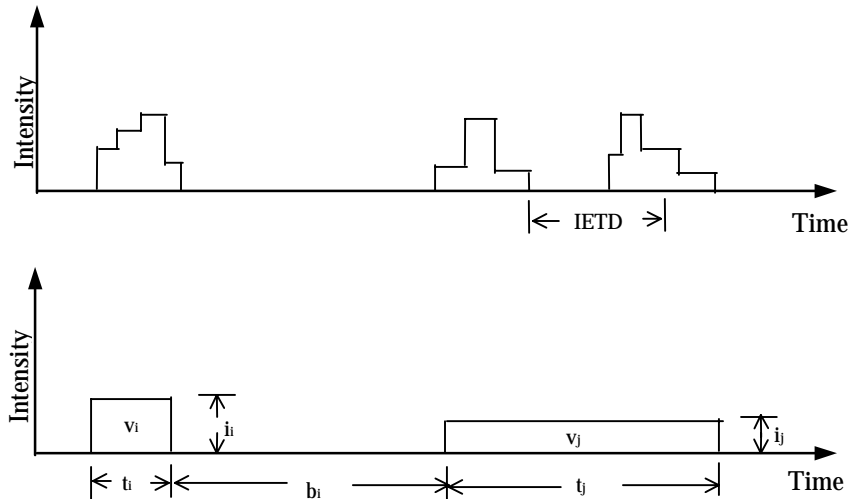
In this research, an analytical probabilistic modeling approach is employed as an alternative to continuous simulation. The basic premise for both the continuous simulation and analytical modeling approaches remains same – long-term meteorology is the input to the model. Continuous simulation attempts to predict the system response of the output variable (i.e., dependent variable) time series in the exact sequence that would occur from the input time series (historical or synthetically derived rainfall), and post-processed statistical analysis provides the average, and/or long-term performance of the output variable. The analytical probabilistic approach fits probability distributions to the rainfall event characteristics (e.g., rainfall event volume, duration, intensity, interevent time) determined from the same rainfall record otherwise used for continuous simulation. These fitted probability density functions (PDFs) are used to represent the independent variables and the parameters of the PDFs constitute the input to the model. The deterministic functional relationships (e.g., hydrologic and pollutant buildup and washoff processes) between the independent and dependent variables of continuous simulation models constitute the transformation function of the analytical probabilistic models, albeit in a simplified manner. Using derived probability distribution theory [Benjamin and Cornell, 1970], the PDFs of the dependent variables are derived from those of the independent variables and the transformation functions. Often closed-form solutions of the dependent variable PDFs, which depict the system performance measures in terms of the independent variables, are obtained [Adams and Papa, 2000]. The modeling performance of the analytical approach relative to continuous simulation is determined by how well the PDFs of the input variables are formulated and the transformation functions are simplified. Since the PDFs of meteorological inputs are derived from the statistical analysis of long-term rainfall records, the mathematically derived PDFs of system outputs reflect the long-term performance of the drainage system under analysis. This approach is intended to approximate continuous simulation modeling and is recommended for the preliminary planning and design stage because of its computational efficiency.

The advantage of such analytical methods is their generality; however, closed-form solutions generally require simplified system representations. Such methodologies have been applied in previous research to develop models for urban hydrology and storm water runoff control analysis [e.g., Eagleson, 1972; Howard, 1976; Adams and Bontje, 1984; Loganathan and Delleur, 1984; Guo and Adams, 1998]. A systematic application of such techniques to the development of analytical models for stormwater management analysis can be found elsewhere [Adams and Papa, 2000].

## **Example - Development of an Analytical Probabilistic Model**

### **Rainfall Data Analysis**

The development of analytical runoff quality models begins with a probabilistic representation of rainfall characteristics, through a statistical analysis of the long-term historical rainfall record. The available continuous chronological rainfall record is first discretized into individual rainfall events separated by a minimum period without rainfall – termed the interevent time definition (IETD). If the time interval between two consecutive rainfalls is greater than the IETD, the rainfall events are considered as two separate events. Once this criterion is established, the rainfall record is transformed into a time series of individual rainfall events and each rainfall event can be characterized by its volume ( $v$ ), duration ( $t$ ), interevent time ( $b$ ) and average intensity ( $i$ ). Next, a frequency analysis is conducted on the magnitudes of the time series of rainfall event characteristics, from which histograms are developed. Probability density functions are then fitted to these histograms. Although gamma distributions may better represent some climates, exponential probability distribution functions often fit such histograms satisfactorily for many climatic regions [e.g., Eagleson, 1972; Howard, 1976; Adams et al., 1986; Guo and Adams, 1998]. Moreover, the exponential distribution has the advantage of easier mathematical manipulation. An average annual number of events can also be obtained from the statistical calculations. In the development of the analytical runoff quality model proposed herein, the exponential PDFs of event rainfall volume and interevent time are utilized. Parameters of the exponential PDFs of rainfall volume and interevent time are denoted by  $\lambda$  and  $\mu$ , and the values of these parameters can be obtained by taking the inverse of the average event volume,  $\bar{v}$ , and average interevent time,  $\bar{b}$ , respectively. The selection of the IETD is governed by the intended application. An IETD of six to twelve hours is used for the analysis of urban runoff quality in this research.



**Figure 5: Discretization of long-term rainfall record**

### **Development of analytical expression for annual average runoff volume**

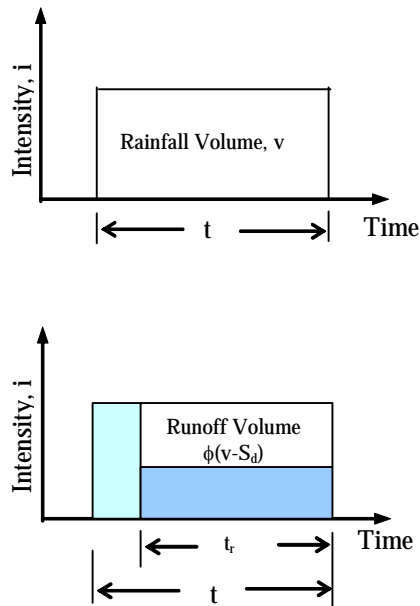
The analytical probabilistic models are intended for screening and planning level analysis of urban stormwater management systems. Accordingly, the models are developed based on simplified system representations. Generally an analytical model employs a single urban catchment as the system. The urban catchment is characterized by its hydrologic parameters such as depression storage and runoff coefficient. Most of the models are developed on a per unit catchment area basis from which the performance measures for the entire catchment can be calculated.

The estimation of runoff quantity and quality by analytical probabilistic models is primarily based on the PDFs of rainfall characteristics and a rainfall-runoff transformation function employed in the model derivation. From modeling perspective, when rain falls on a catchment, it must satisfy the hydrologic losses including interception, depression storage and infiltration losses, before runoff occurs. If the volume of the rainfall event is sufficient to satisfy these hydrologic losses, then the resulting runoff from various pervious and impervious surfaces makes its way to the catchment outlet either through a drainage system or through natural channels. Processes that transform rainfall to runoff are many and they vary spatially and temporally. It is difficult to accommodate all of them in deterministic models and even more so in analytical probabilistic models.

The estimation of runoff quantity is a prerequisite for the estimation of runoff quality. The rainfall-runoff model used in this study follows the system representation presented by *Adams and Bontje* [1984], which employs a depression storage volume and a runoff coefficient to evaluate the resulting event runoff volume. The continuous simulation model STORM uses the same representation for runoff generation. This linear hydrologic model of the rainfall-runoff transformation employed herein is as follows:

$$v_r = \begin{cases} 0 & v \leq S_d \\ \phi(v - S_d) & v > S_d \end{cases} \quad (1)$$

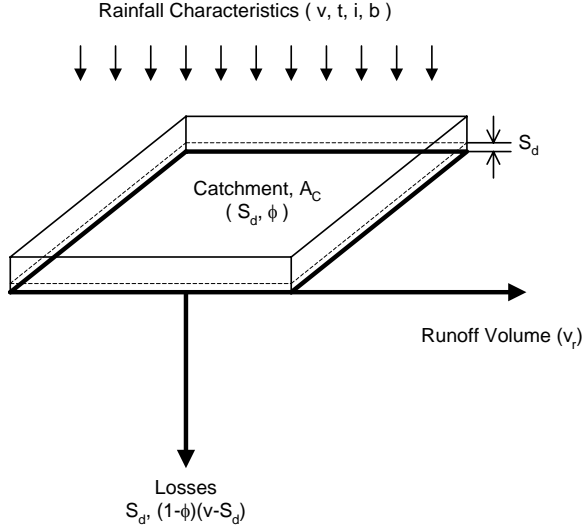
where  $v_r$  is the runoff volume (mm), and the rainfall volume,  $v$  (mm) must satisfy the volume of depression storage,  $S_d$  (mm), before any runoff can be generated. For rainfall volumes greater than  $S_d$ , the runoff volume is determined by the product of a dimensionless runoff coefficient,  $\phi$ , and the excess of rainfall over depression storage.



**Figure 6: Rainfall-runoff Transformation**

The runoff coefficient is a spatially and temporally average constant that is selected based on land use and is typically estimated from the percentage of impervious area. It is noted that the volumes are normalized by the catchment area and are expressed in terms of a uniform depth across the entire catchment.





**Figure 7: Schematic Representation of Rainfall and Runoff Process in a Urban Catchment**

In this system representation, it is assumed that the duration of the runoff event is equal to the duration of the rainfall event. The event rainfall volume can be described by an exponential PDF as follows:

$$f_V(v) = \zeta e^{-\zeta v}, \quad \zeta = 1/\bar{v} \quad (2)$$

where  $\bar{v}$  is the mean rainfall event volume (mm). Given the marginal PDF of event rainfall volume and the rainfall-runoff transformation function (1), the cumulative distribution function (CDF) of event runoff volume,  $F_{V_r}(v_r)$ , can be obtained using derived probability distribution theory as follows:

$$\begin{aligned} F_{V_r}(v_r) &= \Pr[V_r \leq v_r] = \Pr[v_r = 0] + \Pr\left[S_d < V \leq \frac{v_r}{\phi} + S_d\right] \\ &= \int_{v=0}^{S_d} f_V(v) dv + \int_{v=S_d}^{\frac{v_r}{\phi} + S_d} f_V(v) dv = 1 - e^{-\zeta\left(\frac{v_r}{\phi} + S_d\right)} \end{aligned} \quad (3)$$

The PDF of the event runoff volume,  $f_{V_r}(v_r)$ , can be obtained by taking the derivative of  $F_{V_r}(v_r)$  as follows:

$$f_{V_r}(v_r) = \frac{d}{dv_r} F_{V_r}(v_r) = \frac{d}{dv_r} \left[ 1 - e^{-\zeta \left( \frac{v_r + S_d}{\phi} \right)} \right] = \frac{\zeta}{\phi} e^{-\zeta \left( \frac{v_r + S_d}{\phi} \right)}, \quad v_r > 0 \quad (4)$$

The expected value of the event runoff volume,  $E[V_r]$  is obtained as follows:

$$E[V_r] = 0 \cdot p_{V_r}(0) + \int_0^{\infty} v_r f_{V_r}(v_r) dv_r = \int_{v_r=0}^{\infty} v_r \cdot \frac{\zeta}{\phi} e^{-\zeta \left( \frac{v_r + S_d}{\phi} \right)} dv_r = \frac{\phi}{\zeta} e^{-\zeta S_d} \quad (5)$$

Equation (5) represents the model for expected runoff volume per event from urban catchments which is a function of the rainfall volume PDF parameter ( $\zeta$ ) and catchment characteristics parameters  $\phi$  and  $S_d$ . From the expected event runoff volume, the average annual runoff volume,  $R$ , can be obtained as

$$R = \theta \cdot E[V_r] = \theta \frac{\phi}{\zeta} e^{-\zeta S_d} \quad (6)$$

where  $\theta$  is the average annual number of rainfall events.

Using the equation (6), the average annual runoff volume can be obtained for an urban catchment. Utilizing the derived distribution approach, analytical expressions for average annual spill volume from a storage reservoir, number of spill volumes and average annual pollutant load can be derived.

## Conclusions

Combined Sewer Overflows and stormwater runoff are a major source of water pollution problem for the District of Columbia. In order to address the problem, long-term monitoring of runoff quality and modeling of drainage system is necessary. As an initial attempt, Dissolved Oxygen was measured at three locations at the Rock Creek during Fall 2006 and Spring 2007. From the measurement, it is found that there is no evidence of low dissolved oxygen at the measured location of the Rock Creek. As an alternative to continuous simulation and/or to complement continuous simulation, analytical probabilistic models of urban storm water management systems can be developed using derived distribution theory. This is a promising approach to develop analytical expression which can be easily used for solving runoff quantity and quality problems in urban areas.

## References

Adams, B. J., and Bontje, J. B., "Microcomputer Applications of Analytical Models for Urban Stormwater Management," in Engineering Computer Techniques in Stormwater and Flood Management, W. James, (Ed.), ASCE, New York, pp.138-162, 1984.

Adams, B. J., Fraser, H. G., Howard, C. D. D., and Hanafy, M. S., "Meteorological Data Analysis for Urban Drainage System Design," Journal of Environmental Engineering, ASCE, Vol. 112, No. 5, pp. 827-848, 1986.

Adams, B. J., and Zukovs, G., "Combined Sewer System rehabilitation Analysis," in Proceedings, Canadian Society for Civil Engineering Annual Conference, Toronto, Ontario, Vol. II, pp. 171-202, 1986.

Adams, B. J., and Zukovs, G., "Probabilistic Models for Combined Sewer Rehabilitation Analysis," in System Analyses in Water Quality Management, M.B. Beck, (Ed.), Pergamon Press, Oxford, England, pp. 97-108, 1987.

Adams, B. J. and Papa, F., Urban Stormwater Management Planning with Analytical Probabilistic Models, John Wiley and Sons, New York, 2000.

Benjamin, J. R., and Cornell, C.A., Probability, Statistics and Decision for Civil Engineers, McGraw-Hill, New York, NY, 1970.

Berbee, R., Rijs, G., Brouwer, R., and Velzen, L., "Characterization and Treatment of Runoff from Highways in the Netherlands Paved with Impervious and Pervious Asphalt," Water Environment Research, Vol. 71, No. 2, pp. 83-190, 1999.

Clesceri, L., Greenberg, A. E., and Eaton, A. D., "Standard Methods for the Examination of Water and Wastewater," 20th Edition, Water Environment Federation, Alexandria, VA, 1998.

DiToro, D. M., and Small, M. J., "Stormwater Interception and Storage," Journal of Environmental Engineering, ASCE, Vol. 105, No. EE1, pp. 43-45, 1979.

Eagleson, P. S., "Dynamics of Flood Frequency", Water Resources Research, Vol. 8, No. 4, pp. 878-898, 1972.

Ellis, J.B., "Pollutional Aspects of Urban Runoff", Proceedings, Urban Runoff Pollution, H. C. Torno et al. (Eds.), Springer-Verlag, Berlin, pp.1-38, 1986.

Ellis, J. B., and Hvitved-Jacobsen, T., "Urban Drainage Impacts on Receiving Waters," *Journal of Hydraulic Research*, Vol. 34, No. 6, pp. 771-784, 1996.

Field R., Borst, M., O'Connor, T.P., Stinson, M.K., Fan, C, Perdek, J.M., and Sullivan, D., "Urban Wet-Weather Flow Management: Research Direction", *Journal of Water Resources Planning and Management*, ASCE, Vol. 124, No. 3, pp.168-180, 1998.

Flatt, P. E., and Howard, C. D. D., "Preliminary Screening Procedure for Economic Storage-Treatment Trade-Offs in Storm Water Control," in *Proceedings, International Symposium on Urban Storm Water Management*, University of Kentucky, Lexington, KY, pp. 219-227, 1978.

Geiger, W. F. and Dorsch, H. R., *Quantity-Quality Simulation (QQS): A Detailed Continuous Planning Model for Urban Runoff Control*, Volume I, Model Testing and Applications, EPA-600/2-80-011, U.S. EPA, Cincinnati, 1980.

Hall, M. J., *Urban Hydrology*, Elsevier Applied Science Publications, New York, NY, 1984.

Guo, Y., and Adams, B. J., "Long Term Performance of Stormwater Quality Control Ponds,' Chapter 7 in *Current Practices in Modeling in Management of Stormwater Impacts*, W James (Ed.), Lewis Publishers, Boca Raton, FL, pp. 99-119, 1994.

Guo Y. and Adams, B. J., "Hydrologic analysis of urban catchments with event-based probabilistic models, 1, Runoff volume, *Water Resources Research*, Vol. 34, pp. 3421-3431, 1998.

Hicks, B. B., "Atmospheric Deposition and Its Effects on Water Quality," *Workshop on Research Needs for Coastal Pollution in Urban Areas*, E. R. Christensen and C. R. O'Melia (Eds.) Milwaukee, WI, 1997.

Hilborn, J., and Still, M., *Canadian Perspectives on Air Pollution*, SOE Report No. 90-1, Environment Canada, Ottawa, Ontario, 1990.

Huber, W. C. and Dickinson, R. E., *Stormwater Management Model, Version 4: User's Manual*, Environmental Protection Agency, Athens, GA., 1988.

Howard, C. D. D., "Theory of Storage and Treatment Plant Overflows", *Journal of Environmental Engineering*, ASCE, Vol. 102, No. EE4, pp. 709-722, 1976.

James, W., and Boregowda, S., "Continuous Mass-Balance of Pollutant Buildup Processes", *Proceedings, Urban Runoff Pollution*, H. C. Torno et al. (Eds.), Springer-Verlag, Berlin, pp. 243-272, 1986.

Johanson, R. C., Imhoff, J. C., and Davis, H. H., User's Manual for Hydrological Simulation Program-Fortran (HSPF), U.S., EPA, Athens, GA, 1984.

Klemm, R. F., and Gray, J. M. L., A Study of the Chemical Composition of Particulate Matter and Aerosols over Edmonton, Prep. for the Research Management Division by the Alberta Research Council, Report RMD 82/9, 1982.

Loganathan, G. V. and Delleur, J. W., "Effects of Urbanization on Frequencies of Overflows and Pollutant Loadings from Storm Sewer Overflows: A Derived Distribution Approach", Water Resources Research, Vol. 20, No. 7, pp. 857-865, 1984.

Loganathan, G. V., Delleur, J. W., and Segarra, R. I., "Planning Detention Storage for Stormwater Management," Journal of Environmental Planning and Management, Vol. 111, No. 4, pp. 382-398, 1985.

Marsalek, J., Brownlee, B., Mayer, T., Lawal, S., and Larkin, G. A., "Heavy Metals and PAHs in Stormwater Runoff from the Skyway Bridge, Burlington, Ontario," Water Quality Research Journal of Canada, Vol. 32, No. 4, pp. 815-827, 1997.

Marsalek, J., "Challenges in Urban Drainage: Environmental Impacts, Impact Mitigation, Methods of Analysis and Institutional Issues", Proceedings, Hydroinformatics Tools for Planning, Design, Operation and Rehabilitation of Sewer Systems, J. Marsalek et al. (Eds.), Kluwer Academic Publishers, London, pp. 1-24, 1998.

Moffa, P. E. (Ed.), Control and Treatment of Combined-Sewer Overflows, Van Nostrand Reinhold, New York, NY, 1990.

Novotny, V., and Olem, H., Water Quality Prevention, Identification, and Management of Diffuse pollutants, Van Nostrand Reinhold, New York, 1994.

Novotny, V., Sung, H. M., Bannerman R., and Baum, K.: "Estimating Non-point Pollution from small Urban Watersheds", Journal of WPCF, Vol. 57, No. 4, pp.339-348, 1985.

Papa, F., Adams, B. J. and Guo, Y., "A Family of Analytical Probabilistic Models for Urban Stormwater Management Planning", Water Resources and the Urban Environment, Proceedings of the 25th Annual Conference on Water Resources Planning and Management and the 1998 National Conference on Environmental Engineering, ASCE, Chicago, June 6-10, pp. 404-409, 1998.

Randall, C. W., Grizzard, T.J., Helsel, D. R., and Griffin, D. M., "Comparison of Pollutant Mass Loads in Precipitation and Runoff in Urban Areas," Proceedings, Urban

Stormwater Quality, Management and Planning, B. C. Yen, (Ed.), Water Resources Publication, Littleton, CO, pp. 29-38, 1982.

Sartor, J. D., Boyd, G. B., and Agardy, F. J., "Water Pollution Aspects of Street Surfaces Contaminants", Journal of the Water Pollution Control Federation, Vol. 46, No. 3, pp. 458-467, 1974.

Sansalone, J.J., and Buchberger, S.G., "Partitioning and First Flush of Metals in Urban Roadway Stormwater", Journal of Environmental Engineering, ASCE, Vol. 123, No. 2, pp. 134-143, 1997.

Schwarz, R. B., "Distributed Storage for Urban Storage for Urban Stormwater Control: An Analytical Model with Economic Optimization," M.A.Sc. thesis, Department of Civil Engineering, University of Toronto, Toronto, Ontario, 1980.

Schwarz, R. B., and Adams, B. J., "Distributed Storage for Urban Runoff Control," in Proceedings, 2nd International Conference on Urban Storm Drainage, Urbana, IL, pp. 360-369, 1981.

Segarra-Garcia, R. and Loganathan, V. G., "Stormwater Detention Storage Design under Random Pollutant Loading", Journal of Water Resources Planning Management., ASCE, Vol. 118, No. 5, pp.475-490, 1992.

Terstriep, M. L., Noel, D. C., and Bender, G. M., "Sources of Urban Pollutants- Do We Know Enough?", Proceedings, Urban Runoff Quality - Impact and Quality Enhancement Technology, B. Urbonas and L. A. Roesner (Eds.), ASCE, New York, NY, pp. 107-121, 1986.

Thomson, N. R., McBean, E.A., Snodgrass, W., and Mostrenko, I.: "Sample Size Needs for Characterizing Pollutant Concentration in Highway Runoff," Journal of Environmental Engineering, ASCE, Vol. 123, No. 10, 1997. pp. 1061-1065.

Torno, H.C et al., (Eds): Urban Runoff Pollution, Springer-Verlag, New York, 1986.  
U.S. Environmental Protection Agency, A Statistical Method for Assessment of Urban Stormwater Loads-Impacts-Controls, Report EPA-440/3-79-023, Water Planning Division, Washington, D.C., 1979.

U.S. Army Corps of Engineers, Urban Storm Water Runoff, STORM, Hydrologic Engineering Center, Davis, California, 723-S8-L2520, May 1974.

U.S. Environmental Protection Agency, A Statistical Method for the Assessment of Urban Stormwater, Office of Water Planning and Standards, EPA 440/3-79-023, Washington, D.C., 1983a.

U.S. Environmental Protection Agency, Results of the Nationwide Urban Runoff Program, Vol. I, Final Report, Water Planning Division, US EPA, NTIS No. PB84-185552, Washington, D.C., 1983b.

U.S. Environmental Protection Agency, Combined Sewer Overflows, Guidance For Monitoring and Modeling, 1999.

Wanielista, M. P., and Yousef, Y.A., Stormwater Management, Wiley, New York, NY, 1993.

U.S. Geological Survey, Water Quality , Sediment Quality, and Stream-Channel Classification of Rock Creek, Washington DC, 1999-2000.

Waller, D., and Hart, W. C., "Solids, Nutrients and Chlorides in Urban Runoff", Proceedings, Urban Runoff Pollution, H. C. Torno et al., (Eds.), Springer-Verlag, Berlin, pp. 59-85, 1986.

WEF Manual of Practice No.23, Urban Runoff Quality Management, ASCE, Alexandria, VA, 1998.

# Effect of Best Management Practices on contaminant levels in storm water runoff to the Anacostia River

## Basic Information

<b>Title:</b>	Effect of Best Management Practices on contaminant levels in storm water runoff to the Anacostia River
<b>Project Number:</b>	2006DC79B
<b>Start Date:</b>	3/1/2006
<b>End Date:</b>	2/28/2007
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	District of Columbia
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Solute Transport, Nutrients, Water Quality
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Dr. Charles Glass



## **Publication**

**“Monitoring the Effectiveness of Best Management  
Practice in Removing Pollutants from Urban  
Stormwater Runoff”**

**“Bioretention, DC Sandfilter, and BaySaver”**

**Site Locations: Benning Road Bridge, DC Village, and  
W Street Parking Facility**

**Duration: October 1, 2004 – December 31, 2006**

Reported by

Professor: Dr. Charles Glass

Submitted to

District of Columbia  
Department of Transportation, Water Quality Division

**December 14, 2006**

## TABLE OF CONTENTS

Acronyms .....	iii
Synopsis .....	1
Methodology .....	6
Results .....	10
Benning Road Bioretention.....	18
DC Village DC Sand Filter .....	37
W Street BaySaver .....	55
Conclusion .....	81

## Acronyms

- Heavy Metals: As: Arsenic; Cd: Cadmium; Cr: Chromium; Cu: Copper;
- Hg: Mercury; Pb: Lead; Zn: Zinc
- $\text{NH}_3\text{-N}$ : Nitrogen as ammonia
- $\text{NO}_2\text{-N}$ : Nitrogen as nitrite
- $\text{NO}_3\text{-N}$ : Nitrogen as nitrate
- $\text{PO}_4^{3-}\text{-P}$ : Phosphorus as phosphate
- DO: Dissolved Oxygen
- BOD: Biological Oxygen Demand
- FC: Fecal Coliform
- TSS: Total Suspended Solids
- TDS: Total Dissolved Solids
- T: Temperature
- In: Influent concentration
- Out: Effluent concentration
- Avg.: Average
- St dev.: Standard deviation
- BMP: Best Management Practices

## Synopsis

This report is based on field sampling that was conducted between February 14, 2005 and October 27, 2006 to measure the effectiveness of the bioretention site at the Benning Road Bridge over the Anacostia River, the DC Sand filter underneath a parking lot at DC Village, and a BaySaver underneath the parking lot at the W Street parking lot in removing pollutants from urban stormwater runoff. Influent and effluent samples were collected from 15, 12, and 18 at Benning Road, DC Village, and W Street respectively. Only major rainfall events, greater than 0.1 inches of rain, with an antecedent dry period of 72 hours, in compliance with EPA regulations for further analysis in the laboratory were monitored.

The report is divided into four sections; methodology, results, conclusions, and appendix. The methodology section presents the basic methods used for all three sites and highlights the instruments that were used in investigating the amount of pollutants present in the runoff. The results section includes tabular and graphical representations of the physical, chemical and biological characteristics of concern tested in each of the 15 sample events and analysis behind the overall numbers that result from compiling all of the data for a given parameter together. All values presented are averaged values of triplicate measurements and their corresponding standard deviations are shown in the tabular form. The appendix comprises all of the raw data results from the laboratory analysis performed during this project.

In general, after all of the analysis, it is the view of Dr. Glass that the results imply that the DC Sand filter is working properly and is properly maintained. The bioretention at Benning Road was not performing well during the study and it is believed

to be undersized for the amount of runoff that results during an average storm in this area. The BaySaver did not perform well for the majority of this investigation; however, once the device was cleaned performance did improve substantially. All of the devices, no matter whether they were maintained or designed properly, did perform better than if there was no device present at all, for at least some parameters of interest.

Benning Road Bioretention Site



DC Village Sand Filter





W Street Parking Facility BaySaver



# Methodology

## Introduction

In order to capture the highest concentration of water pollutants the focus is normally on “first flush” discharge samples thus, samples are normally collected after a major storm event after at least 72 hours of extended dry period has elapsed from one

<b>Table 1: Analytical Techniques for Each Contaminant</b>	
<b>Contaminant</b>	<b>Analytical Technique</b>
Cd, Cr, Cu, Hg, Pb, As, Zn	<i>Atomic Absorption Spectrometer with Furnace Module</i>
$\text{NH}_4^+\text{-N}$	<i>Ion Chromatography - Cation</i>
$\text{NO}_2^-\text{-N}$ , $\text{NO}_3^-\text{-N}$ , $\text{PO}_4^{3-}\text{-P}$	<i>Ion Chromatography - Anion</i>
BOD	<i>5-day Biological Oxygen Demand Involving the Use of Dissolved Oxygen Meter</i>
DO	<i>Dissolved Oxygen Meter</i>
TSS	<i>Total Suspended Solids Dried at 103-105°C</i>
PAH	<i>High Pressure Liquid Chromatography</i>
TDS	<i>Total Dissolved Solids Dried at 600°C</i>
Temperature	<i>Thermocouple</i>
<i>pH</i>	<i>pH-probe</i>

event to another. Rain events are monitored by checking the local weather station or weather related internet sites. Stormwater runoff samples from the all sites are collected into cleaned 4 liter jars for further analysis in the lab.

## Collection Procedure

Sample collection took place shortly after a rain event began or from ISCO samplers that were programmed prior to the event in order to ensure accuracy in measured parameters. Samples were collected into storage bins that are placed at specific points of the bioretention system to collect both inlet and outlet discharge samples. The inlet and outlet samples discharged into the bins are then transferred into two precleaned airtight jars having a capacity of 4 liters. At the other two sites water was collected directly into the pre-cleaned glass jars. After collection, specific parameters such as pH, dissolved oxygen (DO) level and temperature are measured on site and reference is made to the laboratory manual in performing the required test. The collected discharge samples were then transported to the lab for other laboratory analysis.

### **Laboratory Analysis**

As soon as the sample gets to the lab the pH, DO and temperature were measured again using the procedures in the laboratory manual to determine any deviation in on-site measurements. Approximately 200 ml of inlet and outlet samples are put into 250 ml beakers for the necessary measurements and all parameters in triplicate to eliminate any errors. Organic content of storm water run off samples were determined from chemical oxygen demand (COD) and biological oxygen demand (BOD) analysis. Method of analyzing the COD level can be found in the Hach Water analysis handbook. The BOD levels of the samples were also measured as soon as the samples reached the lab. In order to accomplish this, a total of 6 BOD bottles with air tight stoppers are filled with samples. Three of the BOD bottles contain the inlet discharge samples and the other 3 BOD bottles contained the outlet discharge samples. In filling the bottles care was taken to ensure that air was not trapped in the bottles. The bottles were then placed in boxes and stored in a

dark area for 5 days. At the end of the 5 days, the DO levels of both inlet and outlet samples were measured and the BOD level was determined from calculation. To determine the solid content of the samples, total suspended solids (TSS) and total dissolved solids (TDS) measurements are taken within 24 hrs of sample collection by following the procedure in the Standard Methods for the Examination of Water and Wastewater (Standard Methods, 20<sup>th</sup> Ed.)..

Nutrients of concern analyzed in the laboratory include; total phosphorus, nitrite ( $\text{NO}_2^- - \text{N}$ ), nitrate ( $\text{NO}_3^- - \text{N}$ ), phosphate ( $\text{PO}_4^{-3} - \text{P}$ ) and ammonia. The Hach Water analysis handbook gives a precise method of measuring the total phosphorus content.  $\text{NO}_2^- - \text{N}$ ,  $\text{NO}_3^- - \text{N}$ ,  $\text{PO}_4^{-3} - \text{P}$  and ammonia were analyzed with the Dionex IC DX- 120 instrument and the technique is based on ion chromatography (IC) and liquid chromatography (LC). Both inlet and outlet discharge samples were filtered prior to any IC analysis. Part-per billion (ppb) concentrations of heavy metals in the samples were analyzed using atomic absorption spectroscopy (AAS) and both inlet and outlet samples were filtered prior to AAS analysis. Ideally for accuracy in test results, it is recommended that all IC and AAS analysis should be performed on fresh samples or within 24hrs of sample collection however samples that cannot be analyzed within this time frame can be preserved on short term basis (1 to 2 days) or long period (6 months) for future analysis (Standard Methods, 20<sup>th</sup> Ed.). Short term preservation can be achieved by refrigerating the samples at 4°C. Acid preservation is not recommended for nitrites since this may cause bacterial conversion of  $\text{NO}_2^-$  to  $\text{NO}_3^-$ . Samples for  $\text{NO}_3^-$  analysis can be preserved longer by addition of 2 mL concentrated  $\text{H}_2\text{SO}_4$  and then refrigerated at 4°C. Samples that have to be stored for a longer time before any phosphate analysis can be preserved by

adding 40 mg HgCl<sub>2</sub>/L to the samples before refrigerating at 4°C. In the case of ammonia preservation for up to 28 days for future analysis is possible by either freezing at -20°C with any acid addition or by adding acid until the pH is less than 2 before refrigerating at 4°C. Prior to refrigeration at 4°C, samples for heavy metal analysis can be preserved by acidifying with conc. nitric acid (HNO<sub>3</sub>) until the pH is less than 2 (Standard Methods, 20<sup>th</sup> Ed.).

## Results

In the field of stormwater management there are many variables that cause fluctuations in the performance of stormwater devices. The three devices monitored in this study have drastically varying performance characteristics. In addition, the three sites monitored were drastically different sites with different designs for capturing flow, different overall areas which lead to largely varying peak flow rates, and all three sites were designed with different purposes in mind. When monitoring the devices from varying sites there are no set rules that reveal what makes a site a good performing site and another a bad performing site. Unlike in drinking water treatment and wastewater treatment, the guidelines for stormwater devices do not call for a give concentration to meet, but rather typically are designed to retain a certain amount of flow.

There are, however, a range of values that have been presented in Table 2 from the National Stormwater Best Management Practices Database that show a broad range of values that are found in stormwater. This overview of the range of values found in previous studies encompasses all of the concentrations of parameters going into the three sites of this study, with a few noteworthy exceptions. The heavy metals concentrations of Cadmium, Chromium, Arsenic, and Mercury were found to be higher in the runoff from the Benning Road bridge and the W Street Parking lot than the maximum values found in the National database. The DC Village parking lot had no values that exceeded the values found in the National database. This is most likely the result of the DC Village parking lot being a very small area with relatively little use in comparison to the Benning Road Bridge and the W Street industrial parking lot. The DC Village parking lot never contained more than 15 cars throughout the course of this study, while the Benning Road

bridge is a major thoroughfare in the city with thousands of car traffic per day and the W Street Parking lot stores over 100 heavy vehicles and contains piles of asphalt, sand, and other road materials.

**Table 2: From the ASCE Maximum and Minimum Values for Water Quality Parameters in the National Stormwater Best Management Practices Database**

<b>Water Quality Parameter</b>	<b>Maximum Value</b>	<b>Minimum Value-</b>	<b>Unit</b>
<b>CADMIUM, DISSOLVED</b>	0.008	-0.0075	mg/l
<b>CHROMIUM, DISSOLVED</b>	0.012	-0.0005	mg/l
<b>COD</b>	2030	-12.14	mg/l
<b>COPPER, DISSOLVED</b>	0.05	-0.005	mg/l
<b>IRON, DISSOLVED</b>	0.518	0.004	mg/l
<b>LEAD, DISSOLVED</b>	0.2905	-0.005	mg/l
<b>NITRATE NITROGEN, TOTAL</b>	28	-5	mg/l
<b>NITRITE PLUS NITRATE</b>	9.09	-0.01	mg/l
<b>NITROGEN, AMMONIA, TOTAL</b>	9	-0.5	mg/l
<b>OIL &amp; GREASE</b>	66.7	-1.5	mg/l
<b>OXYGEN, DISSOLVED</b>	13.93	0.02	mg/l
<b>pH (STANDARD UNITS)</b>	10.3	4.2	SU
<b>PHOSPHORUS, DISSOLVED</b>	8.42	0.0022	mg/l
<b>PHOSPHORUS, TOTAL</b>	80.2	-0.1	mg/l
<b>RESIDUE, TOTAL FILTRABLE</b>	11000	38	mg/l
<b>RESIDUE, TOTAL NONFILTRABLE</b>	7100	-12.5	mg/l
<b>TEMPERATURE, WATER</b>	33.22	9.6	°C
<b>ZINC, DISSOLVED</b>	2.618	-0.05	mg/l

(Negative if below detection limit, zero values excluded)

Perhaps a better comparison between the values found in the USEPA's priority and non-priority pollutants for fresh water, and the values found going into and out of the three sites is more appropriate. With these values, that take into the impact the pollutants have on aquatic life and the possibility of the use of the water as drinking water downstream, the heavy metal concentrations coming from the sites are of larger concern. Many of the parameters found on the priority pollutants list are found in excess going into and out of the three sites monitored, again with the exception of the DC Village site.

**Table 3 Chronic Priority Pollutants for Fresh Water (USEPA)**

<b>Pollutant</b>	<b>Chronic Concentration (ppb)</b>
<b>Copper</b>	<b>9</b>
<b>Cadmium</b>	<b>0.25</b>
<b>Zinc</b>	<b>120</b>
<b>Chromium</b>	<b>11</b>
<b>Lead</b>	<b>2.5</b>
<b>Arsenic</b>	<b>150</b>
<b>Mercury</b>	<b>0.77</b>

**Table 4 Non-Priority Pollutants (USEPA)**

<b>Pollutant</b>	<b>Concentration (mg/L)</b>
<b>pH</b>	<b>6.5-9.0</b>
<b>Dissolved Oxygen</b>	<b>Dependent</b>
<b>Temperature</b>	<b>Dependent</b>
<b>TSS</b>	<b>80</b>
<b>TDS</b>	<b>250</b>
<b>PAH</b>	<b>0</b>
<b>Total Nitrogen</b>	<b>10</b>
<b>Total Phosphorus</b>	<b>0.1</b>



Comparing the values found in Tables 3 and 4 with the values for the measured parameters in Table 5 that contains the summary of results for the Benning Road bioretention it is evident that several parameters are excessive. Copper, Cadmium, Lead, and Mercury had average concentrations into and out of the BMP in excess of the priority pollutant concentrations. All of the non-priority pollutants were in a reasonable range of values, however the efficiency of removal did not compare well to other bioretention studies.

The results of the DC Sand Filter at DC Village are shown in Table 6. When comparing the values in Table 6 with the priority and non-priority pollutants found in Table 4 and 5, only Cadmium exceeded the concentration found on the priority pollutants list in both the influent and the effluent. TSS exceeded the value found in the non-priority pollutant list however the value of the effluent was sufficiently below this concentration due to the performance of the filter.

Prior to the cleaning of the BaySaver at the W Street parking lot, every parameter was elevated when compared to stormwater runoff from the other two sites, as can be seen in Table 7. When compared to Table 3 and Table 4, Copper, Cadmium, Mercury, TSS, and TP were all elevated both going into and coming out of the BaySaver. After the BaySaver was cleaned all of the values decreased however these values decreased for the influent and the effluent. Thus after only sampling 3 events where no significant difference between the concentrations entering or leaving the device, no conclusions can be made to the devices performance after maintenance. The removal efficiency of the BaySaver for all parameters both pre- and post-cleaning was poor. No one pollutant was removed at above 90%. The system is designed to store pollutants not remove them.

Table 5 Summary of Bioretention Data

<b>Contaminant</b>	<b>Influent Avg. and Std. Dev.</b>	<b>Effluent Avg. and Std. Dev</b>	<b><i>Removal Efficiency</i></b>
<b>pH</b>	<b>8.09 ± 0.46</b>	<b>7.75 ± 0.46</b>	
<b>D.O.</b>	<b>5.87 ± 1.87</b>	<b>5.80 ± 0.88</b>	
<b>Temp. (°C)</b>	<b>19 ± 3.5</b>	<b>18.3 ± 4.1</b>	
<b>TSS</b>	<b>176 ± 396</b>	<b>24 ± 28</b>	<b>86%</b>
<b>TDS</b>	<b>146 ± 353</b>	<b>14 ± 24</b>	<b>91%</b>
<b>Cu</b>	<b>23 ± 29</b>	<b>11 ± 29</b>	<b>53%</b>
<b>Cd</b>	<b>9 ± 32</b>	<b>2 ± 9</b>	<b>78%</b>
<b>Zn</b>	<b>70 ± 32</b>	<b>52 ± 27</b>	<b>26%</b>
<b>Cr</b>	<b>10 ± 7</b>	<b>5 ± 4</b>	<b>50%</b>
<b>Pb</b>	<b>47 ± 179</b>	<b>16 ± 56</b>	<b>66%</b>
<b>As</b>	<b>29 ± 112</b>	<b>31 ± 119</b>	<b>-6%</b>
<b>Hg</b>	<b>54 ± 126</b>	<b>42 ± 86</b>	<b>22%</b>
<b>TP</b>	<b>0.5 ± 0.4</b>	<b>0.2 ± 0.2</b>	<b>60%</b>
<b>PO<sub>4</sub><sup>-3</sup></b>	<b>0.0 ± 0.1</b>	<b>0.0 ± 0.1</b>	<b>0%</b>
<b>NO<sub>2</sub><sup>-</sup></b>	<b>0.4 ± 0.6</b>	<b>0.3 ± 0.5</b>	<b>-25%</b>
<b>NO<sub>3</sub><sup>-</sup></b>	<b>0.2 ± 0.3</b>	<b>0.2 ± 0.2</b>	<b>0%</b>
<b>NH<sub>4</sub><sup>+</sup></b>	<b>22 ± 55</b>	<b>16 ± 40</b>	<b>27%</b>
<b><i>COD</i></b>	<b>112 ± 92</b>	<b>66 ± 43</b>	<b>41%</b>

Table 6 Summary of DC Sand Filter Data

<b>Contaminant</b>	<b>Influent Avg. and Std. Dev.</b>	<b>Effluent Avg. and Std. Dev</b>	<b><i>Removal Efficiency</i></b>
<b>pH</b>	<b>6.6 ± 0.9</b>	<b>6.6 ± 0.3</b>	
<b>D.O.</b>	<b>6.2 ± 1.2</b>	<b>6.7 ± 1.7</b>	
<b>Temp. (°C)</b>	<b>22.8 ± 4.6</b>	<b>22.8 ± 4.7</b>	
<b>TSS</b>	<b>96 ± 232</b>	<b>11 ± 3.2</b>	<b>88%</b>
<b>TDS</b>	<b>54 ± 125</b>	<b>10 ± 2</b>	<b>81%</b>
<b>Cu</b>	<b>6 ± 4</b>	<b>4 ± 3</b>	<b>33%</b>
<b>Cd</b>	<b>1 ± 1</b>	<b>3 ± 6</b>	<b>-200%</b>
<b>Zn</b>	<b>12 ± 2</b>	<b>12 ± 2</b>	<b>0%</b>
<b>Cr</b>	<b>0.3 ± 0.2</b>	<b>0.3 ± 0.2</b>	<b>0%</b>
<b>Pb</b>	<b>0.3 ± 0.2</b>	<b>0.4 ± 0.4</b>	<b>0%</b>
<b>As</b>	<b>2.3 ± 0.8</b>	<b>2.2 ± 1.0</b>	<b>0%</b>
<b>Hg</b>	<b>0.8 ± 0.8</b>	<b>0.8 ± 1.2</b>	<b>0%</b>
<b>TP</b>	<b>0.3 ± 0.4</b>	<b>0.2 ± 0.2</b>	<b>40%</b>
<b>PO<sub>4</sub><sup>-3</sup></b>	<b>0.2 ± 0.5</b>	<b>0.2 ± 0.6</b>	<b>0%</b>
<b>NO<sub>2</sub><sup>-</sup></b>	<b>0.2 ± 0.4</b>	<b>0.2 ± 0.4</b>	<b>0%</b>
<b>NO<sub>3</sub><sup>-</sup></b>	<b>0.3 ± 0.4</b>	<b>1.1 ± 1.4</b>	<b>-300%</b>
<b>NH<sub>4</sub><sup>+</sup></b>	<b>2.8 ± 3.1</b>	<b>1.3 ± 0.7</b>	<b>53%</b>
<b>COD</b>	<b>62 ± 43</b>	<b>38 ± 41</b>	<b>39%</b>

Table 7 Summary of BaySaver Pre-Cleaning Data

<b>Contaminant</b>	<b>Influent Avg. and Std. Dev.</b>	<b>Effluent Avg. and Std. Dev</b>	<b><i>Removal Efficiency</i></b>
<b>pH</b>	<b>6.8 ± 0.4</b>	<b>6.8 ± 0.5</b>	
<b>D.O.</b>	<b>7.8 ± 1.4</b>	<b>7.4 ± 1.4</b>	
<b>Temp. (°C)</b>	<b>22.9 ± 5.1</b>	<b>22.6 ± 4.1</b>	
<b>TSS</b>	<b>290 ± 499</b>	<b>111 ± 64</b>	<b>62%</b>
<b>TDS</b>	<b>230 ± 426</b>	<b>75 ± 30</b>	<b>67%</b>
<b>Cu</b>	<b>12 ± 8</b>	<b>10 ± 6</b>	<b>17%</b>
<b>Cd</b>	<b>12 ± 31</b>	<b>4 ± 9</b>	<b>64%</b>
<b>Zn</b>	<b>20 ± 15</b>	<b>19 ± 10</b>	<b>4%</b>
<b>Cr</b>	<b>5.1 ± 7.1</b>	<b>2.7 ± 2.0</b>	<b>46%</b>
<b>Pb</b>	<b>48 ± 137</b>	<b>1.2 ± 1.3</b>	<b>97%</b>
<b>As</b>	<b>38 ± 112</b>	<b>10 ± 10</b>	<b>74%</b>
<b>Hg</b>	<b>98 ± 128</b>	<b>90 ± 163</b>	<b>9%</b>
<b>TP</b>	<b>0.6 ± 0.3</b>	<b>0.4 ± 0.2</b>	<b>24%</b>
<b>PO<sub>4</sub><sup>-3</sup></b>	<b>0.3 ± 0.3</b>	<b>13 ± 22</b>	<b>-37%</b>
<b>NO<sub>2</sub><sup>-</sup></b>	<b>1.5 ± 5.3</b>	<b>0.8 ± 2.2</b>	<b>48%</b>
<b>NO<sub>3</sub><sup>-</sup></b>	<b>0.8 ± 1.3</b>	<b>1.7 ± 3.0</b>	<b>-107%</b>
<b>NH<sub>4</sub><sup>+</sup></b>	<b>1.4 ± 1.2</b>	<b>1.0 ± 1.2</b>	<b>27%</b>
<b>COD</b>	<b>118 ± 43</b>	<b>102 ± 47</b>	<b>13%</b>

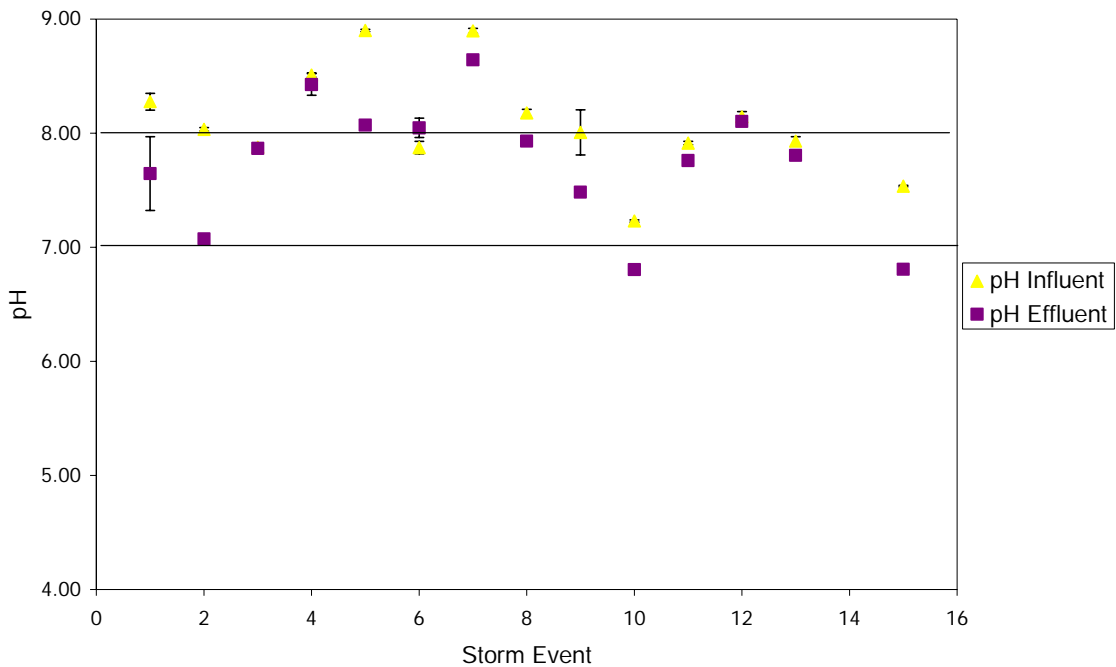
Table 8 Summary of BaySaver Post-Cleaning Data

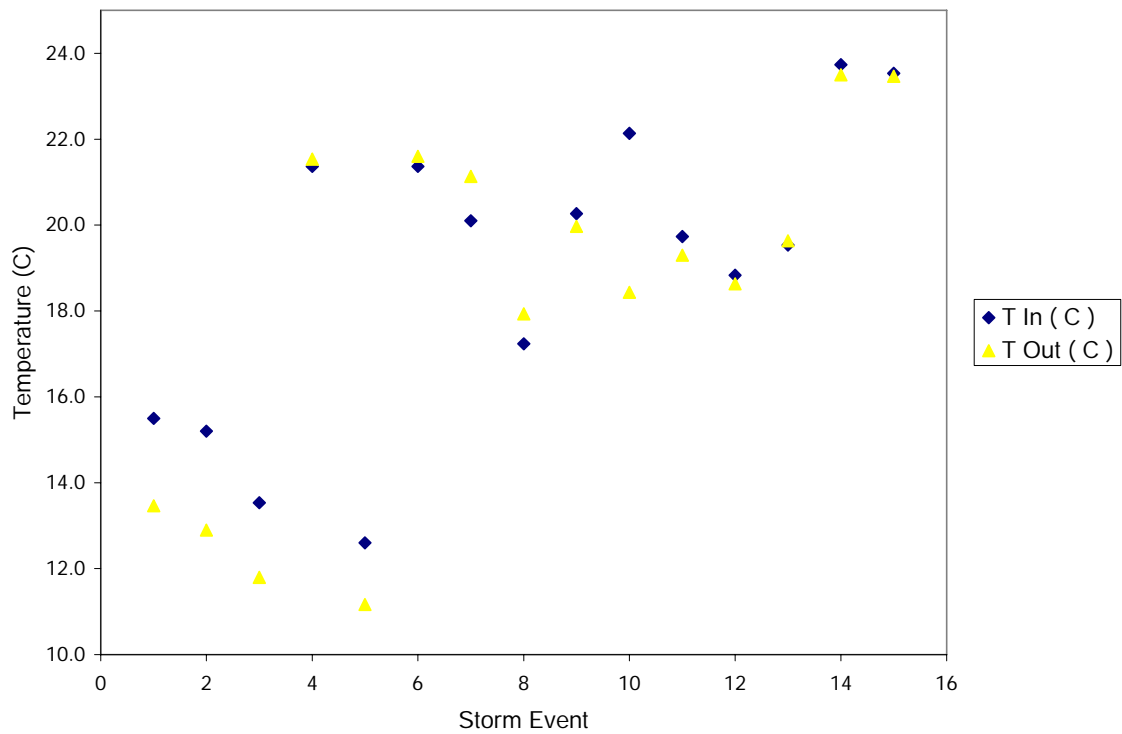
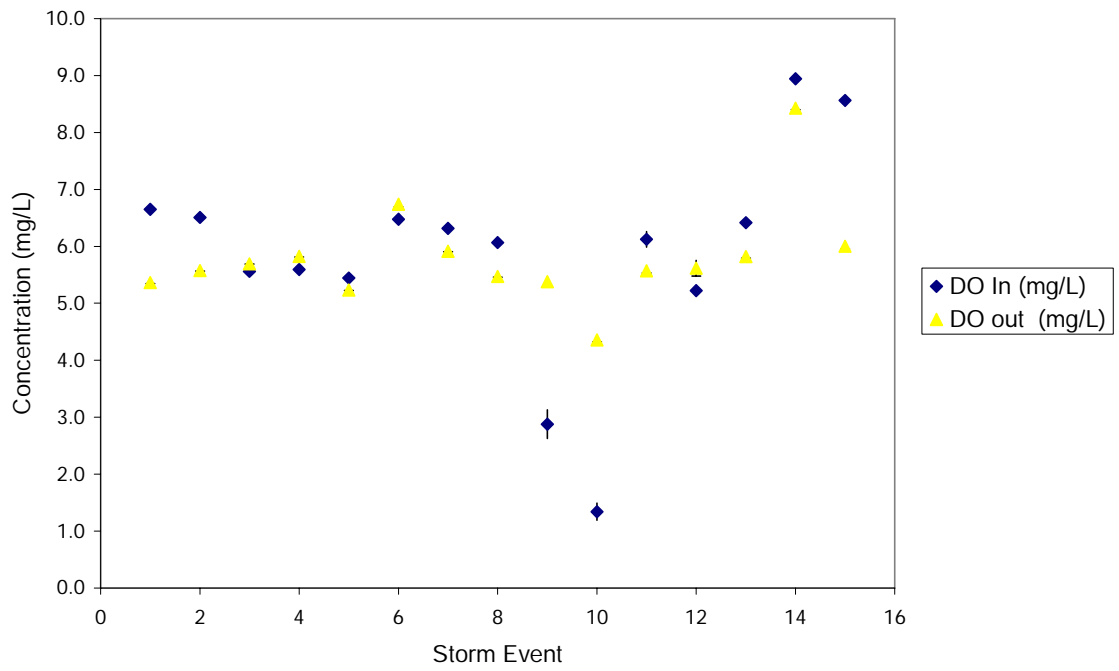
<b>Contaminant</b>	<b>Influent Avg. and Std. Dev.</b>	<b>Effluent Avg. and Std. Dev</b>	<b><i>Removal Efficiency</i></b>
<b>pH</b>	<b>6.8 ± 0.9</b>	<b>7.2 ± 0.5</b>	
<b>D.O.</b>	<b>9.2 ± 0.5</b>	<b>8.0 ± 1.2</b>	
<b>Temp. (°C)</b>	<b>18 ± 4.8</b>	<b>19 ± 4.0</b>	
<b>TSS</b>	<b>3.3 ± 3.0</b>	<b>3.1 ± 2.7</b>	<b>7%</b>
<b>TDS</b>	<b>64 ± 15</b>	<b>73 ± 30</b>	<b>-15%</b>
<b>Cu</b>	<b>8 ± 5</b>	<b>11 ± 1</b>	<b>-41%</b>
<b>Cd</b>	<b>154 ± 37</b>	<b>170 ± 28</b>	<b>-10%</b>
<b>Zn</b>	<b>3 ± 6</b>	<b>17 ± 2</b>	<b>-4%</b>
<b>Cr</b>	<b>1.8 ± 1.1</b>	<b>2.5 ± 0.8</b>	<b>-37%</b>
<b>Pb</b>	<b>0.8 ± 0.5</b>	<b>0.8 ± 0.8</b>	<b>0%</b>
<b>As</b>	<b>3.5 ± 5.1</b>	<b>8.4 ± 2.9</b>	<b>-141%</b>
<b>Hg</b>	<b>0 ± 0</b>	<b>0 ± 0</b>	<b>0%</b>
<b>TP</b>	<b>0.4 ± 0.4</b>	<b>0.7 ± 0.4</b>	<b>-70%</b>
<b>PO<sub>4</sub><sup>-3</sup></b>	<b>0.2 ± 0.0</b>	<b>0.1 ± 0.1</b>	<b>50%</b>
<b>NO<sub>2</sub><sup>-</sup></b>	<b>0.2 ± 0.2</b>	<b>0.4 ± 0.4</b>	<b>-100%</b>
<b>NO<sub>3</sub><sup>-</sup></b>	<b>0.1 ± 0.2</b>	<b>0 ± 0</b>	<b>100%</b>
<b>NH<sub>4</sub><sup>+</sup></b>	<b>0.7 ± 0.8</b>	<b>0.5 ± 0.9</b>	<b>29%</b>
<b>COD</b>	<b>43 ± 19</b>	<b>41 ± 21</b>	<b>5%</b>

## Results for the Bioretention Site

### 1. Storm event number, date of event, pH, DO, and temperature values.

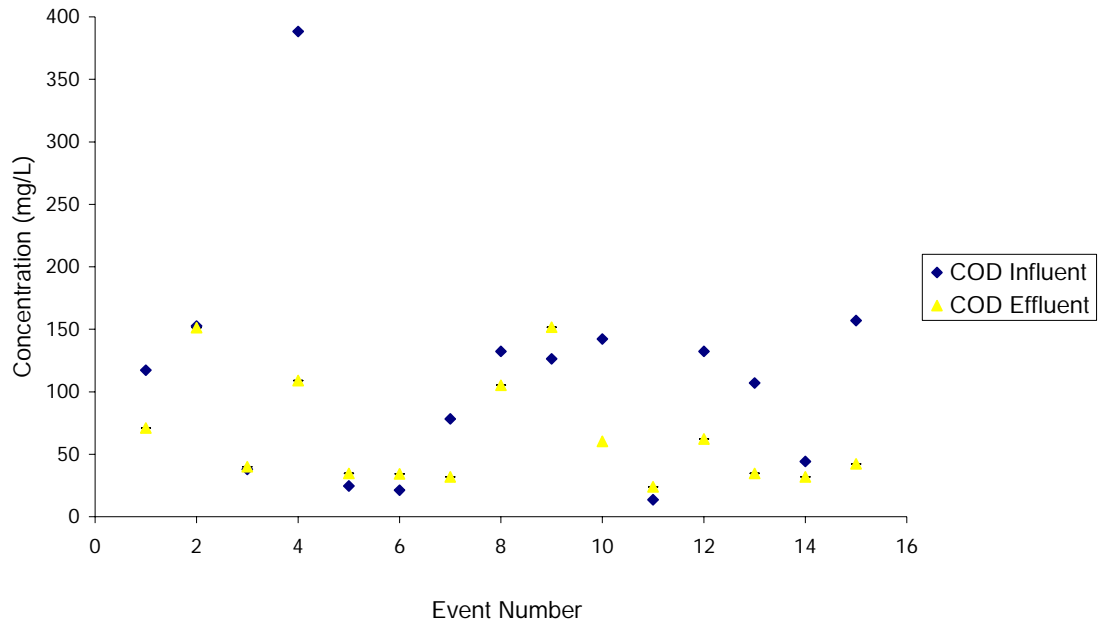
Storm No	Date	pH Influent	St. Dev.	pH Effluent	St. Dev.	DO In (mg/L)	St. Dev.	DO out (mg/L)	St. Dev.	T In (C)	St. Dev.	T Out (C)	St. Dev.
1	2/14/2005	8.3	0.1	7.6	0.3	6.7	0.1	5.4	0.0	15.5	2.2	13.5	2.8
2	2/24/2005	8.0	0.0	7.1	0.0	6.5	0.0	5.6	0.0	15.2	0.8	12.9	0.9
3	3/8/2005	7.9	0.0	7.9	0.0	5.6	0.0	5.7	0.0	13.5	0.3	11.8	0.2
4	3/20/2005	8.5	0.0	8.4	0.1	5.6	0.0	5.8	0.0	21.4	0.1	21.5	0.1
5	3/24/2005	8.9	0.0	8.1	0.0	5.4	0.0	5.2	0.0	12.6	0.2	11.2	0.2
6	4/4/2005	7.9	0.1	8.0	0.1	6.5	0.1	6.7	0.0	21.4	0.1	21.6	0.1
7	4/8/2005	8.9	0.0	8.6	0.0	6.3	0.0	5.9	0.0	20.1	0.4	21.1	0.1
8	4/22/2005	8.2	0.0	7.9	0.0	6.1	0.1	5.5	0.0	17.2	0.1	17.9	0.2
9	4/29/2005	8.0	0.2	7.5	0.0	2.9	0.3	5.4	0.1	20.3	0.2	20.0	0.2
10	5/16/2005	7.2	0.0	6.8	0.0	1.3	0.2	4.4	0.0	22.1	0.1	18.4	0.1
11	5/20/2005	7.9	0.0	7.8	0.0	6.1	0.1	5.6	0.0	19.7	0.1	19.3	0.0
12	5/24/2005	8.1	0.0	8.1	0.0	5.2	0.0	5.6	0.1	18.8	0.1	18.6	0.1
13	6/3/2005	7.9	0.0	7.8	0.0	6.4	0.0	5.8	0.0	19.5	0.1	19.6	0.1
14	6/7/2005					8.9	0.0	8.4	0.0	23.7	0.1	23.5	0.0
15	6/30/2005	7.5	0.0	6.8	0.0	8.6	0.0	6.0	0.1	23.5	0.1	23.5	0.1



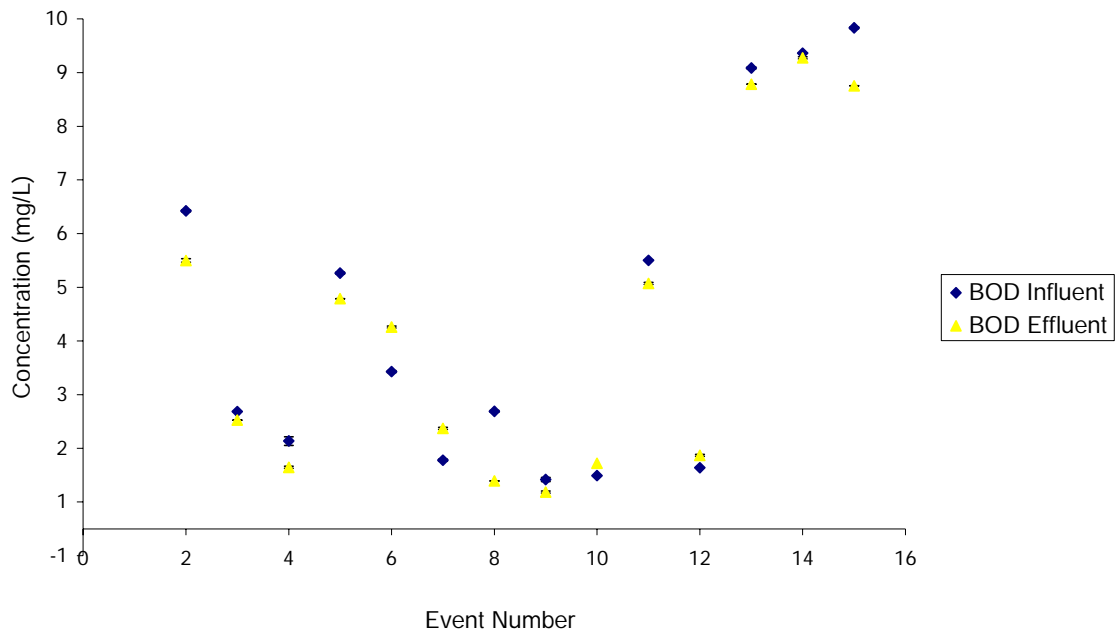


## 2. Storm event number, date of event, chemical and biological oxygen demand values.

No	Storm Date	COD Influent (mg/L)	St. Dev	COD Effluent (mg/L)	St. Dev.	BOD Influent (mg/L)	St. Dev	BOD Effluent (mg/L)	St. Dev.
1	2/14/2005	117.3	0.6	71.0	2.0				
2	2/24/2005	152.7	2.5	151.3	4.2	5.9	0.1	5.0	0.0
3	3/8/2005	38.0	1.7	40.0	1.0	2.2	1.1	2.0	1.2
4	3/20/2005	388.3	2.9	109.0	14.7	1.6	0.0	1.1	0.1
5	3/24/2005	24.7	4.5	34.7	0.6	4.8	0.1	4.3	0.0
6	4/4/2005	21.3	15.9	34.3	1.2	2.9	0.3	3.8	0.1
7	4/8/2005	78.3	3.1	32.0	1.0	1.3	0.0	1.9	0.1
8	4/22/2005	132.3	2.5	105.3	1.5	2.2	0.8	0.9	0.2
9	4/29/2005	126.3	8.7	151.7	3.5	0.9	0.1	0.7	0.0
10	5/16/2005	142.3	0.6	60.3	1.5	1.0	0.1	1.2	0.2
11	5/20/2005	13.7	0.6	24.0	2.0	5.0	0.2	4.6	0.5
12	5/24/2005	132.3	1.5	62.3	0.6	1.1	0.1	1.4	0.2
13	6/3/2005	107.0	3.6	34.7	0.6	8.6	0.1	8.3	0.2
14	6/7/2005	44.3	3.1	32.0	1.0	8.9	0.0	8.8	0.1
15	6/30/2005	157.0	0.0	42.3	1.5	9.3	0.0	8.3	0.1

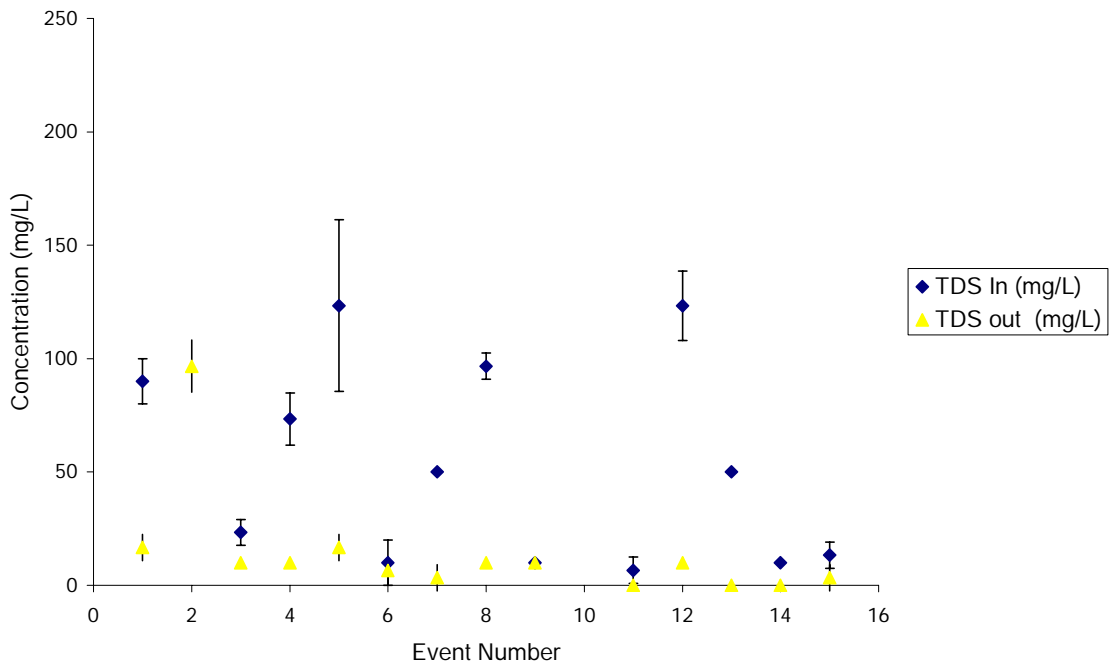
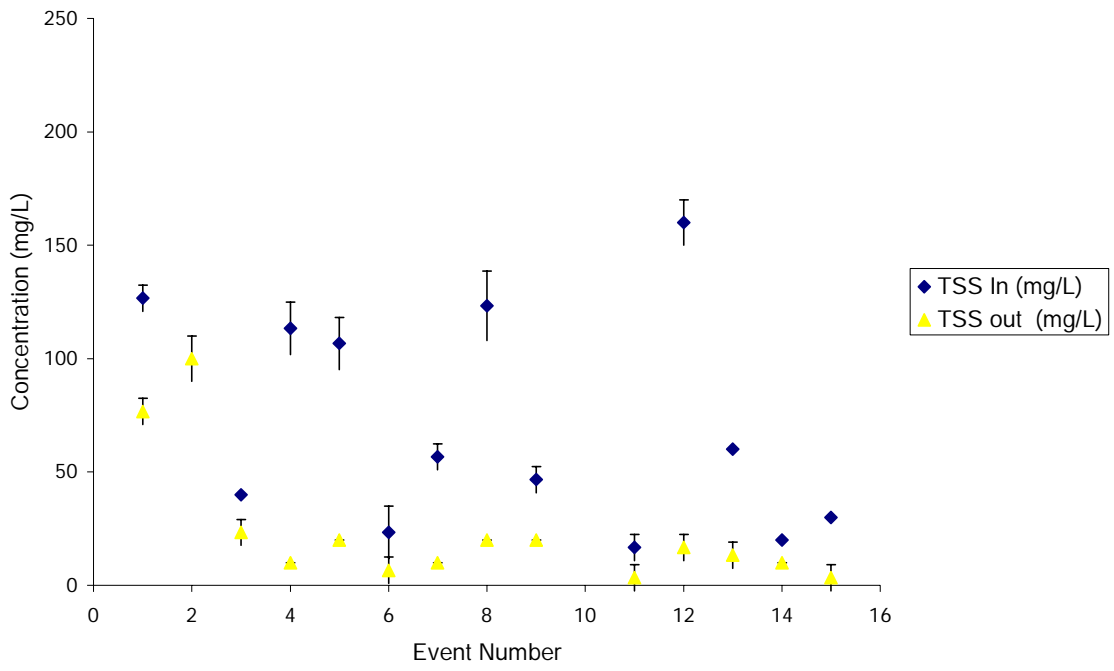






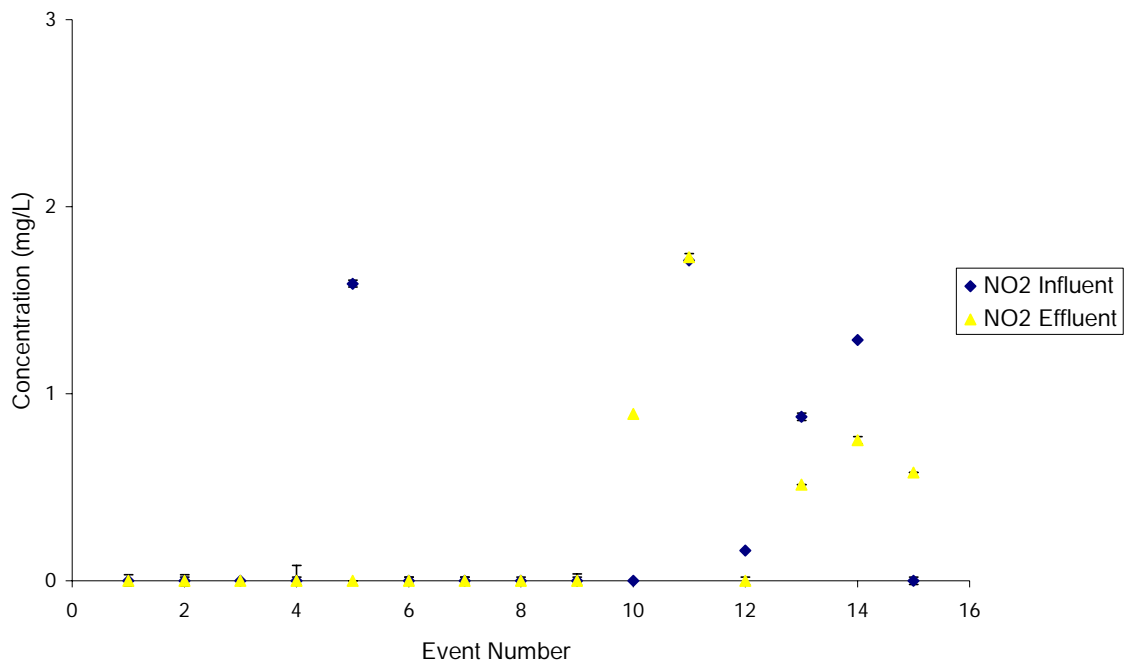
**3. Storm event number, date of event, total suspended and total dissolved solid values.**

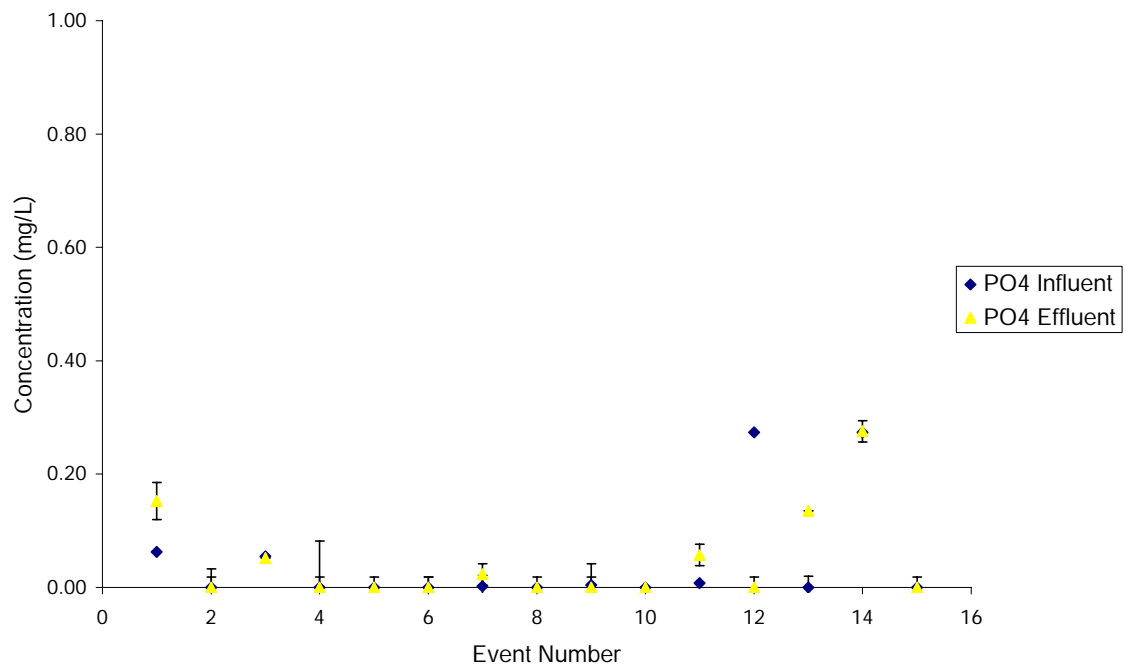
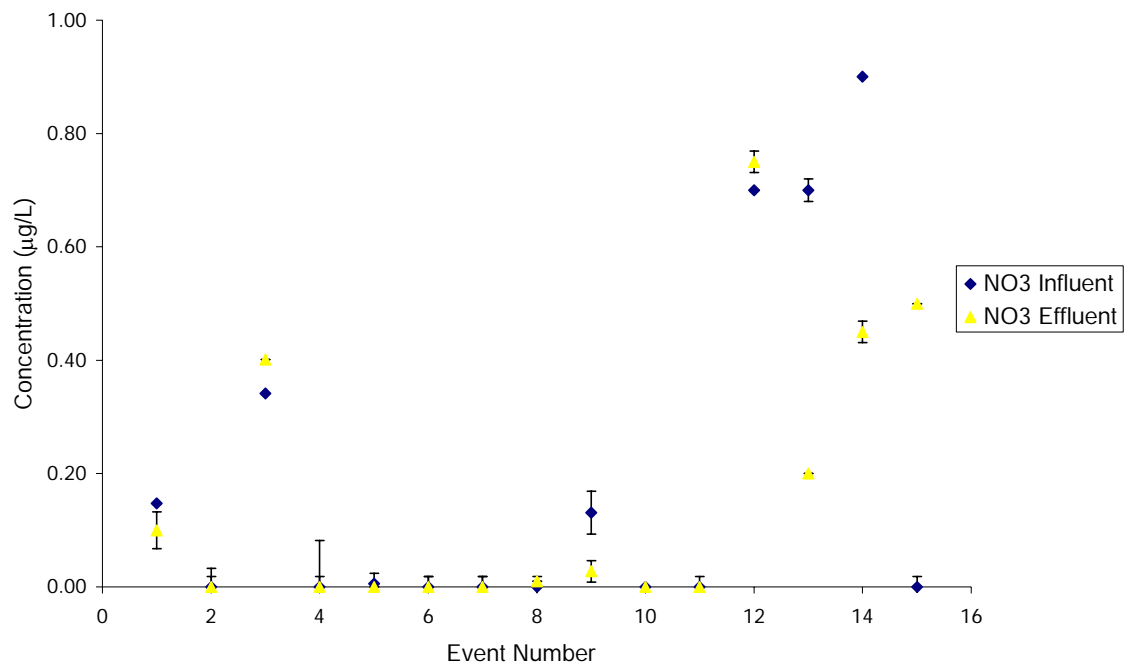
Storm No	Date	TSS In (mg/L)	St. Dev	TSS out (mg/L)	St. Dev.	TDS In (mg/L)	St. Dev	TDS out (mg/L)	St. Dev.
1	2/14/2005	126.7	5.8	76.7	5.8	90.0	10.0	16.7	5.8
2	2/24/2005	1543.3	90.7	100.0	10.0	1363.3	73.7	96.7	11.5
3	3/8/2005	40.0	0.0	23.3	5.8	23.3	5.8	10.0	0.0
4	3/20/2005	113.3	11.5	10.0	0.0	73.3	11.5	10.0	0.0
5	3/24/2005	106.7	11.5	20.0	0.0	123.3	37.9	16.7	5.8
6	4/4/2005	23.3	11.5	6.7	5.8	10.0	10.0	6.7	5.8
7	4/8/2005	56.7	5.8	10.0	0.0	50.0	0.0	3.3	5.8
8	4/22/2005	123.3	15.3	20.0	0.0	96.7	5.8	10.0	0.0
9	4/29/2005	46.7	5.8	20.0	0.0	10.0	0.0	10.0	0.0
10	5/16/2005								
11	5/20/2005	16.7	5.8	3.3	5.8	6.7	5.8	0.0	0.0
12	5/24/2005	160.0	10.0	16.7	5.8	123.3	15.3	10.0	0.0
13	6/3/2005	60.0	0.0	13.3	5.8	50.0	0.0	0.0	0.0
14	6/7/2005	20.0	0.0	10.0	0.0	10.0	0.0	0.0	0.0
15	6/30/2005	30.0	0.0	3.3	5.8	13.3	5.8	3.3	5.8



#### 4. Storm event number, date of event, NO<sub>2</sub>, NO<sub>3</sub>, and PO<sub>4</sub> concentration values

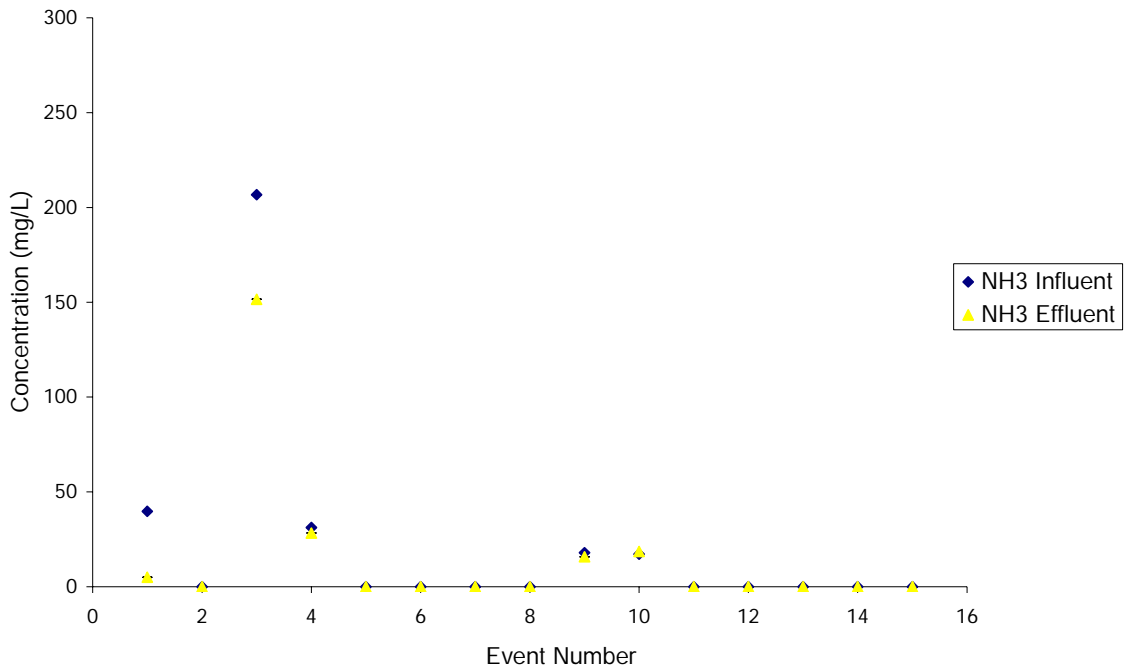
Storm No	Date	NO2 Influent mg/L	St. Dev	NO2 Effluent mg/L	St. Dev.	NO3 Influent mg/L	St. Dev	NO3 Effluent mg/L	St. Dev.	PO4 Influent mg/L	St. Dev	PO4 Effluent mg/L	St. Dev.
1	2/14/2005	0.0	0.0	0.0	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.2	0.0
2	2/24/2005	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3	3/8/2005	0.0	0.0	0.0	0.0	0.3	0.0	0.4	0.0	0.1	0.0	0.1	0.0
4	3/20/2005	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5	3/24/2005	1.6	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
6	4/4/2005	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
7	4/8/2005	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8	4/22/2005	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
9	4/29/2005	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0
10	5/16/2005	0.0	0.0	0.9	1.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
11	5/20/2005	1.7	0.0	1.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0
12	5/24/2005	0.2	0.3	0.0	0.0	0.7	0.0	0.8	0.1	0.3	0.0	0.0	0.0
13	6/3/2005	0.9	0.0	0.5	0.0	0.7	0.0	0.2	0.0	0.0	0.0	0.1	0.2
14	6/7/2005	1.3	0.0	0.8	0.0	0.9	0.0	0.5	0.1	0.3	0.0	0.3	0.0
15	6/30/2005	0.0	0.0	0.6	0.0	0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0





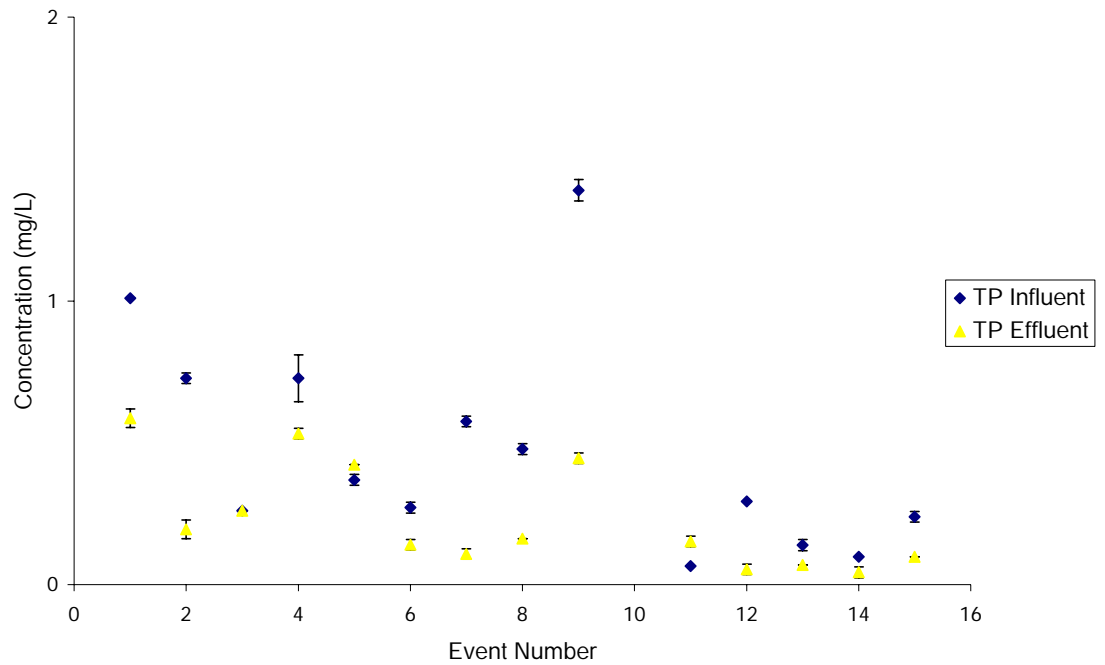
5. Storm event number, date of event, and ammonia concentration values.

Storm No	Date	NH3 Influent mg/L	St. Dev	NH3 Effluent mg/L	St. Dev.
1	2/14/2005	39.8	10.5	5.0	4.3
2	2/24/2005	No meas	No meas	No meas	No meas
3	3/8/2005	206.7	8.0	151.5	13.4
4	3/20/2005	31.2	0.3	28.3	0.5
5	3/24/2005	0.0	0.0	0.0	0.0
6	4/4/2005	0.0	0.0	0.0	0.0
7	4/8/2005	0.0	0.0	0.0	0.0
8	4/22/2005	0.0	0.0	0.0	0.0
9	4/29/2005	18.0	0.1	15.8	0.1
10	5/16/2005	17.3	0.1	18.6	0.6
11	5/20/2005	0.0	0.0	0.0	0.0
12	5/24/2005	0.0	0.0	0.0	0.0
13	6/3/2005	0.0	0.0	0.0	0.0
14	6/7/2005	0.0	0.0	0.0	0.0
15	6/30/2005	0.0	0.0	0.0	0.0



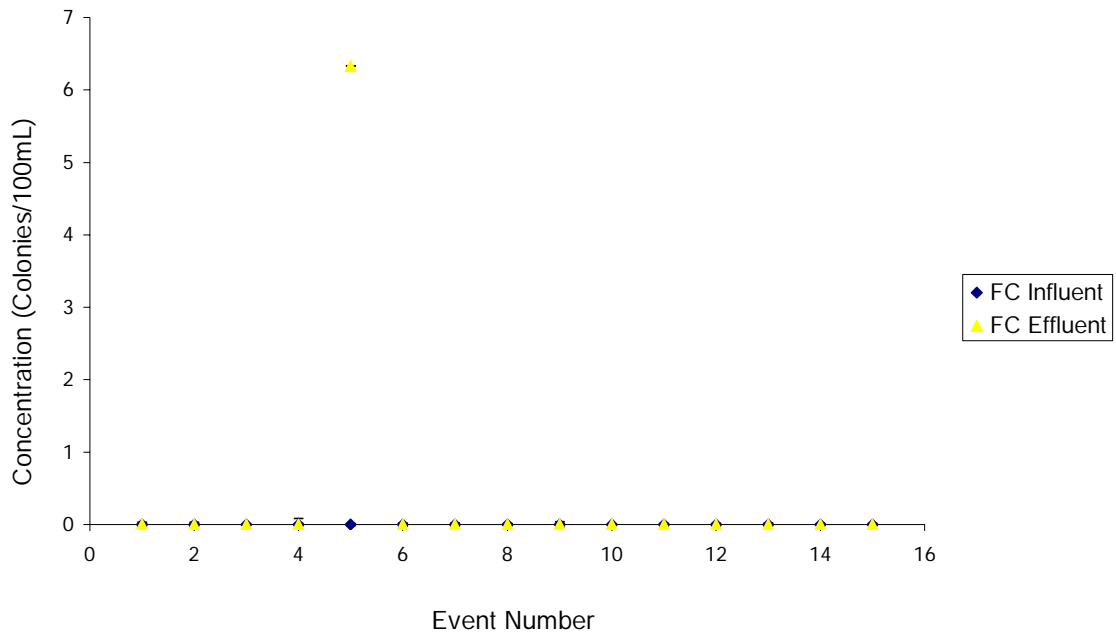
6. Storm event number, date of event, and TP concentration values.

Storm No	Date	TP Influent mg/L	St. Dev	TP Effluent mg/L	St. Dev.
1	2/14/2005	1.0	0.0	0.6	0.0
2	2/24/2005	0.7	0.0	0.2	0.0
3	3/8/2005	0.3	0.0	0.3	0.0
4	3/20/2005	0.7	0.1	0.5	0.0
5	3/24/2005	0.4	0.0	0.4	0.0
6	4/4/2005	0.3	0.0	0.1	0.0
7	4/8/2005	0.6	0.0	0.1	0.0
8	4/22/2005	0.5	0.0	0.2	0.0
9	4/29/2005	1.4	0.0	0.4	0.0
10	5/16/2005				
11	5/20/2005	0.1	0.0	0.2	0.0
12	5/24/2005	0.3	0.0	0.1	0.0
13	6/3/2005	0.1	0.0	0.1	0.0
14	6/7/2005	0.1	0.0	0.0	0.0
15	6/30/2005	0.2	0.0	0.1	0.0



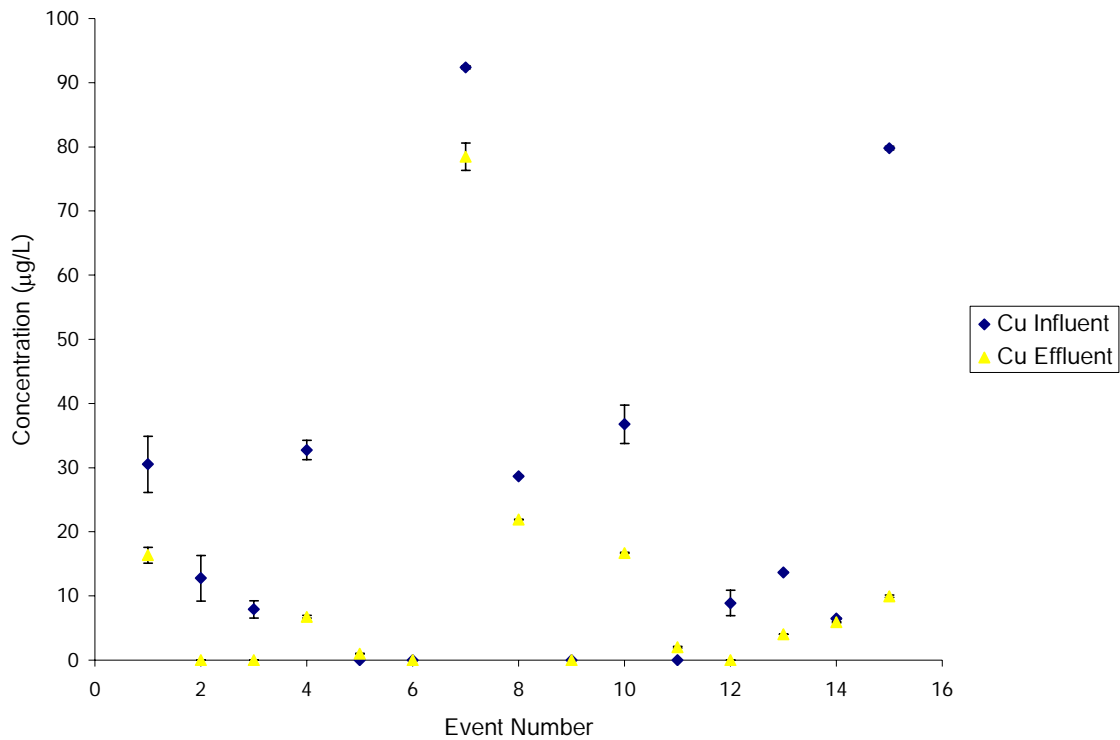
7. Storm event number, date of event, and Fecal coliforms concentration values.

Storm No	Date	FC Influent	St. Dev	FC Effluent	St. Dev.
1	2/14/2005	0.0	0.0	0.0	0.0
2	2/24/2005	0.0	0.0	0.0	0.0
3	3/8/2005	0.0	0.0	0.0	0.0
4	3/20/2005	0.0	0.0	0.0	0.0
5	3/24/2005	0.0	0.0	6.3	11.0
6	4/4/2005	0.0	0.0	0.0	0.0
7	4/8/2005	0.0	0.0	0.0	0.0
8	4/22/2005	0.0	0.0	0.0	0.0
9	4/29/2005	0.0	0.0	0.0	0.0
10	5/16/2005	0.0	0.0	0.0	0.0
11	5/20/2005	0.0	0.0	0.0	0.0
12	5/24/2005	0.0	0.0	0.0	0.0
13	6/3/2005	0.0	0.0	0.0	0.0
14	6/7/2005	0.0	0.0	0.0	0.0
15	6/30/2005	0.0	0.0	0.0	0.0



8. Storm event number, date of event, and copper concentration values.

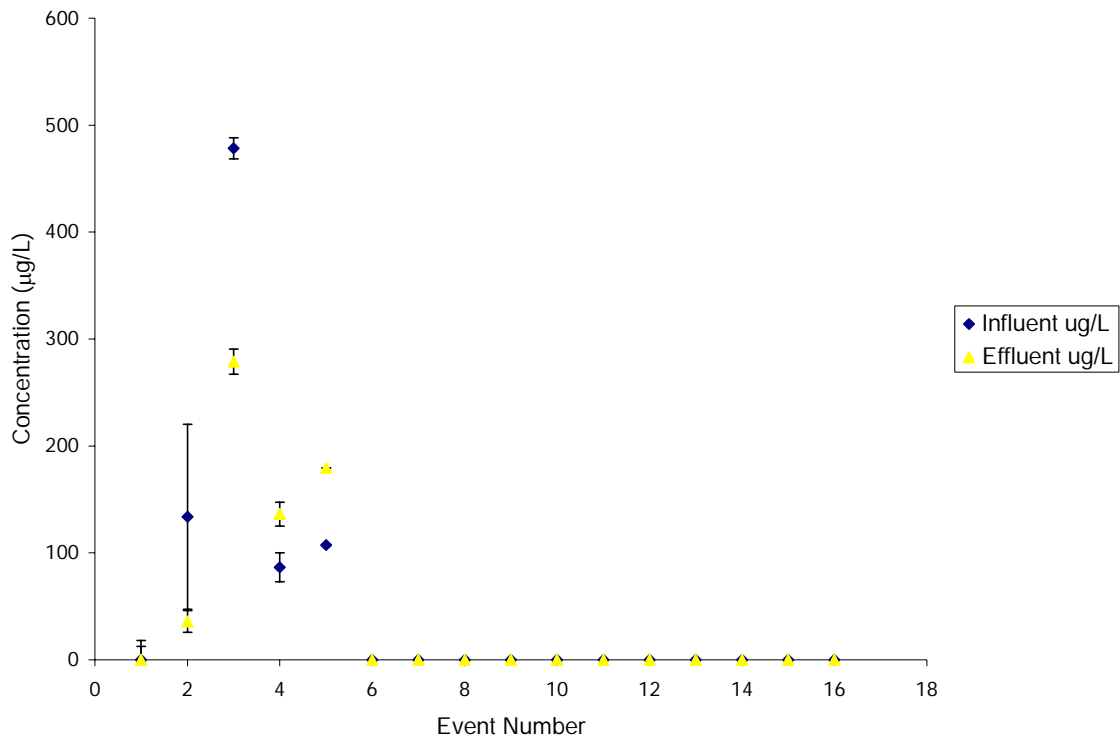
Storm No	Date	Cu Influent (ug/L)	St. Dev	Cu Effluent (ug/L)	St. Dev.
1	2/14/2005	30.5	4.4	16.4	1.2
2	2/24/2005	12.8	3.6	0.0	0.0
3	3/8/2005	7.9	1.3	0.0	0.0
4	3/20/2005	32.8	1.5	6.8	0.2
5	3/24/2005	0.0	0.0	1.0	0.1
6	4/4/2005	0.0	0.0	0.0	0.0
7	4/8/2005	92.4	0.2	78.5	2.1
8	4/22/2005	28.7	0.1	21.9	0.1
9	4/29/2005	0.0	0.0	0.0	0.0
10	5/16/2005	36.8	3.0	16.7	0.1
11	5/20/2005	0.0	0.0	2.0	0.1
12	5/24/2005	8.9	2.0	0.0	0.0
13	6/3/2005	13.7	0.1	4.0	0.0
14	6/7/2005	6.5	0.1	5.9	0.1
15	6/30/2005	79.8	0.3	9.9	0.2





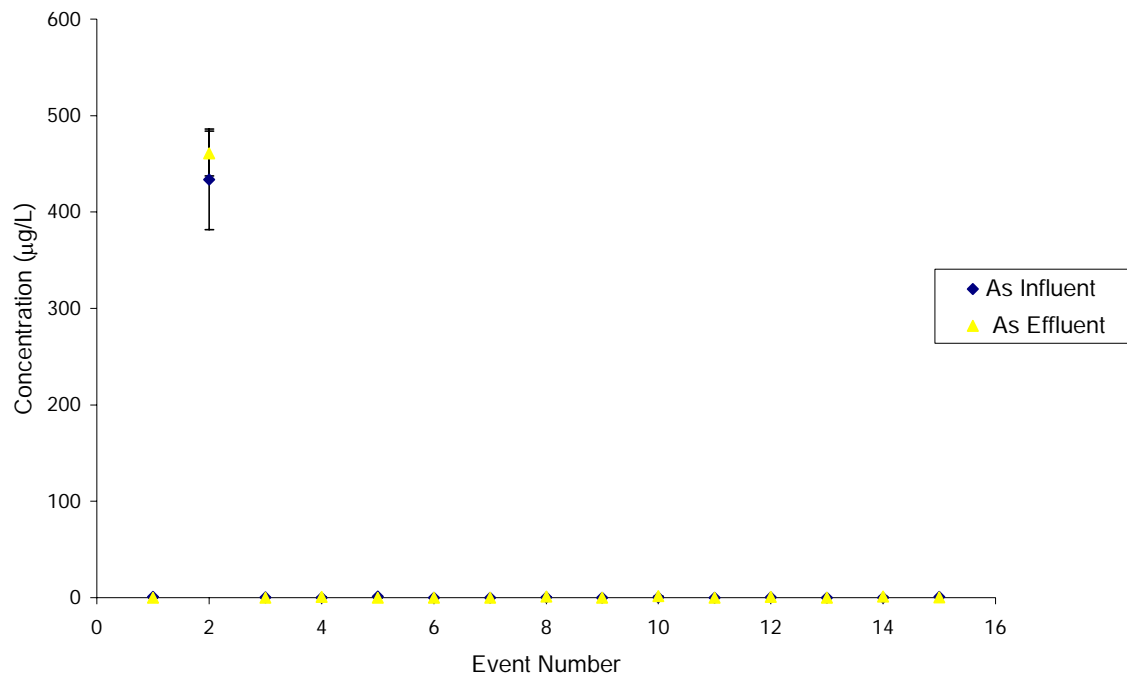
8. Storm event number, date of event, and mercury concentration values.

Storm No	Date	Hg Influent (ug/L)	St. Dev	Hg Effluent (ug/L)	St. Dev.
1	2/14/2005	133.7	18.1	35.8	12.5
2	2/24/2005	478.3	86.4	279.0	10.3
3	3/8/2005	86.5	9.8	136.3	11.7
4	3/20/2005	107.2	13.6	179.3	11.2
5	3/24/2005	0.0	0.0	0.0	0.0
6	4/4/2005	0.0	0.0	0.0	0.0
7	4/8/2005	0.0	0.0	0.0	0.0
8	4/22/2005	0.0	0.0	0.0	0.0
9	4/29/2005	0.0	0.0	0.0	0.0
10	5/16/2005	0.0	0.0	0.0	0.0
11	5/20/2005	0.0	0.0	0.0	0.0
12	5/24/2005	0.0	0.0	0.0	0.0
13	6/3/2005	0.0	0.0	0.0	0.0
14	6/7/2005	0.0	0.0	0.0	0.0
15	6/30/2005	0.0	0.0	0.0	0.0



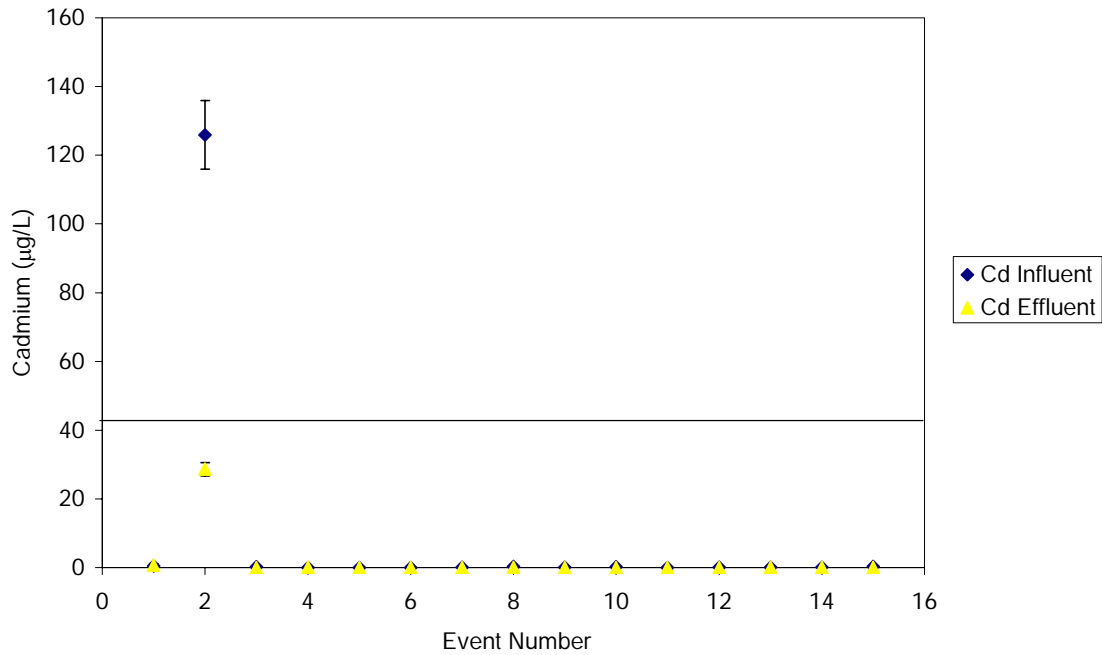
9. Storm event number, date of event, and arsenic concentration values.

Storm No	Date	As Influent	St. Dev	As Effluent	St. Dev.
1	2/14/2005	1.0	0.2	0.0	0.0
2	2/24/2005	433.8	52.1	460.8	23.4
3	3/8/2005	0.6	0.1	0.0	0.0
4	3/20/2005	0.0	0.0	0.8	0.1
5	3/24/2005	1.4	0.2	0.0	0.0
6	4/4/2005	0.0	0.0	0.0	0.0
7	4/8/2005	0.0	0.0	0.0	0.0
8	4/22/2005	0.5	0.0	1.1	0.1
9	4/29/2005	0.0	0.0	0.0	0.0
10	5/16/2005	0.6	0.1	1.7	0.0
11	5/20/2005	0.0	0.0	0.0	0.0
12	5/24/2005	0.3	0.1	1.0	0.1
13	6/3/2005	0.0	0.0	0.0	0.0
14	6/7/2005	0.0	0.0	1.1	0.1
15	6/30/2005	0.9	0.1	0.6	0.0



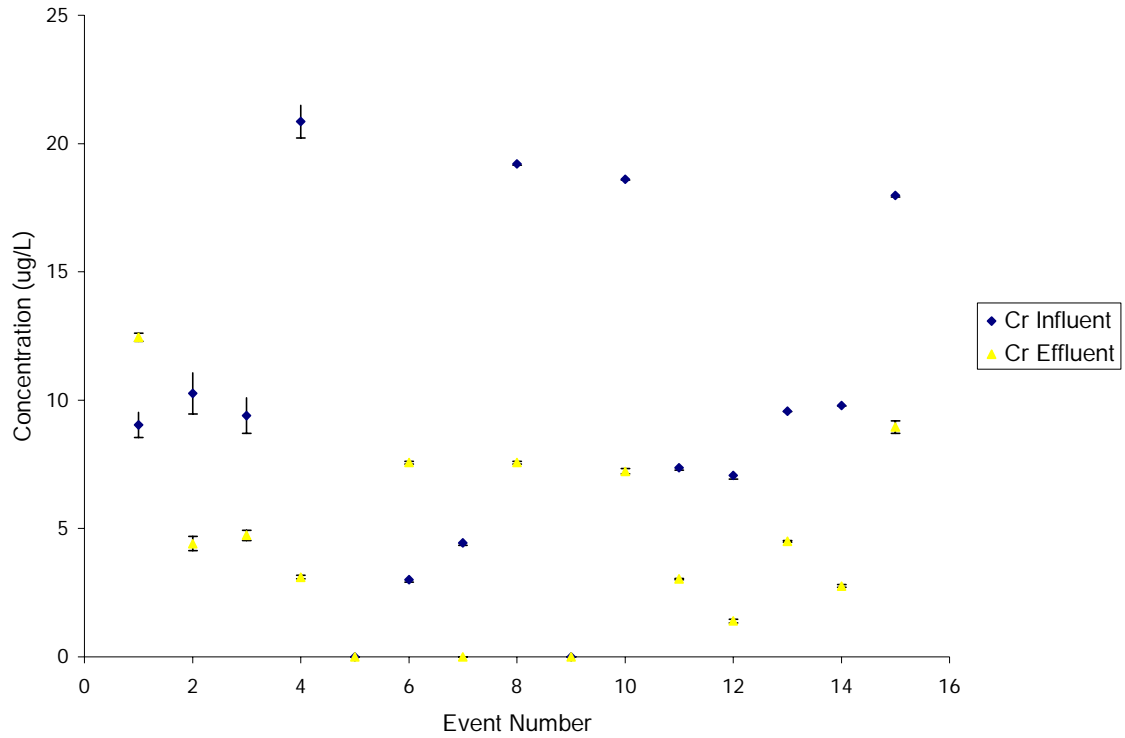
10. Storm event number, date of event, and cadmium concentration values.

Storm No	Date	Cd Influent (ug/L)	St. Dev	Cd Effluent (ug/L)	St. Dev.
1	2/14/2005	0.4	0.0	0.7	0.5
2	2/24/2005	125.9	10.0	28.6	1.9
3	3/8/2005	0.3	0.1	0.0	0.0
4	3/20/2005	0.0	0.0	0.1	0.0
5	3/24/2005	0.0	0.0	0.0	0.0
6	4/4/2005	0.0	0.0	0.0	0.0
7	4/8/2005	0.1	0.0	0.0	0.0
8	4/22/2005	0.4	0.0	0.1	0.0
9	4/29/2005	0.1	0.0	0.0	0.0
10	5/16/2005	0.2	0.0	0.0	0.0
11	5/20/2005	0.0	0.0	0.0	0.0
12	5/24/2005	0.2	0.0	0.0	0.0
13	6/3/2005	0.1	0.0	0.1	0.0
14	6/7/2005	0.1	0.0	0.1	0.0
15	6/30/2005	0.3	0.0	0.2	0.0



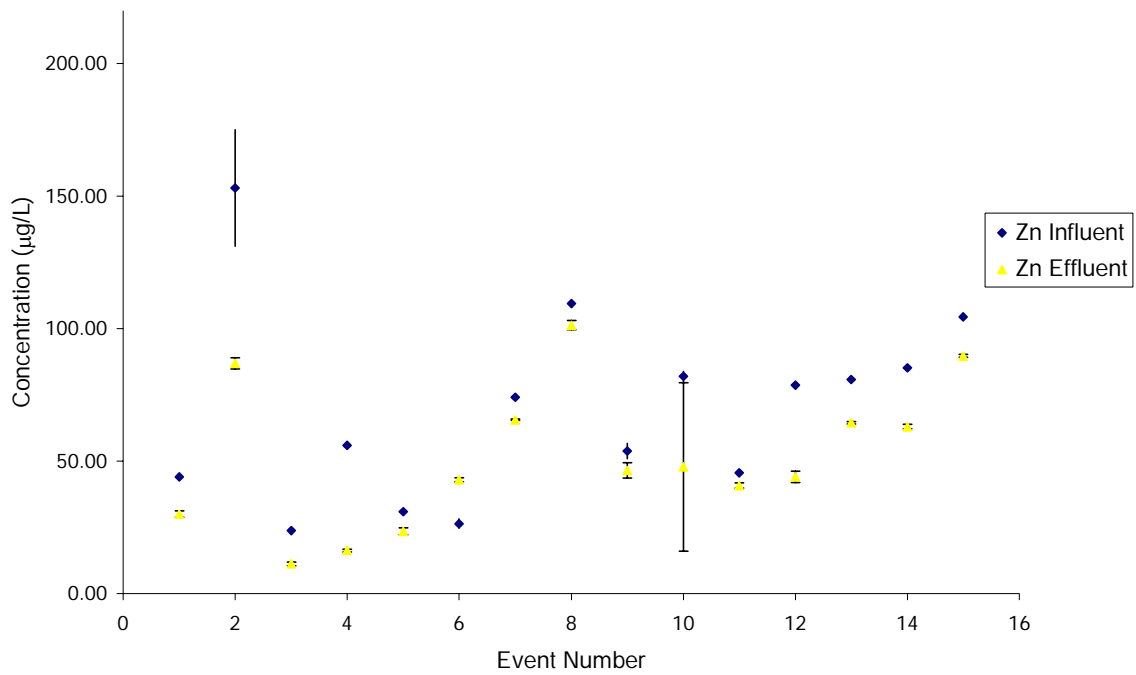
11. Storm event number, date of event, and chromium concentration values.

Storm No	Date	Cr Influent (ug/L)	St. Dev.	Cr Effluent (ug/L)	St. Dev.
1	2/14/2005	9.0	0.5	12.5	0.2
2	2/24/2005	10.3	0.8	4.4	0.3
3	3/8/2005	9.4	0.7	4.7	0.2
4	3/20/2005	20.9	0.6	3.1	0.1
5	3/24/2005	0.0	0.0	0.0	0.0
6	4/4/2005	3.0	0.1	7.6	0.1
7	4/8/2005	4.4	0.1	0.0	0.0
8	4/22/2005	19.2	0.0	7.6	0.1
9	4/29/2005	0.0	0.0	0.0	0.0
10	5/16/2005	18.6	0.0	7.2	0.1
11	5/20/2005	7.4	0.1	3.0	0.0
12	5/24/2005	7.1	0.1	1.4	0.1
13	6/3/2005	9.6	0.0	4.5	0.0
14	6/7/2005	9.8	0.0	2.8	0.1
15	6/30/2005	18.0	0.1	9.0	0.2



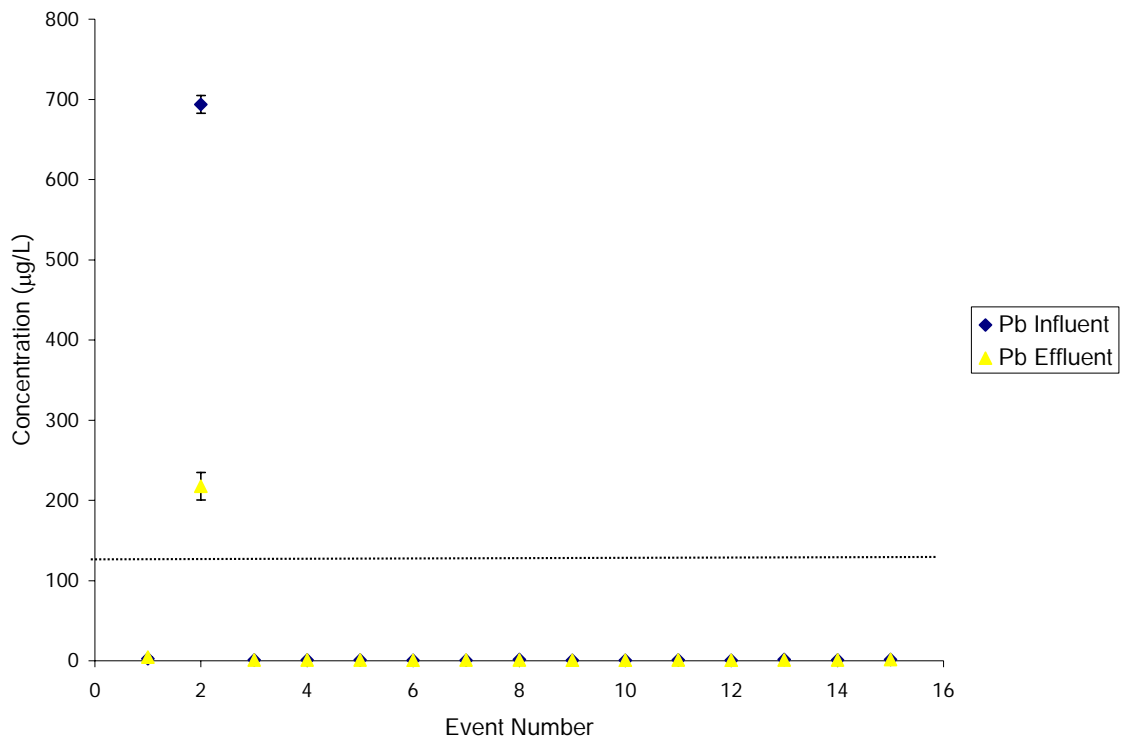
11. Storm event number, date of event, and zinc concentration values.

Storm No	Date	Zn Influent (ug/L)	St. Dev	Zn Effluent (ug/L)	St. Dev.
1	2/14/2005	44.1	0.9	30.1	1.2
2	2/24/2005	153.1	22.0	86.9	2.1
3	3/8/2005	23.9	1.2	11.3	0.7
4	3/20/2005	55.9	1.1	16.2	0.6
5	3/24/2005	31.0	0.7	23.5	1.3
6	4/4/2005	26.4	1.7	43.0	0.7
7	4/8/2005	74.0	0.5	65.6	0.2
8	4/22/2005	109.5	0.2	101.3	1.8
9	4/29/2005	53.8	2.9	46.5	2.9
10	5/16/2005	82.0	1.9	47.8	31.8
11	5/20/2005	45.6	0.3	40.8	1.0
12	5/24/2005	78.7	0.4	44.1	2.1
13	6/3/2005	80.8	0.1	64.5	0.5
14	6/7/2005	85.2	0.4	63.0	0.8
15	6/30/2005	104.4	0.4	89.7	0.5



12. Storm event number, date of event, and lead concentration values.

Storm No	Date	Pb Influent (ug/L)	St. Dev	Pb Effluent (ug/L)	St. Dev.
1	2/14/2005	2.5	0.1	4.7	0.1
2	2/24/2005	693.6	11.2	217.8	17.1
3	3/8/2005	1.2	0.1	1.1	0.3
4	3/20/2005	1.0	0.2	1.0	0.0
5	3/24/2005	1.1	0.1	0.8	0.0
6	4/4/2005	0.7	0.1	0.6	0.1
7	4/8/2005	0.5	0.0	0.9	0.0
8	4/22/2005	1.3	0.0	0.8	0.0
9	4/29/2005	0.5	0.0	0.5	0.0
10	5/16/2005	0.7	0.0	0.4	0.0
11	5/20/2005	0.8	0.0	0.9	0.0
12	5/24/2005	0.6	0.1	0.5	0.0
13	6/3/2005	1.5	0.1	1.1	0.0
14	6/7/2005	0.8	0.0	1.2	0.0
15	6/30/2005	1.5	0.0	1.3	0.0



## PAH Measurements

### Compounds Measured for:

- 1 Indeno (1,2,3 - cd)pyrene
- 2 Benzo(ghi)perylene
- 3 Dibenzo(a,h)anthracene
- 4 Benzo(a)Pyrene
- 5 Benzo(k)Flouranthene
- 6 Chrysene
- 7 Benzo(a)Anthracene
- 8 Pyrene
- 9 Flouranthene
- 10 Anthracene
- 11 Phenanthrene
- 12 Acenaphthylene
- 13 Napthalene
- 14 Benzo(b)flouranthene

### Events and the Compounds with concentrations above 0.5 ppb in at least one sample

<u>Storm event 2</u>		Nothing over 1 ppb	
<u>Storm event 5</u>		Nothing over 1 ppb	
<u>Storm event 6</u>			
3	<b>Dibenzo(a,h)anthracene</b>		
	IN6 A	0.29	1.44
	IN6 average	0.29	<b>1.4</b>
	OUT6 C	20.09	100
	Out6 average	20.09	<b>100.5</b>
13	<b>Napthalene</b>		
	OUT6 B	0.0868	0.434
	OUT6 C	0.8763	4.3815
	Out6 average	0.48155	<b>2.41</b>
<u>Storm Event 7</u>			
7	<b>Benzo(a)Anthracene</b>		
	IN7 A	0.4427	2.2135
	IN7 B	0.2448	1.224
	IN7 C	0.2574	1.287
	IN7 average	0.315	<b>1.6</b>
	Out7 average	NA	NA
12	<b>Acenaphthylene</b>		
	IN7 A	0.2168	1.084
	IN7 B	0.0196	0.098
	IN7 average	0.1182	<b>0.59</b>
	OUT7 A	0.0002	0.001
	OUT7 B	0.0003	0.0015
	Out7 average	0.00025	<b>0.00</b>
<u>Storm event 8</u>			
1	<b>Indeno (1,2,3 - cd)pyrene</b>	<b>HPLC conc.</b>	<b>Actual conc. (ppb)</b>

	IN8 average	NA	NA
	OUT8 B	11.3326	56.7
	Out8 average	11.3326	<b>56.7</b>
5	<b>Benzo(k)Flouranthene</b>		
	OUT8 A	0.2142	1.071
	Out8 average	0.2142	<b>1.07</b>
<u>Storm event 10</u>		Nothing over 1 ppb	
<u>Storm event 11</u>			
1	<b>Indeno (1,2,3 - cd)pyrene</b>	<b>HPLC conc.</b>	<b>Actual conc. (ppb)</b>
	IN11 average	NA	NA
	OUT11 A	2.0227	10.1135
	Out11 average	2.0227	<b>10.11</b>
<u>Storm event 12</u>			
3	<b>Dibenzo(a,h)anthracene</b>		
	IN12 average	NA	NA
	OUT12 B	0.1309	0.6545
	Out12 average	0.1309	<b>0.65</b>
<u>Storm event 13</u>		Nothing over 1 ppb	
<u>Storm event 14</u>			
1	<b>Indeno (1,2,3 - cd)pyrene</b>	<b>HPLC conc.</b>	<b>Actual conc. (ppb)</b>
	IN14 B	2.6042	13.0
	IN14 average	2.6042	<b>13.0</b>
	Out14 average	NA	NA
<u>Storm event 15</u>			
13	<b>Napthalene</b>		
	IN15 B	0.0561	0.3
	IN15 average	0.0561	<b>0.3</b>
	OUT15 A	0.008	0.0
	OUT15 B	0.6336	3.2
	OUT15 C	0.0016	0.0
	Out15 average	0.2144	1.1

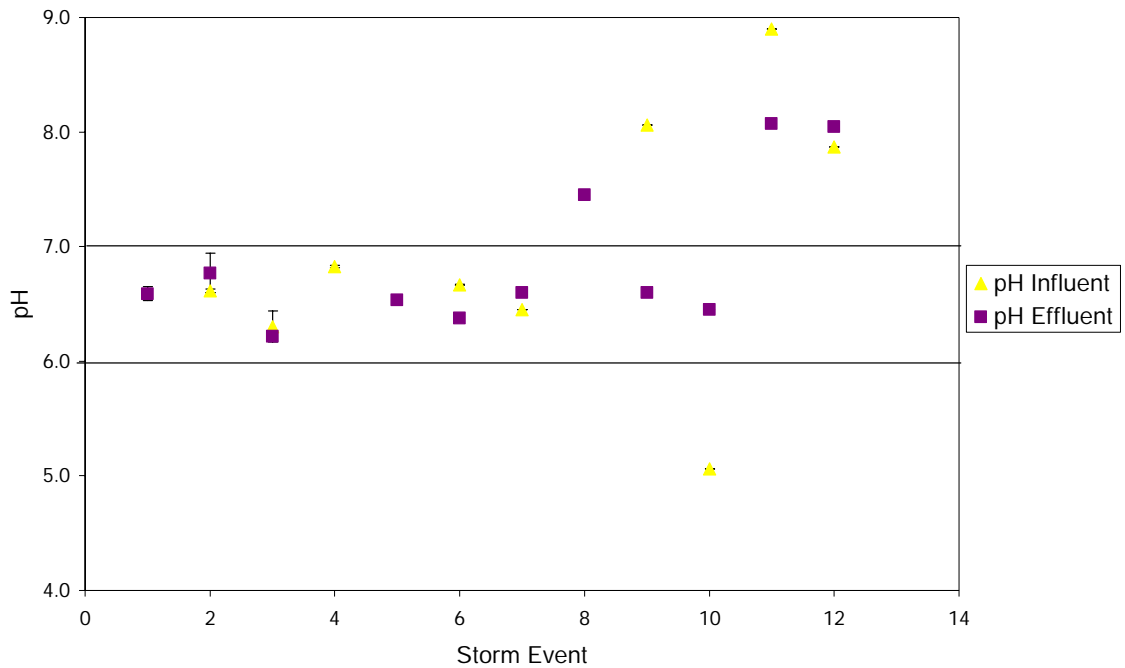


## Results for the DC Sand Filter Site

DDOT project - Site # 2 -DC village  
pH

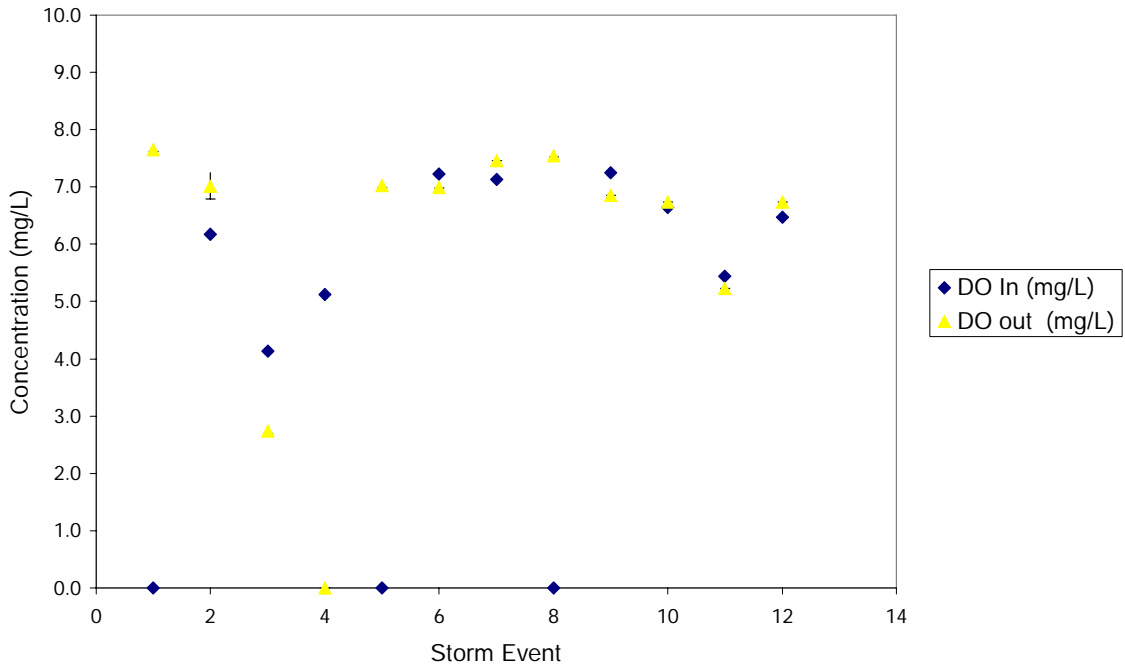
Storm #	pH Influent	St. Dev	pH Effluent	St. Dev.
1	NS	NS	6.6	0.1
2	6.6	0.0	6.8	0.2
3	6.3	0.1	6.2	0.0
4	6.8	0.0	NS	NS
5	NS	NS	6.5	0.0
6	6.7	0.0	6.4	0.0
7	6.5	0.0	6.6	0.0
8	NS	NS	7.5	0.0
9	8.1	0.0	6.6	0.0
10	5.1	0.0	6.5	0.0
11	8.9	0.0	8.1	0.0
12	7.9	0.0	8.0	0.0

Average	7.0	0.0	6.9	0.0
Std. Dev.	1.1	0.0	0.7	0.1



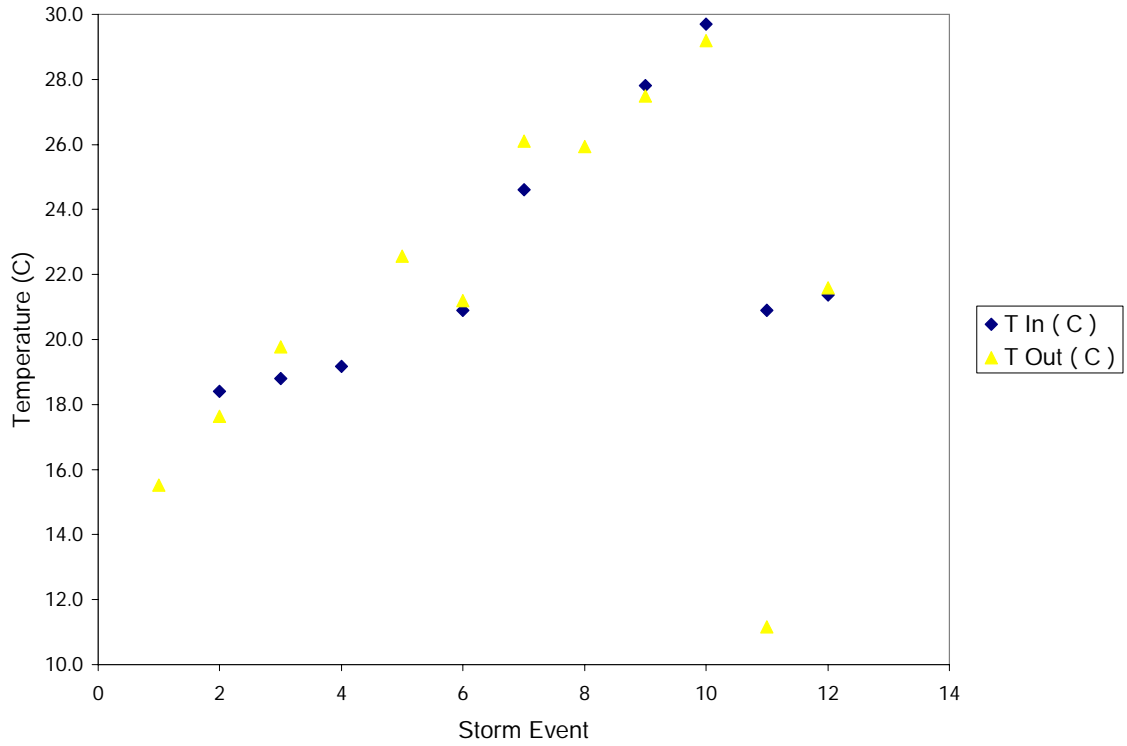
DDOT project - Site # 2 -DC village  
DO

Storm #	DO In (mg/L)	St. Dev	DO out (mg/L)	St. Dev.
1	NS	NS	7.7	0.0
2	6.2	0.0	7.0	0.2
3	4.1	0.0	2.7	0.0
4	5.1	0.0	NS	NS
5	NS	NS	7.0	0.0
6	7.2	0.0	7.0	0.0
7	7.1	0.0	7.5	0.0
8	NS	NS	7.5	0.0
9	7.3	0.0	6.9	0.0
10	6.6	0.0	6.7	0.0
11	5.4	0.0	5.2	0.0
12	6.5	0.0	6.7	0.0
Average	6.2	0.0	6.5	0.0
Std. Dev.	1.1	0.0	1.4	0.1



DDOT project - Site # 2 -DC village  
 Temperature

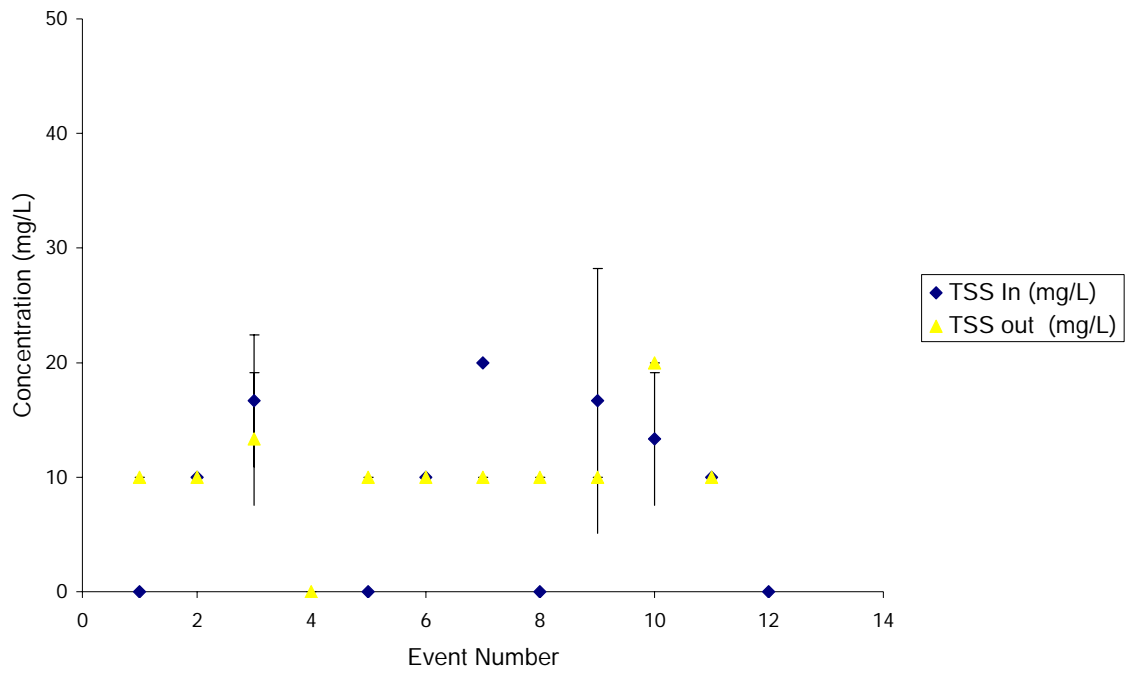
Storm #	T In (C)	St. Dev.	T Out (C)	St. Dev.
1	NS	NS	16	0
2	18	0	18	0
3	19	0	20	0
4	19	0	NS	NS
5	NS	NS	23	0
6	21	0	21	0
7	25	0	26	0
8	NS	NS	26	0
9	28	0	28	0
10	30	0	29	0
11	21	0	11	0
12	21	0	22	0
Average	22.4	0.0	21.7	0.1
Std. Dev.	4.1	0.1	5.5	0.1



DDOT project - Site # 2 -DC village  
 TSS

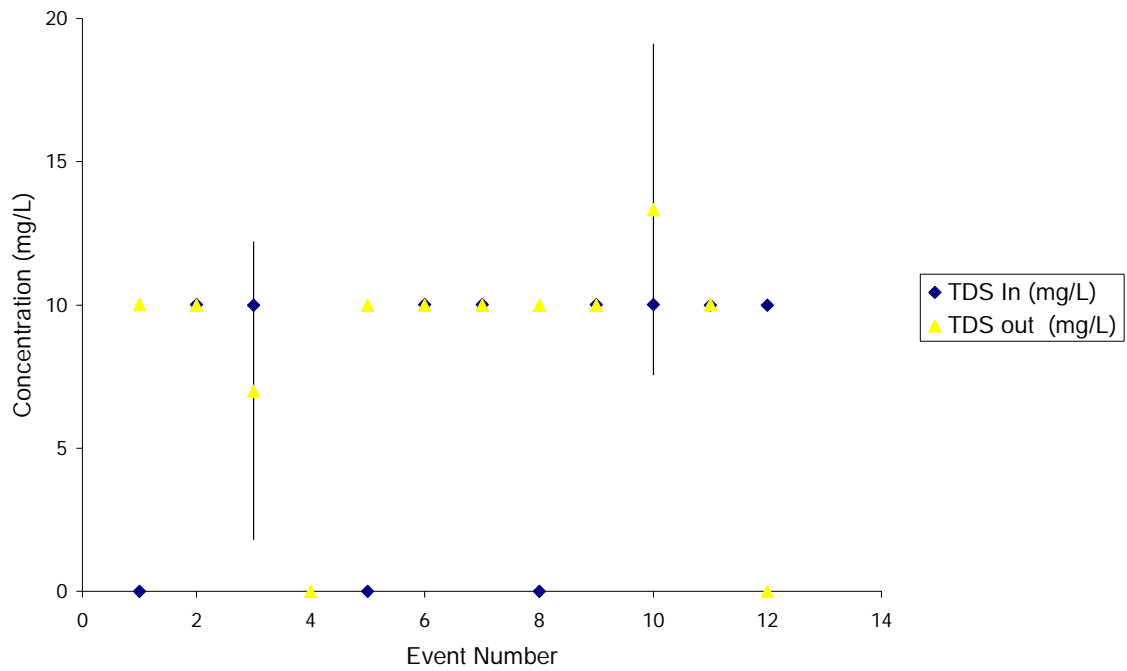
Storm #	TSS In (mg/L)	St. Dev	TSS out (mg/L)	St. Dev.
1	NS	NS	10	0
2	10	0	10	0
3	17	6	13	6
4	670	52	NS	NS
5	NS	NS	10	0
6	10	0	10	0
7	20	0	10	0
8	NS	NS	10	0
9	17	12	10	0
10	13	6	20	0
11	10	0	10	0
12	NS	NS		

	% Removal				
Average	95.8	9.4	11.3	0.6	0.88
Std. Dev.	232.0	17.7	3.2	1.8	



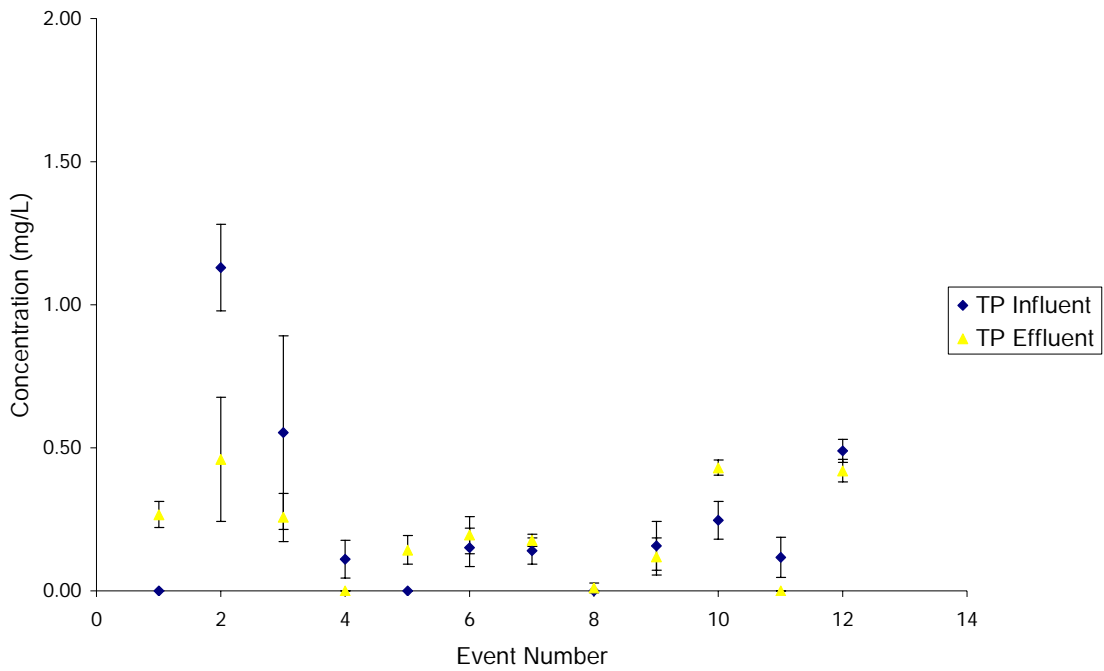
DDOT project - Site # 2 -DC village  
TDS

Storm #	TDS In (mg/L)	St. Dev	TDS out (mg/L)	St. Dev.	
1	NS	NS	10.0	0.0	
2	10.0	0.0	10.0	0.0	
3	10.0	0.0	7.0	5.2	
4	363.3	37.9	NS	NS	
5	NS	NS	10.0	0.0	
6	10.0	0.0	10.0	0.0	
7	10.0	0.0	10.0	0.0	
8	NS	NS	10.0	0.0	
9	10.0	0.0	10.0	0.0	
10	10.0	0.0	13.3	5.8	
11	10.0	0.0	10.0	0.0	
12	10.0	0.0	0.0	0.0	
Average	49.3	4.2	9.1	1.0	% Removal 0.81
Std. Dev.	117.8	12.6	3.3	2.2	



DDOT project - Site # 2 -DC village  
TP

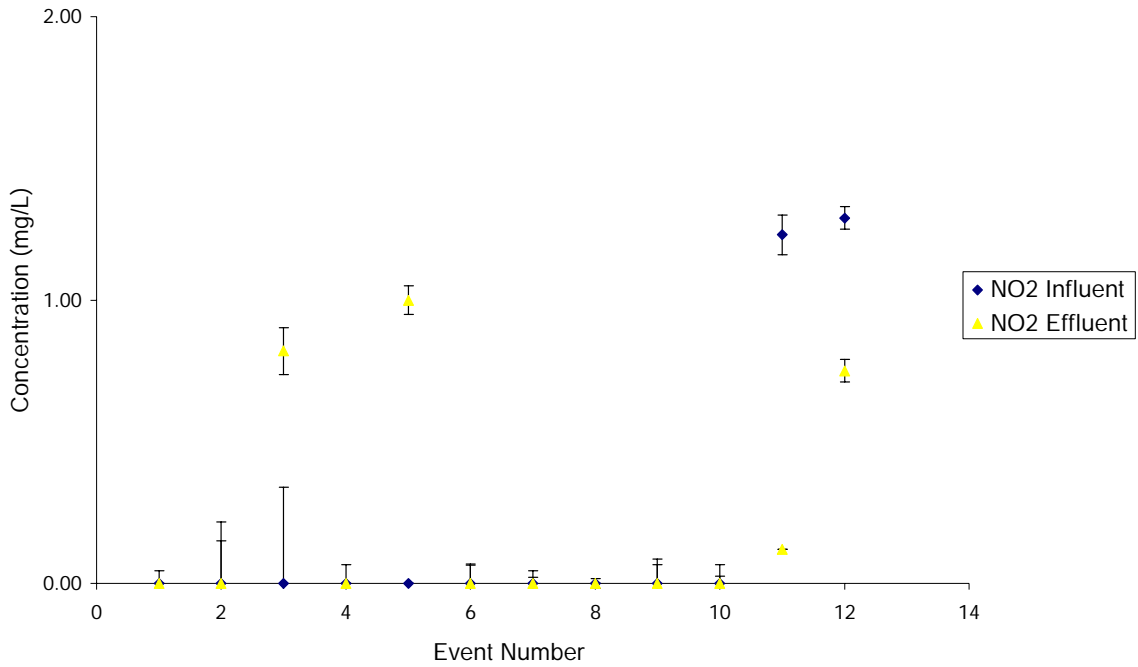
Storm #	TP mg/L		TP mg/L		
	TP Influent	St. Dev.	TP Effluent	St. Dev.	
1	NS	NS	0.27	0.05	
2	1.13	0.15	0.46	0.22	
3	0.55	0.34	0.26	0.08	
4	0.11	0.07	NS	NS	
5	NS	NS	0.14	0.05	
6	0.15	0.07	0.20	0.07	
7	0.14	0.05	0.18	0.02	
8	NS	NS	0.01	0.02	
9	0.16	0.09	0.12	0.07	
10	0.25	0.07	0.43	0.03	
11	0.12	0.1	0.0	0.0	
12	0.5	0.0	0.4	0.0	
Average	0.3	0.1	0.2	0.1	% Removal 0.34
Std. Dev.	0.3	0.1	0.2	0.1	



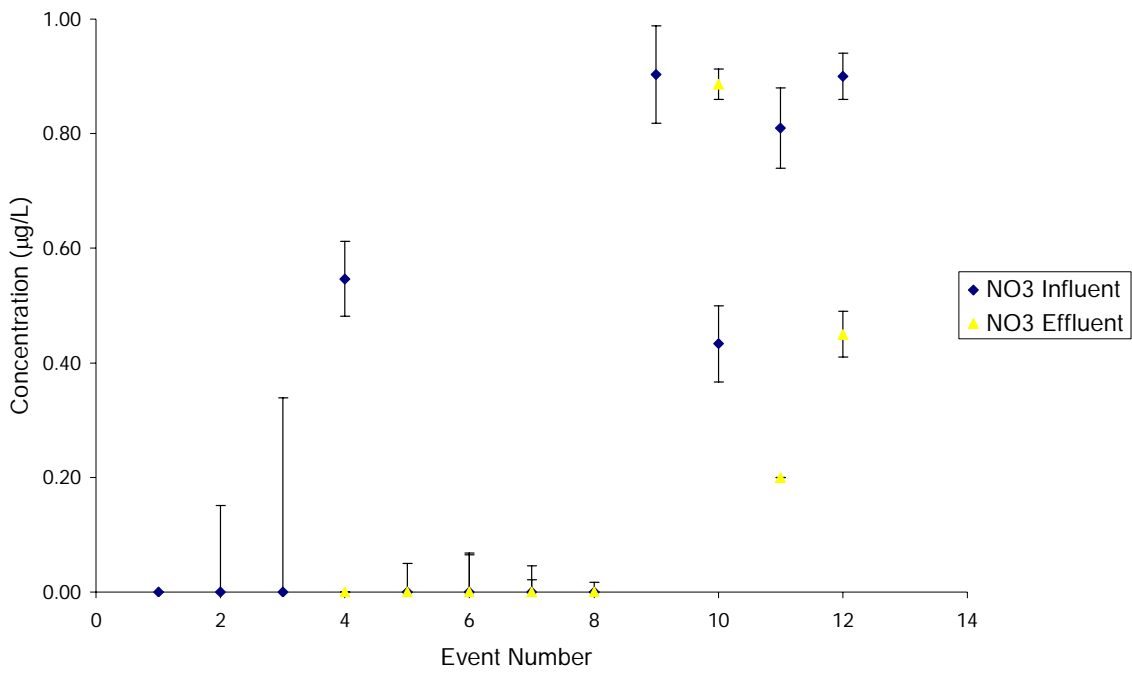
DDOT project - Site # 2 -DC village  
NO2

Storm #	NO2 mg/L		NO2 mg/L	
	NO2 Influent	St. Dev.	NO2 Effluent	St. Dev.
1	NS	NS	0.00	0.00
2	0.00	0.00	0.00	0.00
3	0.00	0.00	0.82	0.16
4	0.00	0.00	NS	NS
5	NS	NS	1.00	0.00
6	0.00	0.00	0.00	0.00
7	0.00	0.00	0.00	0.00
8	NS	NS	0.00	0.00
9	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00
11	1.23	0.10	0.12	0.03
12	1.3	0.0	0.8	0.0

					% Removal
Average	0.3	0.0	0.2	0.0	0.13
Std. Dev.	0.6	0.0	0.4	0.0	



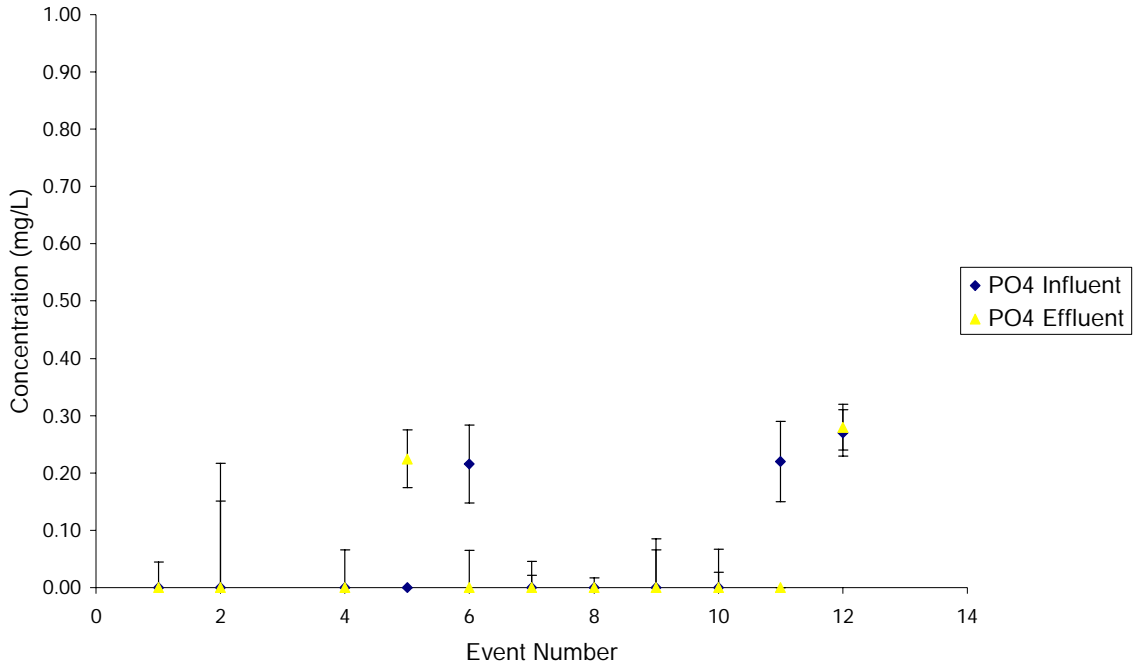
DDOT project - Site # 2 -DC village				
NO3				
	NO3 mg/L		NO3 mg/L	
Storm #	NO3 Influent	St. Dev	NO3 Effluent	St. Dev.
1	NS	NS	3.43	0.75
2	0.00	0.00	3.80	1.51
3	0.00	0.00	1.13	0.12
4	0.55	0.15	NS	NS
5	NS	NS	0.00	0.00
6	0.00	0.00	0.00	0.00
7	0.00	0.00	0.00	0.00
8	NS	NS	0.00	0.00
9	0.90	0.01	1.17	0.09
10	0.43	0.03	0.89	0.44
11	0.81	0.55	0.20	0.15
12	0.9	0.0	0.5	0.1
				% Removal
Average	0.4	0.1	1.0	0.3
Std. Dev.	0.4	0.2	1.4	0.5





DDOT project - Site # 2 -DC village  
PO4

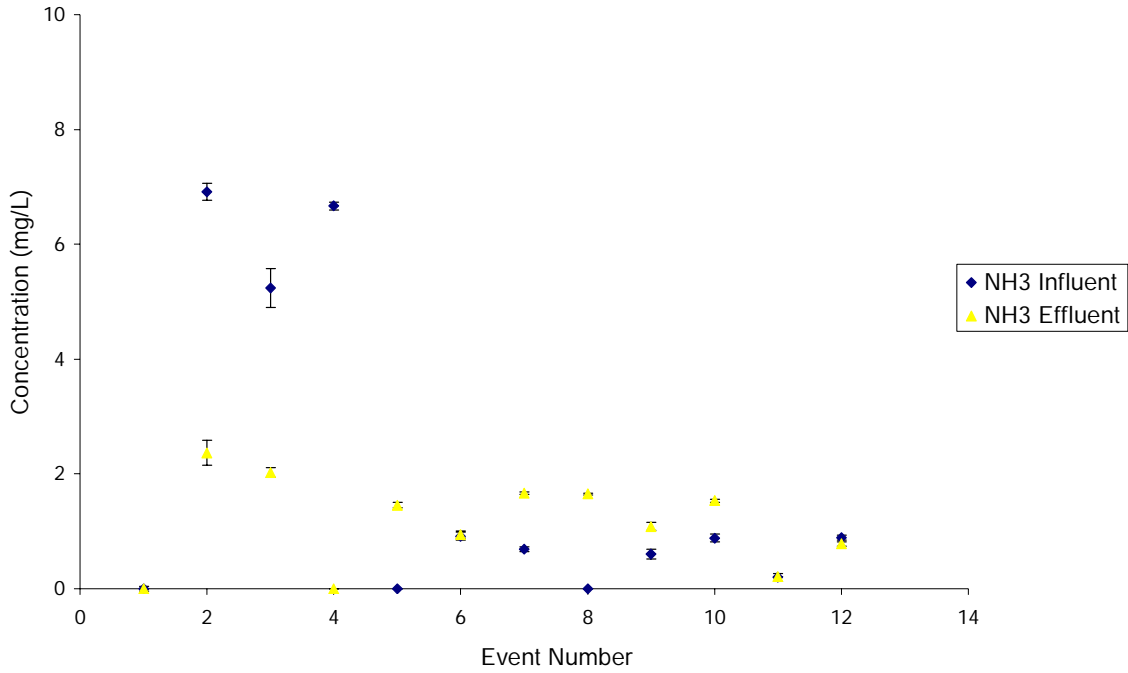
Storm #	PO4 mg/L		PO4 mg/L		% Removal
	PO4 Influent	St. Dev.	PO4 Effluent	St. Dev.	
1	NS	NS	0.00	0.00	
2	0.00	0.00	0.00	0.00	
3	1.55	0.17	2.02	0.11	
4	0.00	0.00	NS	NS	
5	NS	NS	0.22	0.00	
6	0.22	0.01	0.00	0.00	
7	0.00	0.00	0.00	0.00	
8	NS	NS	0.00	0.00	
9	0.00	0.00	0.00	0.00	
10	0.00	0.00	0.00	0.00	
11	0.2	0.0	0.0	0.0	
12	0.3	0.0	0.3	0.0	
Average	0.3	0.0	0.2	0.0	0.09
Std. Dev.	0.5	0.1	0.6	0.0	



DDOT project - Site # 2 -DC village  
NH3

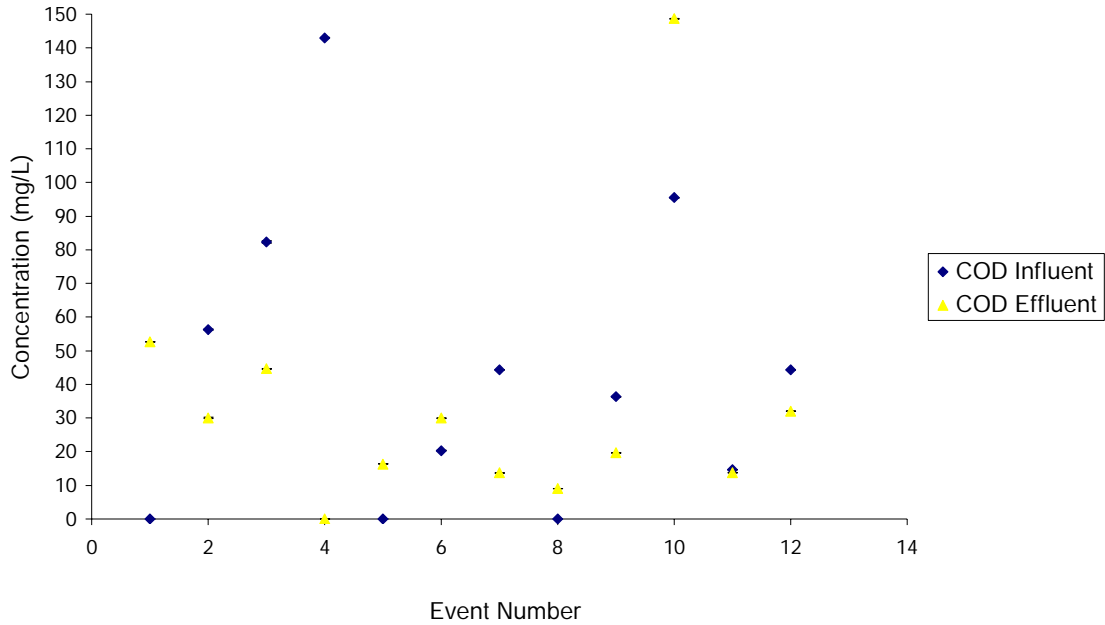
Storm #	NH3 mg/L		NH3 mg/L	
	NH3 Influent	St. Dev.	NH3 Effluent	St. Dev.
1	NS	NS	0.00	0.00
2	6.92	0.05	2.37	0.065
3	5.24	0.50	2.03	0.248
4	6.67	0.45	NS	NS
5	NS	NS	1.46	0.06
6	0.92	0.04	0.95	0.04
7	0.69	0.00	1.67	0.06
8	NS	NS	1.65	0.09
9	0.60	0.08	1.09	0.16
10	0.88	0.06	1.54	0.13
11	0.20	0.01	0.21	0.01
12	0.9	0.0	0.8	0.0

					% Removal
Average	2.6	0.1	1.2	0.1	0.51
Std. Dev.	2.8	0.2	0.7	0.1	



DDOT project - Site # 2 -DC village  
COD

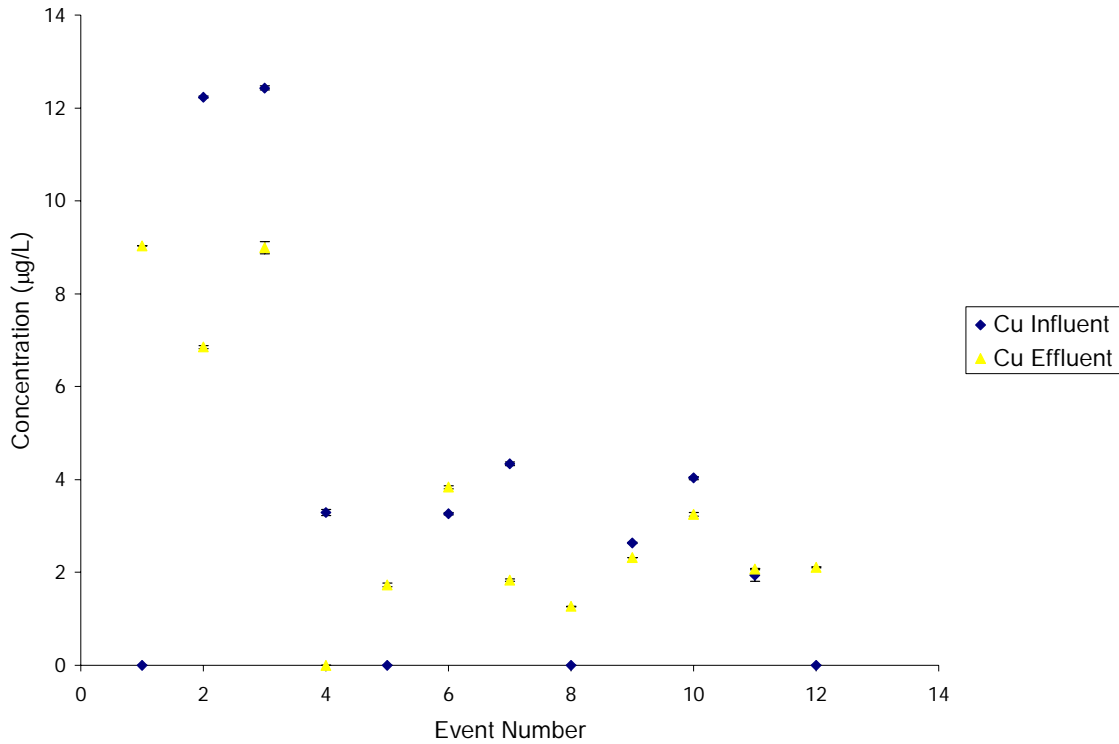
Storm #	COD mg/L		COD mg/L		% Removal
	COD Influent	St. Dev.	COD Effluent	St. Dev.	
1	NS	NS	52.7	0.6	
2	56.3	0.6	30.0	1.0	
3	82.3	2.1	44.7	0.6	
4	143.0	6.1	NS	NS	
5	NS	NS	16.3	0.6	
6	20.3	0.6	30.0	1.0	
7	44.3	2.5	13.7	0.6	
8	NS	NS	9.0	0.0	
9	36.3	0.6	19.7	1.5	
10	95.5	43.1	148.7	7.2	
11	14.7	0.3	13.7	0.1	
12	44.3	3.1	32.0	1.0	
Average	60	6.5	37	1.3	0.37
Std. Dev.	41	13.8	39	2.0	



DDOT project - Site # 2 -DC village  
Cu

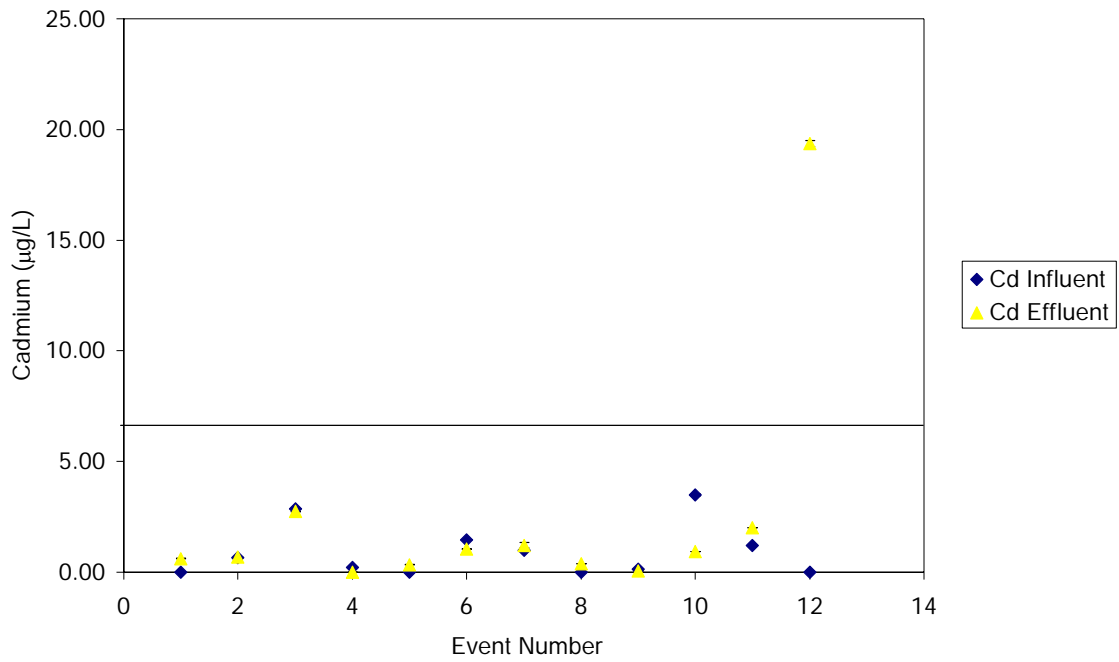
Storm #	(ug/L)		(ug/L)	
	Cu Influent	St. Dev	Cu Effluent	St. Dev.
1	NS	NS	9.0	0.0
2	12.2	0.0	6.9	0.0
3	12.4	0.0	9.0	0.1
4	3.3	0.1	NS	NS
5	NS	NS	1.7	0.0
6	3.3	0.0	3.8	0.0
7	4.3	0.0	1.8	0.0
8	NS	NS	1.3	0.0
9	2.6	0.0	2.3	0.0
10	4.0	0.0	3.2	0.0
11	1.9	0.1	2.1	0.0
12	NS	NS	2.1	0.0

Average	5.5	0.0	3.9	0.0	% Removal	0.29
Std. Dev.	4.3	0.0	2.9	0.0		0.0



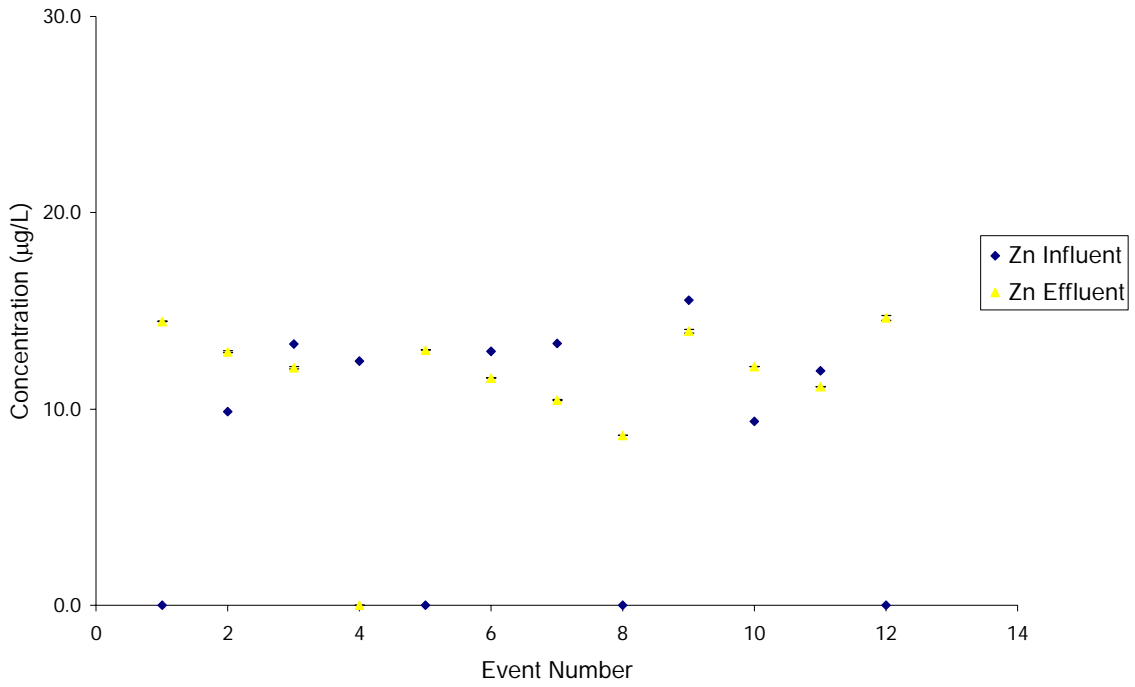
DDOT project - Site # 2 -DC village  
Cd

Storm #	(ug/L)		(ug/L)		% Removal	
	Cd Influent	St. Dev.	Cd Effluent	St. Dev.		
1	NS	NS	0.6	0.0		
2	0.6	0.0	0.7	0.0		
3	2.9	0.0	2.7	0.0		
4	0.2	0.0	NS	NS		
5	NS	NS	0.3	0.0		
6	1.5	0.0	1.0	0.0		
7	1.0	0.0	1.2	0.1		
8	NS	NS	0.4	0.0		
9	0.1	0.0	0.1	0.0		
10	3.5	0.1	0.9	0.0		
11	1.2	0.0	2.0	0.0		
12	NS	NS	19.4	0.1		
Average		1.4	0.0	2.7	0.0	-0.94
Std. Dev.		1.2	0.0	5.6	0.1	



DDOT project - Site # 2 -DC village  
Zn

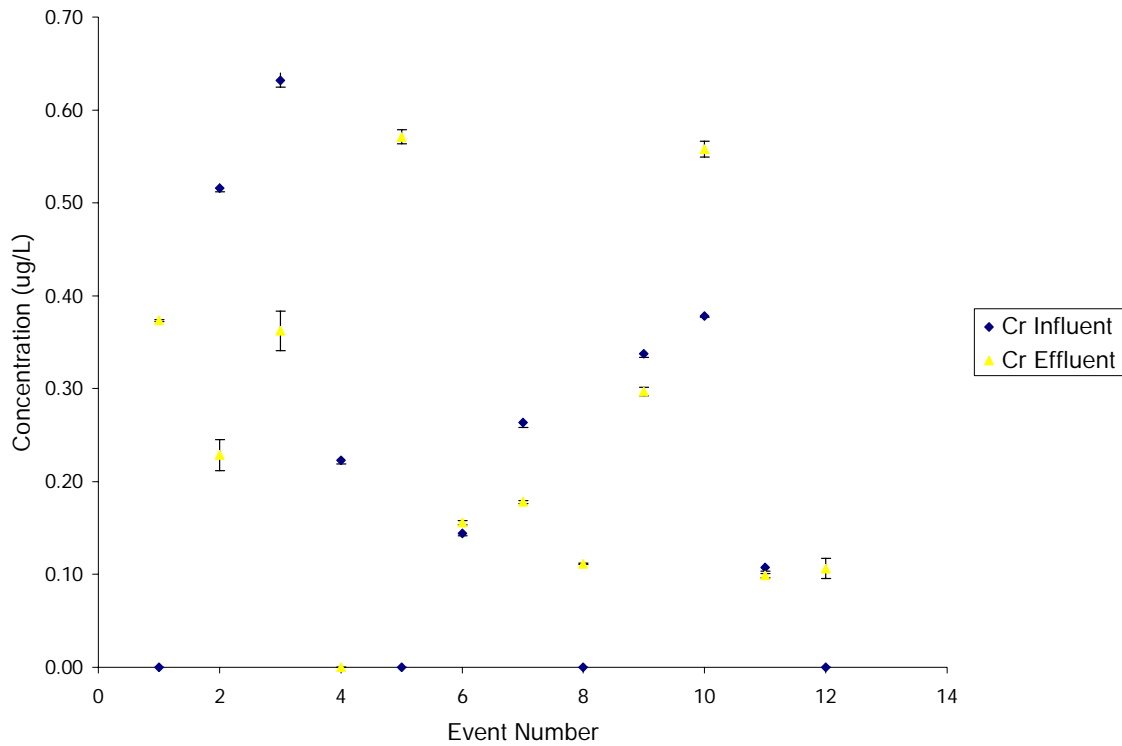
Storm #	(ug/L)		(ug/L)		% Removal
	Zn Influent	St. Dev.	Zn Effluent	St. Dev.	
1	NS	NS	14.5	0.0	
2	9.9	0.1	12.9	0.0	
3	13.3	0.0	12.1	0.1	
4	12.4	0.1	NS	NS	
5	NS	NS	13.0	0.0	
6	12.9	0.0	11.6	0.0	
7	13.3	0.0	10.5	0.0	
8	NS	NS	8.6	0.0	
9	15.5	0.0	14.0	0.1	
10	9.4	0.1	12.2	0.0	
11	11.9	0.0	11.1	0.0	
12	NS	NS	14.6	0.1	
Average	12.3	0.0	12.3	0.0	0.01
Std. Dev.	2.0	0.0	1.8	0.0	



DDOT project - Site # 2 -DC village  
Cr

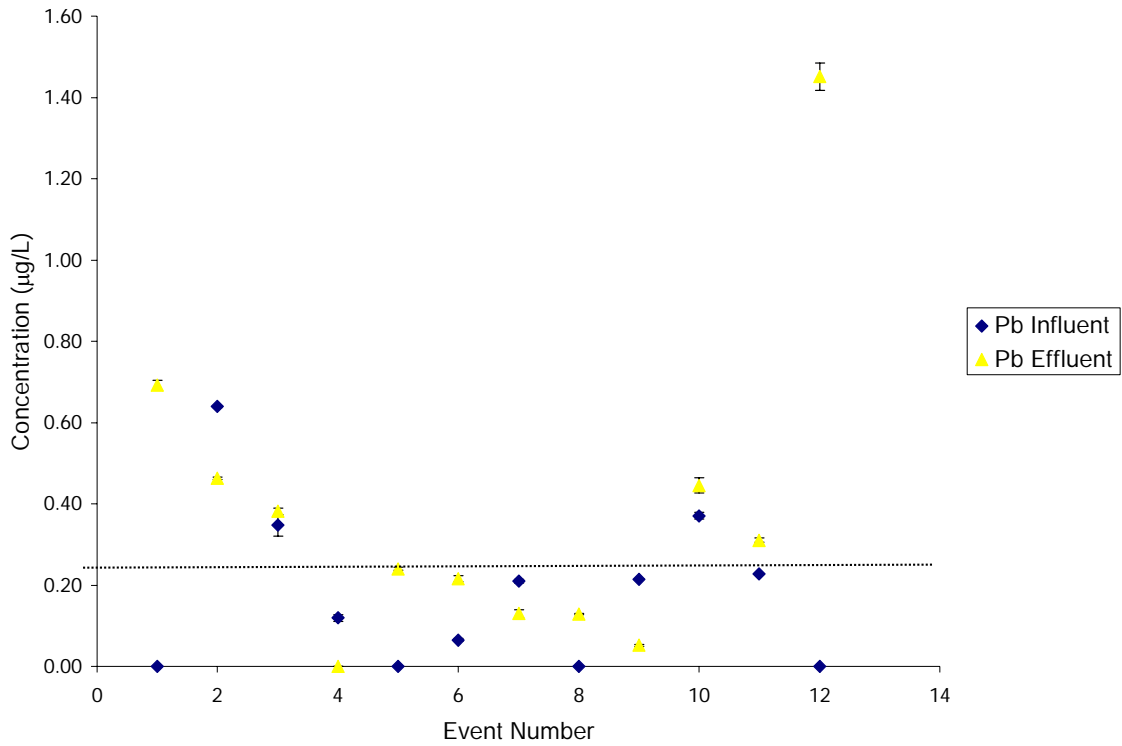
Storm #	(ug/L)		(ug/L)	
	Cr Influent	St. Dev.	Cr Effluent	St. Dev.
1	NS	NS	0.4	0.0
2	0.5	0.0	0.2	0.0
3	0.6	0.0	0.4	0.0
4	0.2	0.0	NS	NS
5	NS	NS	0.6	0.0
6	0.1	0.0	0.2	0.0
7	0.3	0.0	0.2	0.0
8	NS	NS	0.1	0.0
9	0.3	0.0	0.3	0.0
10	0.4	0.0	0.6	0.0
11	0.1	0.0	0.1	0.0
12	NS	NS	0.1	0.0

Average	0.3	0.0	0.3	0.0	% Removal	0.15
Std. Dev.	0.2	0.0	0.2	0.0		0.0



DDOT project - Site # 2 -DC village  
Pb

Storm #	(ug/L)		(ug/L)		% Removal
	Pb Influent	St. Dev.	Pb Effluent	St. Dev.	
1	NS	NS	0.7	0.0	
2	0.6	0.0	0.5	0.0	
3	0.3	0.0	0.4	0.0	
4	0.1	0.0	NS	NS	
5	NS	NS	0.2	0.0	
6	0.1	0.0	0.2	0.0	
7	0.2	0.0	0.1	0.0	
8	NS	NS	0.1	0.0	
9	0.2	0.0	0.1	0.0	
10	0.4	0.0	0.4	0.0	
11	0.2	0.0	0.3	0.0	
12	NS	NS	1.5	0.0	
Average	0.3	0.0	0.4	0.0	-0.50
Std. Dev.	0.2	0.0	0.4	0.0	0.0

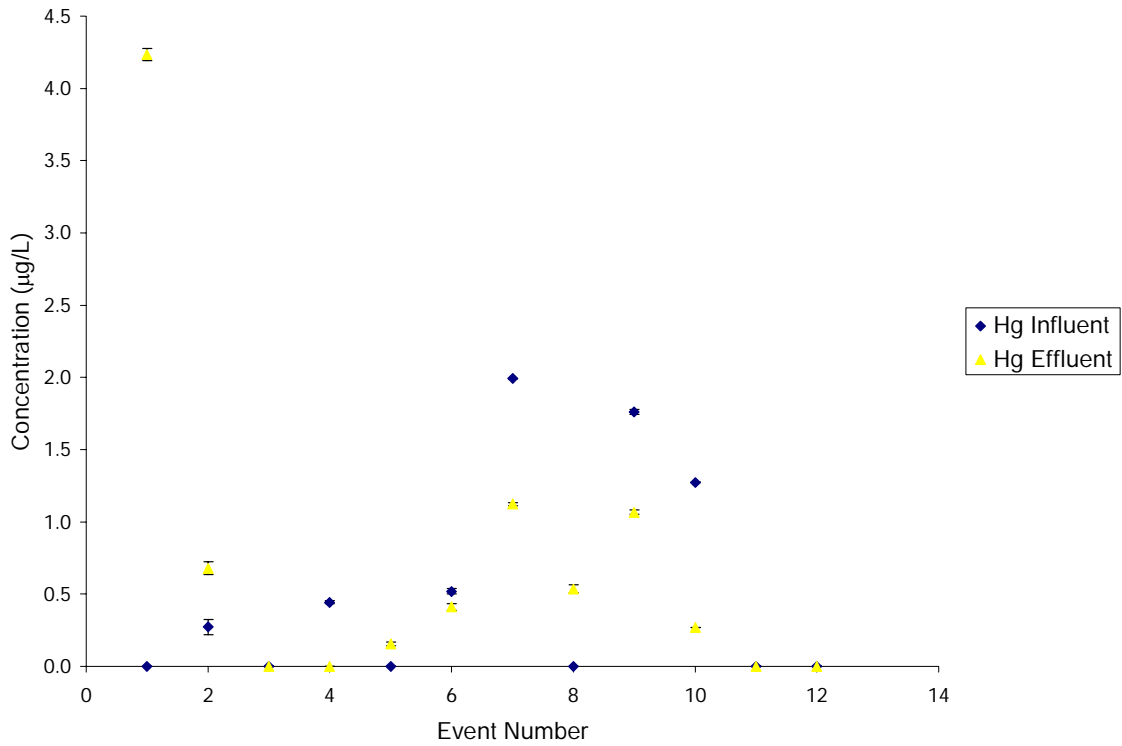




DDOT project - Site # 2 -DC village

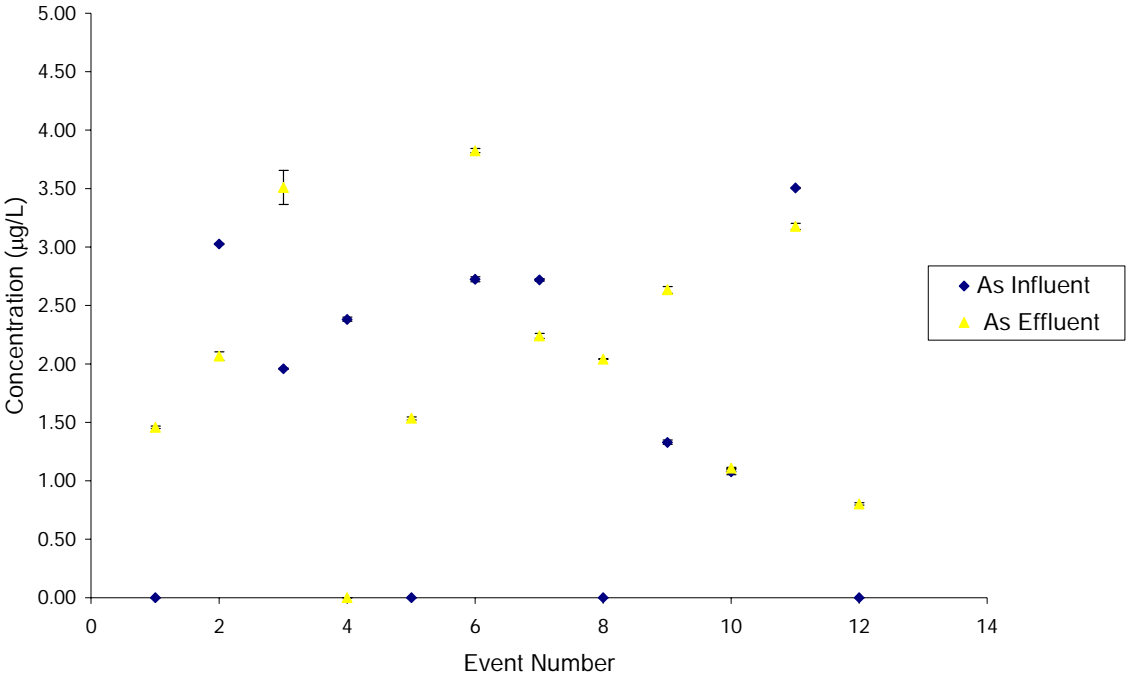
Hg

Storm #	Influent ug/L		Effluent ug/L		% Removal
	Hg Influent	St. Dev.	Hg Effluent	St. Dev.	
1	NS	NS	4.2	0.0	
2	0.3	0.1	0.7	0.0	
3	0.0	0.0	0.0	0.0	
4	0.4	0.0	NS	NS	
5	NS	NS	0.2	0.0	
6	0.5	0.0	0.4	0.0	
7	2.0	0.0	1.1	0.0	
8	NS	NS	0.5	0.0	
9	1.8	0.0	1.1	0.0	
10	1.3	0.0	0.3	0.0	
11	0.0	0.0	0.0	0.0	
12	NS	NS	0.0	0.0	
Average		0.8	0.0	0.8	0.0
Std. Dev.		0.8	0.0	1.2	0.0



DDOT project - Site # 2 -DC village  
As

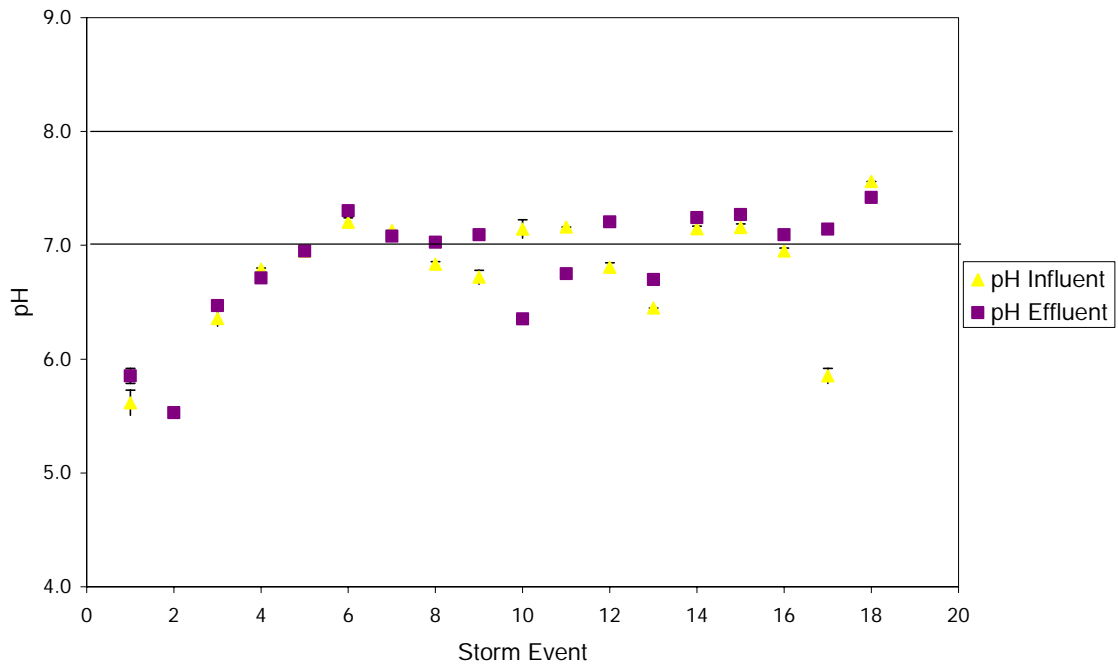
Storm #	As Influent	St. Dev.	As Effluent	St. Dev.	% Removal
1	NS	NS	1.5	0.0	
2	3.0	0.0	2.1	0.0	
3	2.0	0.0	3.5	0.1	
4	2.4	0.0	NS	NS	
5	NS	NS	1.5	0.0	
6	2.7	0.0	3.8	0.0	
7	2.7	0.0	2.2	0.0	
8	NS	NS	2.0	0.0	
9	1.3	0.0	2.6	0.0	
10	1.1	0.0	1.1	0.0	
11	3.5	0.0	3.2	0.0	
12	NS	NS	0.8	0.0	
Average	2.3	0.0	2.2	0.0	0.05
Std. Dev.	0.8	0.0	1.0	0.0	



## W Street BaySaver

### 1. Storm event number, date of event, pH, DO, and temperature values.

Storm #	pH Influent	St. Dev	pH Effluent	St. Dev.
1	5.6	0.1	5.9	0.1
2	NS	NS	5.5	0.0
3	6.4	0.1	6.5	0.0
4	6.8	0.0	6.7	0.0
5	7.0	0.0	7.0	0.0
6	7.2	0.0	7.3	0.0
7	7.1	0.0	7.1	0.0
8	6.8	0.0	7.0	0.0
9	6.7	0.1	7.1	0.0
10	7.1	0.1	6.4	0.0
11	7.2	0.0	6.8	0.0
12	6.8	0.0	7.2	0.0
13	6.5	0.0	6.7	0.0
14	7.1	0.0	7.2	0.0
15	7.2	0.0	7.3	0.0
16	7.0	0.0	7.1	0.0
17	5.9	0.1	7.1	0.1
18	7.6	0.0	7.4	0.0
Samples 1-15				
Average	6.8	0.0	6.8	0.0
Std. Dev.	0.4	0.0	0.5	0.0
Samples 16-18				
Average	6.8	0.0	7.2	0.0
Std. Dev.	0.9	0.0	0.2	0.0



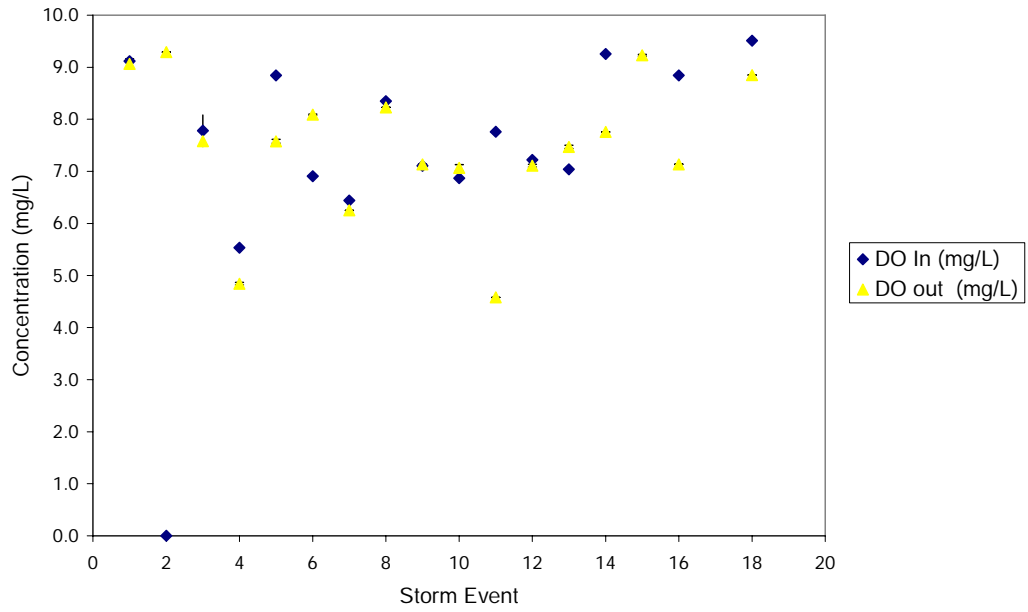
Storm #	DO In (mg/L)	St. Dev	DO out (mg/L)	St. Dev.
1	9.1	0.0	9.1	0.1
2	NS	NS	9.3	0.0
3	7.8	0.3	7.6	
4	5.5	0.0	4.8	0.0
5	8.8	0.1	7.6	0.0
6	6.9	0.0	8.1	0.0
7	6.4	0.0	6.3	0.0
8	8.4	0.0	8.2	0.0
9	7.1	0.0	7.1	0.0
10	6.9	0.0	7.1	0.1
11	7.8	0.0	4.6	0.0
12	7.2	0.1	7.1	0.0
13	7.0	0.0	7.5	0.0
14	9.3	0.0	7.8	0.0
15	11.6	0.0	9.2	0.0
16	8.8	0.1	7.1	0.0
17				
18	9.5	0.0	8.9	0.0

Samples 1-15

Average	7.8	0.0	7.4	0.0
Std. Dev.	1.5	0.1	1.4	0.0

Samples 16-18

Average	9.2	0.0	8.0	0.0
Std. Dev.	0.5	0.0	1.2	0.0



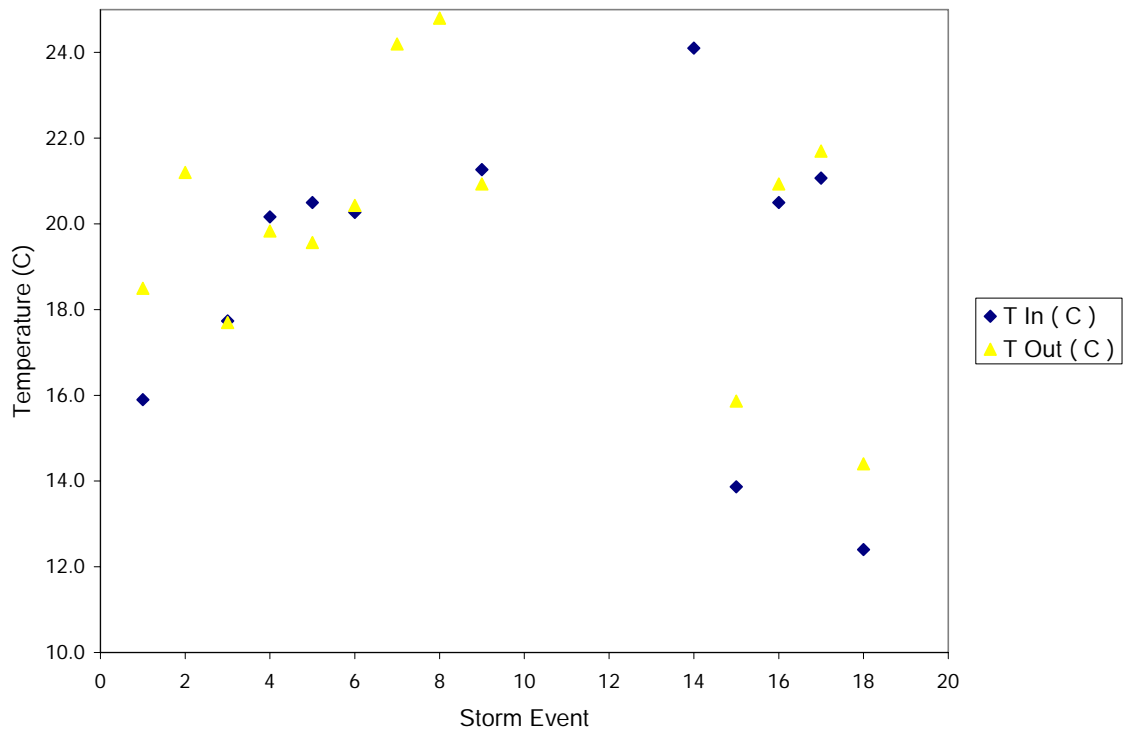
Storm #	T In (C)	St. Dev	T Out (C)	St. Dev.
1	15.90	0.26	18.5	0.0
2	NS	NS	21.2	0.0
3	17.7	0.3	17.7	0.0
4	20.2	0.1	19.8	0.1
5	20.5	0.0	19.6	0.1
6	20.3	0.1	20.4	0.1
7	27.5	0.0	24.2	0.0
8	25.9	0.0	24.8	0.0
9	21.3	0.1	20.9	0.1
10	30.5	0.1	27.8	0.0
11	27.0	0.0	26.8	0.0
12	27.6	0.1	26.2	0.1
13	27.9	0.0	28.5	0.0
14	24.1	0.1	27.0	0.2
15	13.9	0.1	15.9	0.1
16	20.5	0.0	20.9	0.1
17	21.1	0.2	21.7	0.1
18	12.4	0.0	14.4	0.0

Samples 1-15

Average	22.9	0.1	22.6	0.0
Std. Dev.	5.1	0.1	4.1	0.0

Samples 16-18

Average	18.0	0.1	19.0	0.1
Std. Dev.	4.8	0.1	4.0	0.1

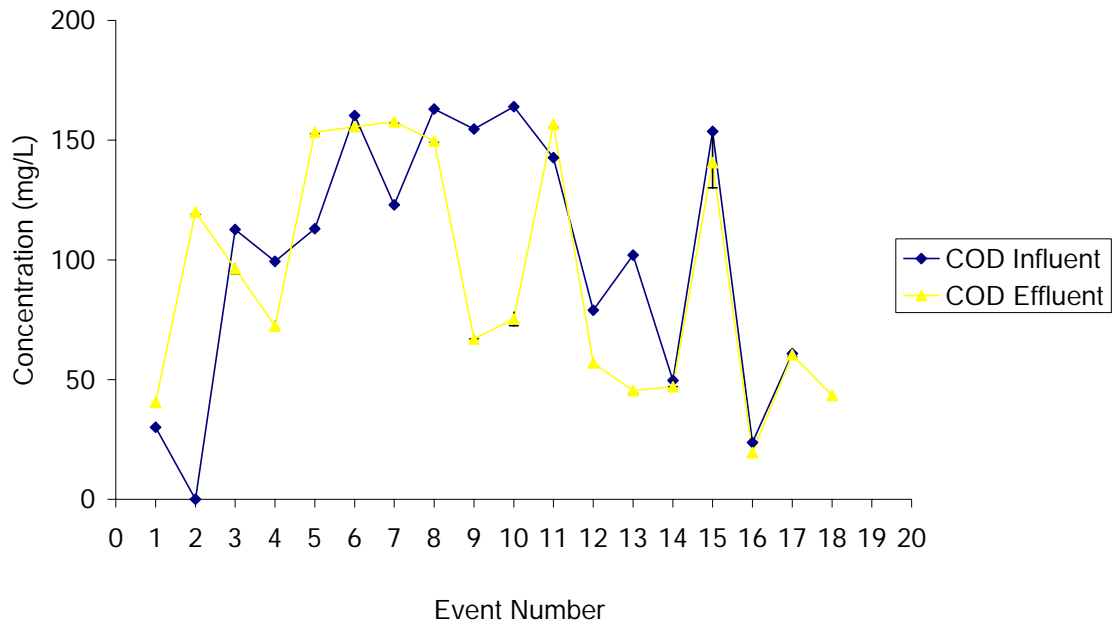


2. Storm event number, date of event, chemical oxygen demand values.

Storm #	COD mg/L COD Influent		COD mg/L COD Effluent	
	Influent	St. Dev.	Effluent	St. Dev.
1	30.1	2.5	41	2
2	NS	NS	120	1
3	113	6	96	2
4	99	1	72	2
5	113	22	153	1
6	160	1	156	1
7	123	2	158	1
8	163	0	150	1
9	155	2	67	0
10	164	1	75	3
11	143	2	157	1
12	79	1	57	2
13	102	2	45	1
14	50	0	47	0
15	154	1	141	11
16	24	1	19	2
17	61	0	60	1
18	45	1	43	2

Samples 1-15				
Average	117.6	3.0	102.3	1.8
Std. Dev.	42.8	5.6	46.7	2.5

Samples 16-18				
Average	43.3	0.9	41.1	1.4
Std. Dev.	18.7	0.8	20.5	0.6

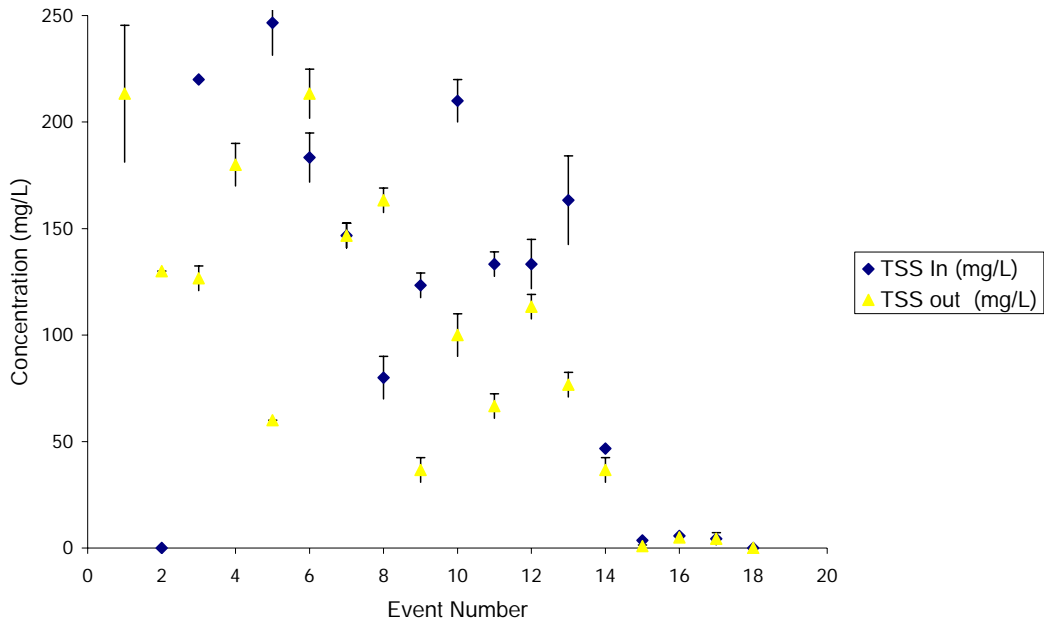


3. Storm event number, date of event, total suspended and total dissolved solid values.

Storm #	TSS In (mg/L)	St. Dev.	TSS out (mg/L)	St. Dev.
1	1993	271	213	32
2	NS	NS	130	0
3	220	0	127	6
4	380	26	180	10
5	247	15	60	0
6	183	12	213	12
7	147	6	147	6
8	80	10	163	6
9	123	6	37	6
10	210	10	100	10
11	133	6	67	6
12	133	12	113	6
13	163	21	77	6
14	47	6	37	6
15	4	46	1	0
16	6	1	5	1
17	4	5	4	3
18	0	0	0	0

Samples 1-15					% Removal
Average	290	31.8	111	7.4	0.62
Std. Dev.	499	69.7	65	7.7	
Samples 16-18					% Removal

Average	3.3	1.9	3.1	1.2	0.07
Std. Dev.	3.0	2.6	2.7	1.5	



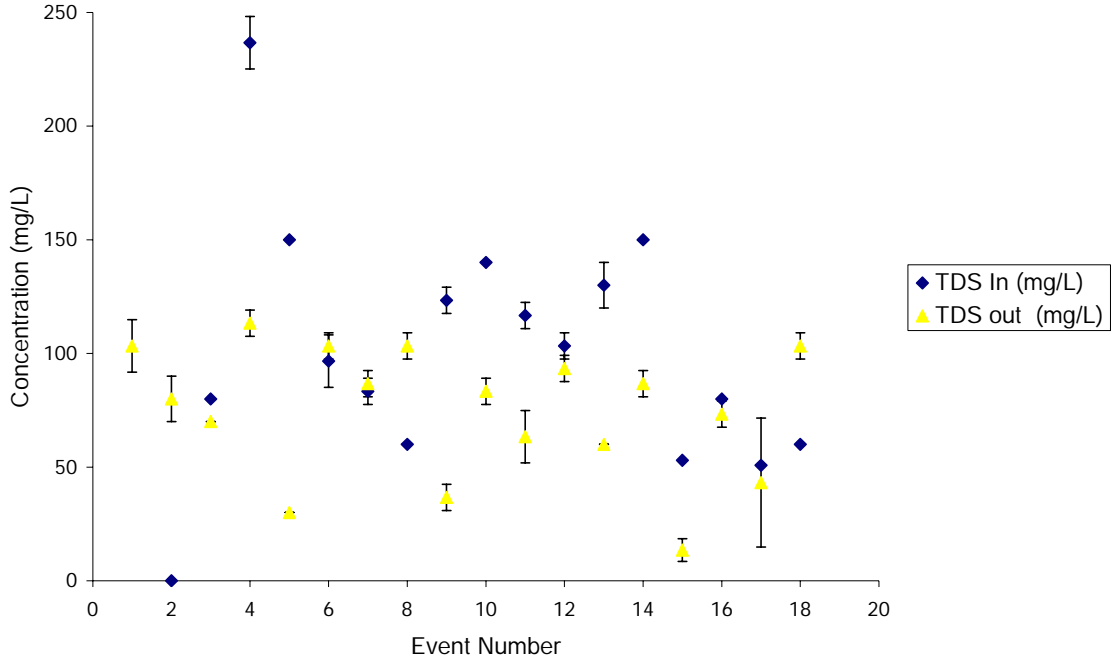
Storm #	TDS In (mg/L)	St. Dev	TDS out (mg/L)	St. Dev.
1	1700	184	103	12
2	NS	NS	80.000	10.000
3	80	0	70	0
4	237	12	113	6
5	150	0	30	0
6	97	12	103	6
7	83	6	87	6
8	60	0	103	6
9	123	6	37	6
10	140	0	83	6
11	117	6	63	12
12	103	6	93	6
13	130	10	60	0
14	150	0	87	6
15	53	56	14	5
16	80	10	73	6
17	51	48	43	28
18	60	0	103	6

					% Removal
Samples 1-15					
Average	230	21	75	6	0.67
Std. Dev.	426	49	30	4	

					% Removal
Samples 16-18					



Average	64	19	73	13	-0.15
Std. Dev.	15	26	30	13	

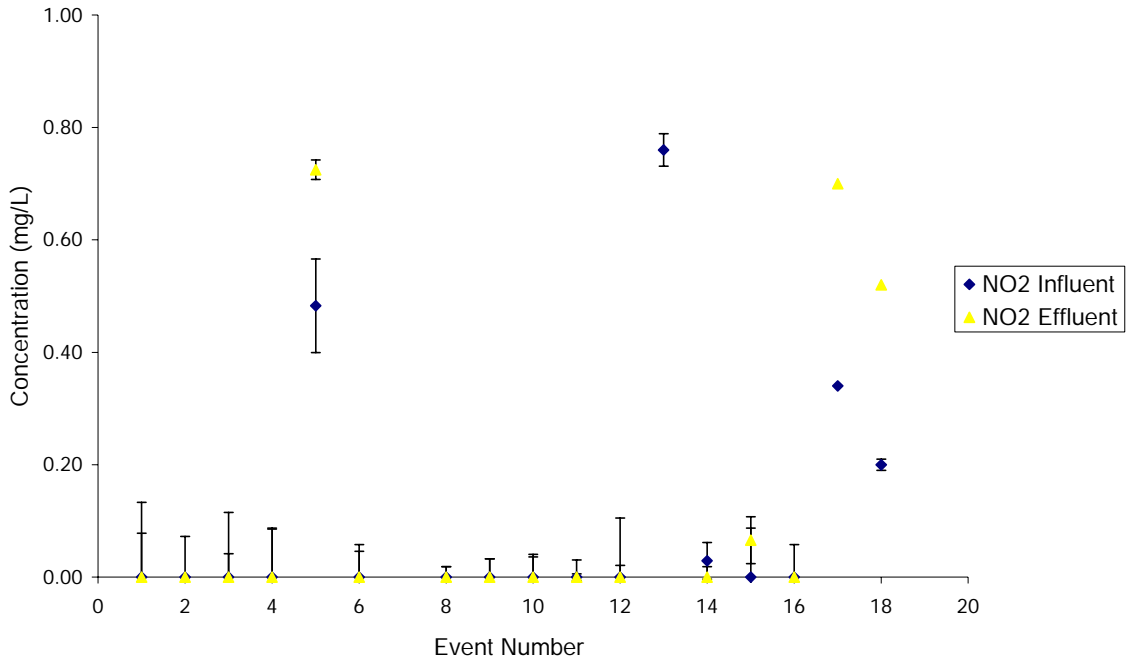


**4. Storm event number, date of event, NH<sub>3</sub>, NO<sub>2</sub>, NO<sub>3</sub>, and PO<sub>4</sub> concentration values**

Storm #	NO <sub>2</sub> mg/L NO <sub>2</sub> Influent		NO <sub>2</sub> mg/L NO <sub>2</sub> Effluent	
	St. Dev	St. Dev	St. Dev	St. Dev
1	0.0	0.0	0.0	0.0
2	NS	NS	0.0	0.0
3	0.0	0.0	0.0	0.0
4	0.0	0.0	0.0	0.0
5	0.5	0.1	0.7	0.2
6	0.0	0.0	0.0	0.0
7	20.0	1.0	8.3	0.6
8	0.0	0.0	0.0	0.0
9	0.0	0.0	0.0	0.0
10	0.0	0.0	0.0	0.0
11	0.0	0.0	0.0	0.0
12	0.0	0.0	0.0	0.0
13	0.8	0.2	2.7	1.0
14	0.0	0.0	0.0	0.0
15	0.0	0.0	0.1	0.1
16	0.0	0.0	0.0	0.0
17	0.3	0.2	0.7	0.0
18	0.2	0.0	0.5	0.0

Samples 1-15		% Removal	
Average	St. Dev	Average	St. Dev
1.5	0.1	0.8	0.1
		0.48	

Std. Dev.	5.3	0.3	2.2	0.3	
Samples 16-18					% Removal
Average	0.2	0.1	0.4	0.0	-1.26
Std. Dev.	0.2	0.1	0.4	0.0	



Storm #	NO3 mg/L		NO3 mg/L	
	NO3 Influent	St. Dev	NO3 Effluent	St. Dev.
1	1.2	2.0	9.5	0.9
2	NS	NS	3.7	1.0
3	1.7	0.3	7.6	0.5
4	0.0	0.0	0.0	0.0
5	0.0	0.0	0.0	0.0
6	0.5	0.1	0.7	0.2
7	4.8	0.3	0.1	0.0
8	1.7	0.0	0.1	0.1
9	0.1	0.1	0.0	0.0
10	0.7	0.1	1.4	0.6
11	0.0	0.0	2.1	0.8
12	0.0	0.0	0.1	0.1
13	0.2	0.0	0.1	0.0
14	0.3	0.1	0.3	0.0
15	0.5	0.1	0.2	0.1
16	0.4	0.1	0.0	0.0
17	0.0	0.0	0.0	0.0
18	0.0	0.0	0.0	0.0

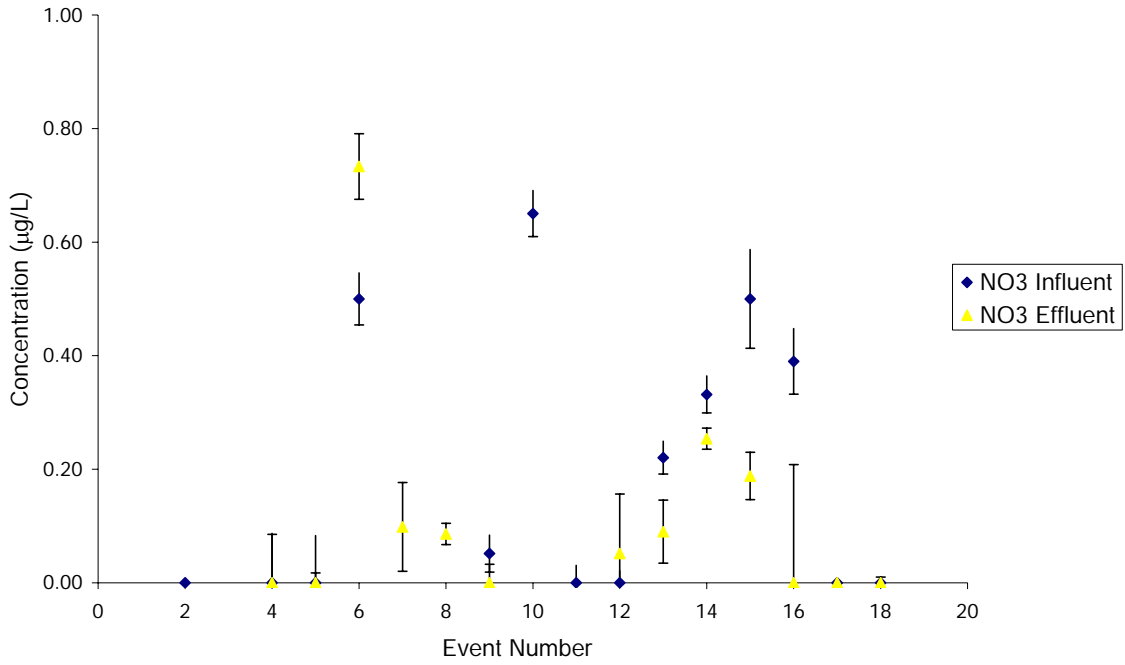
Samples 1-15					% Removal
Average	0.8	0.2	1.7	0.3	-1.07

Std. Dev. 1.3 0.5 3.0 0.4

Samples 16-18

Average 0.1 0.0 0.0 0.0 1.00  
 Std. Dev. 0.2 0.1 0.0 0.0

% Removal

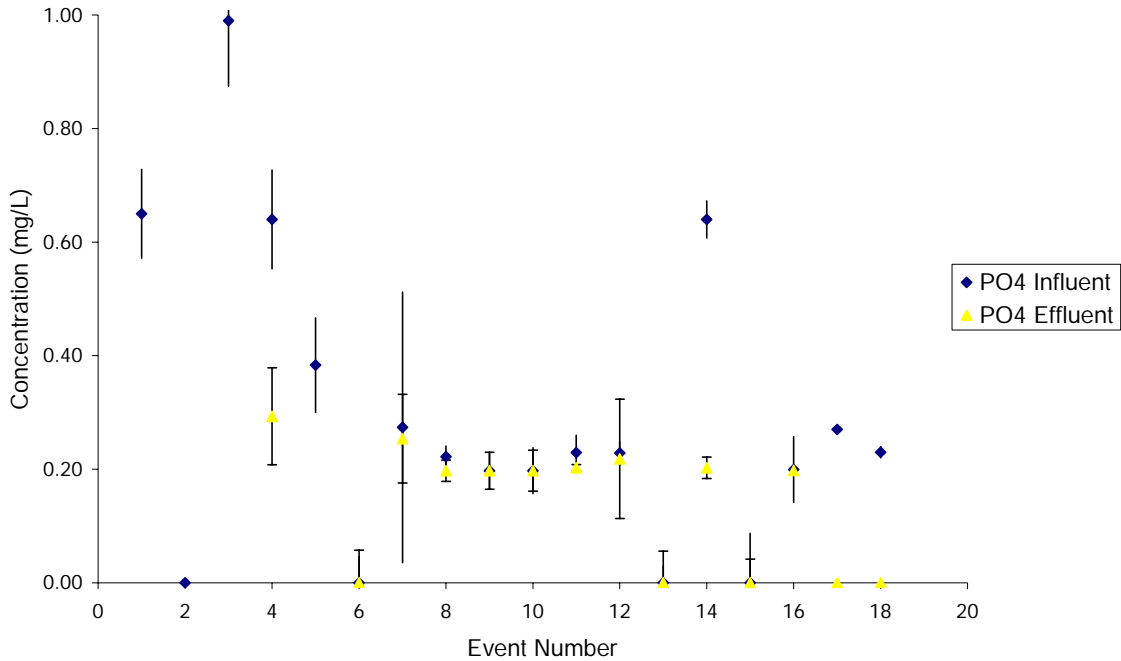


Storm #	PO4 mg/L		PO4 mg/L	
	PO4 Influent	St. Dev	PO4 Effluent	St. Dev.
1	0.65	0.61	48.14	0.14
2	NS	NS	45.60	0.96
3	0.99	0.23	47.45	1.08
4	0.64	0.13	0.29	0.12
5	0.38	0.08	48.33	7.09
6	0.00	0.00	0.00	0.00
7	0.27	0.04	0.25	0.00
8	0.22	0.02	0.20	0.00
9	0.20	0.00	0.20	0.00
10	0.20	0.00	0.20	0.00
11	0.23	0.05	0.20	0.00
12	0.23	0.00	0.22	0.00
13	0.00	0.00	0.00	0.00
14	0.64	0.13	0.20	0.00
15	0.00	0.00	0.00	0.00
16	0.20	0.00	0.20	0.00
17	0.27	0.03	0.00	0.00
18	0.23	0.05	0.00	0.00

Samples 1-15

%

					Removal
Average	0.3	0.1	12.8	0.6	-37.38
Std. Dev.	0.3	0.2	21.6	1.8	
					%
Samples 16-18					Removal
Average	0.2	0.0	0.1	0.0	0.72
Std. Dev.	0.0	0.0	0.1	0.0	



**5. Storm event number, date of event, and ammonia concentration values.**

Storm #	NH3 mg/L		NH3 mg/L	
	NH3 Influent	St. Dev	NH3 Effluent	St. Dev.
1	1.3	0.2	1.4	0.1
2	NS	NS	0.0	0.0
3	2.6	0.1	1.8	0.1
4	1.6	0.1	0.3	0.0
5	1.3	0.2	0.5	0.1
6	2.2	0.1	1.6	0.1
7	0.8	0.0	0.7	0.0
8	1.0	0.0	0.9	0.0
9	0.9	0.0	0.8	0.0
10	4.9	0.8	4.8	0.4
11	0.9	0.0	0.9	0.0
12	0.6	0.2	0.7	0.1
13	1.0	0.1	0.9	0.1
14	0.2	0.0	0.2	0.0
15	0.8	0.0	0.3	0.1
16	1.6	0.1	1.6	0.1

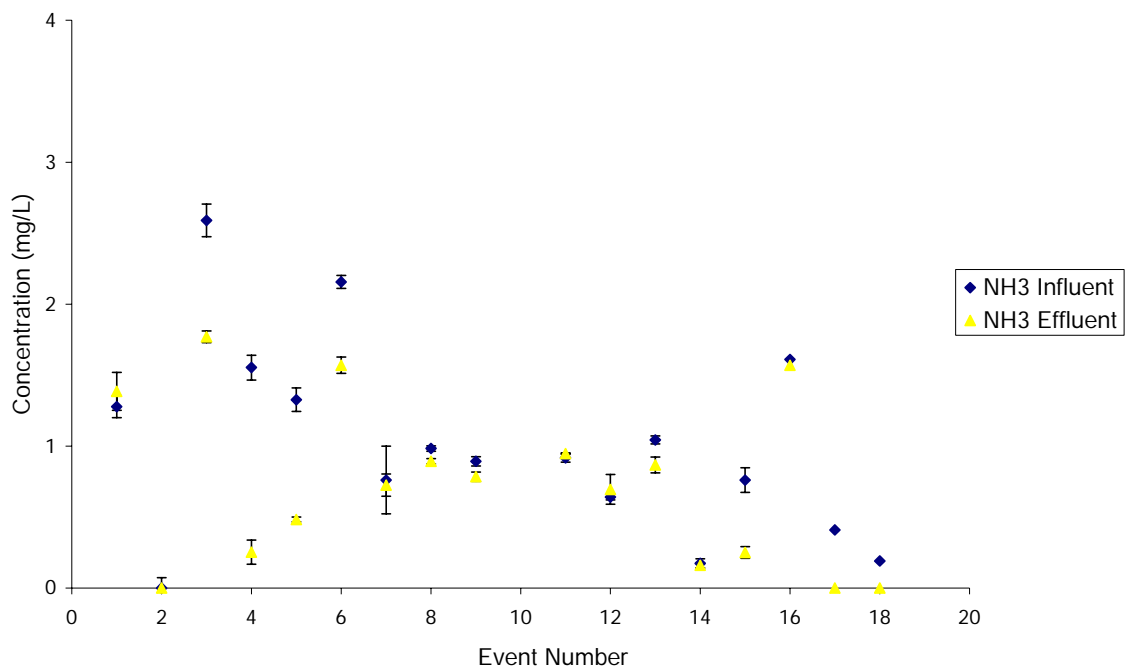
17	0.4	0.2	0.0	0.0
18	0.2	0.0	0.0	0.0

Samples 1-15

Average	1.4	0.1	1.0	0.1	% Removal	0.27
Std. Dev.	1.2	0.2	1.2	0.1		

Samples 16-18

Average	0.7	0.1	0.5	0.0	% Removal	0.29
Std. Dev.	0.8	0.1	0.9	0.1		



**6. Storm event number, date of event, and TP concentration values.**

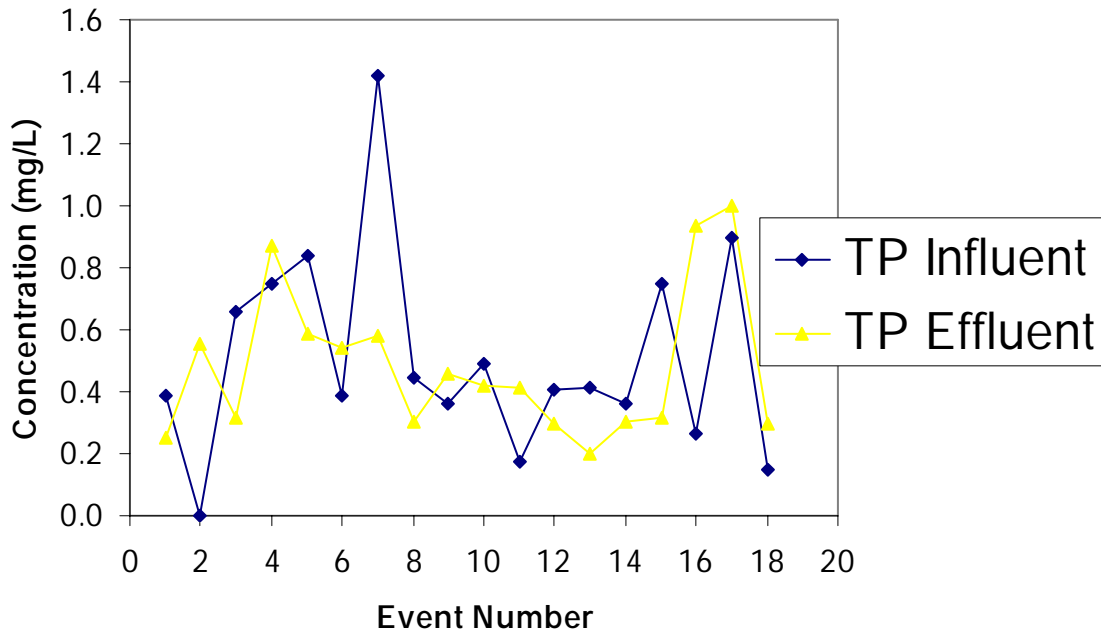
Storm #	TP mg/L		TP mg/L	
	Influent	St. Dev	Effluent	St. Dev.
1	0.4	0.1	0.3	0.1
2	NS	NS	0.6	0.1
3	0.7	0.1	0.3	0.0
4	0.8	0.1	0.9	0.1
5	0.8	0.1	0.6	0.0
6	0.4	0.0	0.5	0.1
7	1.4	0.2	0.6	0.1
8	0.4	0.0	0.3	0.0
9	0.4	0.0	0.5	0.0
10	0.5	0.0	0.4	0.0
11	0.2	0.0	0.4	0.0
12	0.4	0.0	0.3	0.1
13	0.4	0.0	0.2	0.1

14	0.4	0.0	0.3	0.0
15	0.8	0.1	0.3	0.0
16	0.3	0.1	0.9	0.2
17	0.9	0.0	1.0	0.0
18	0.2	0.0	0.3	0.0

					% Removal
Samples 1-15					
Average	0.6	0.1	0.4	0.1	0.24
Std. Dev.	0.3	0.1	0.2	0.0	

					% Removal
Samples 16-18					
Average	0.4	0.0	0.7	0.1	-0.70
Std. Dev.	0.4	0.0	0.4	0.1	

## TP



### 7. Storm event number, date of event, and copper concentration values.

Storm #	(ug/L)		(ug/L)	
	Cu Influent	St. Dev	Cu Effluent	St. Dev.
1	29.38	0.10	14.14	0.52
2	NS	NS	21.07	0.01
3	10.5	0.0	20.6	0.1
4	8.3	0.0	9.4	0.0
5	6.0	0.1	8.5	0.3
6	9.2	0.0	14.0	0.0
7	25.5	0.2	10.1	0.1
8	25.0	0.0	13.0	0.0
9	7.6	0.1	6.7	0.0
10	12.8	0.0	6.6	0.0

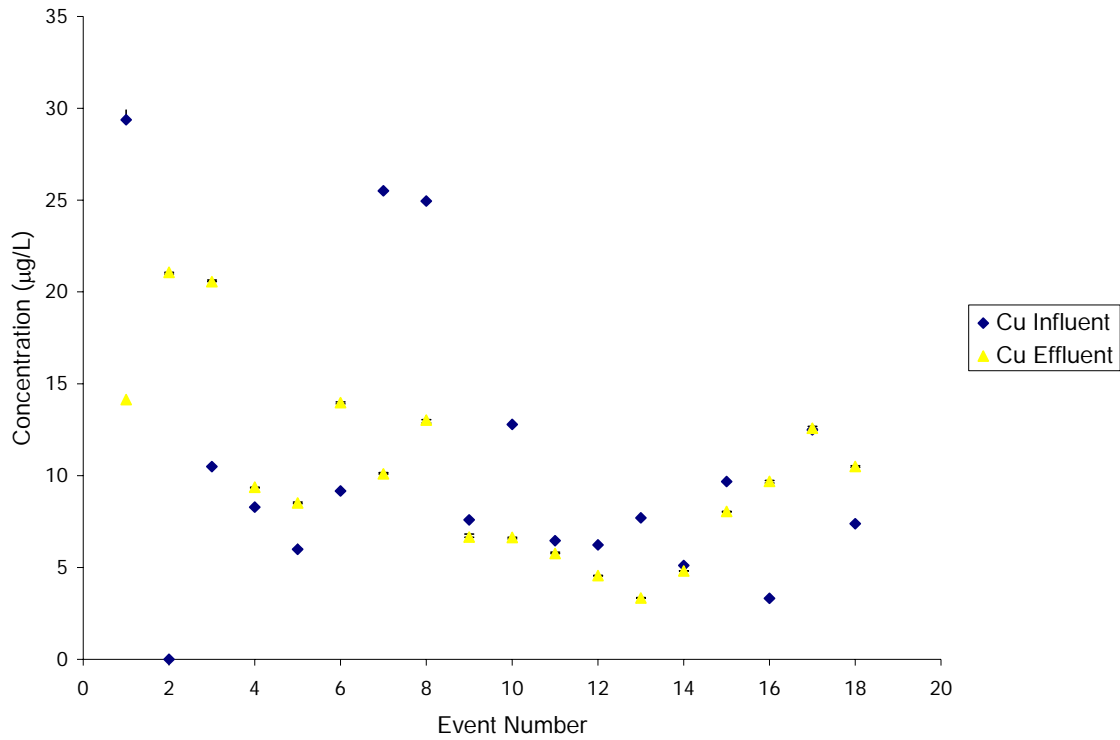
11	6.5	0.0	5.8	0.0
12	6.2	0.0	4.6	0.0
13	7.7	0.0	3.3	0.0
14	5.1	0.0	4.8	0.0
15	9.7	0.1	8.1	0.1
16	3.3	0.0	9.7	0.0
17	12.5	0.1	12.6	0.1
18	7.4	0.1	10.5	0.1

Samples 1-15

Average	12	0	10	0	0.17
Std. Dev.	8	0	6	0	

Samples 16-18

Average	8	0	11	0	-0.41
Std. Dev.	5	0	1	0	



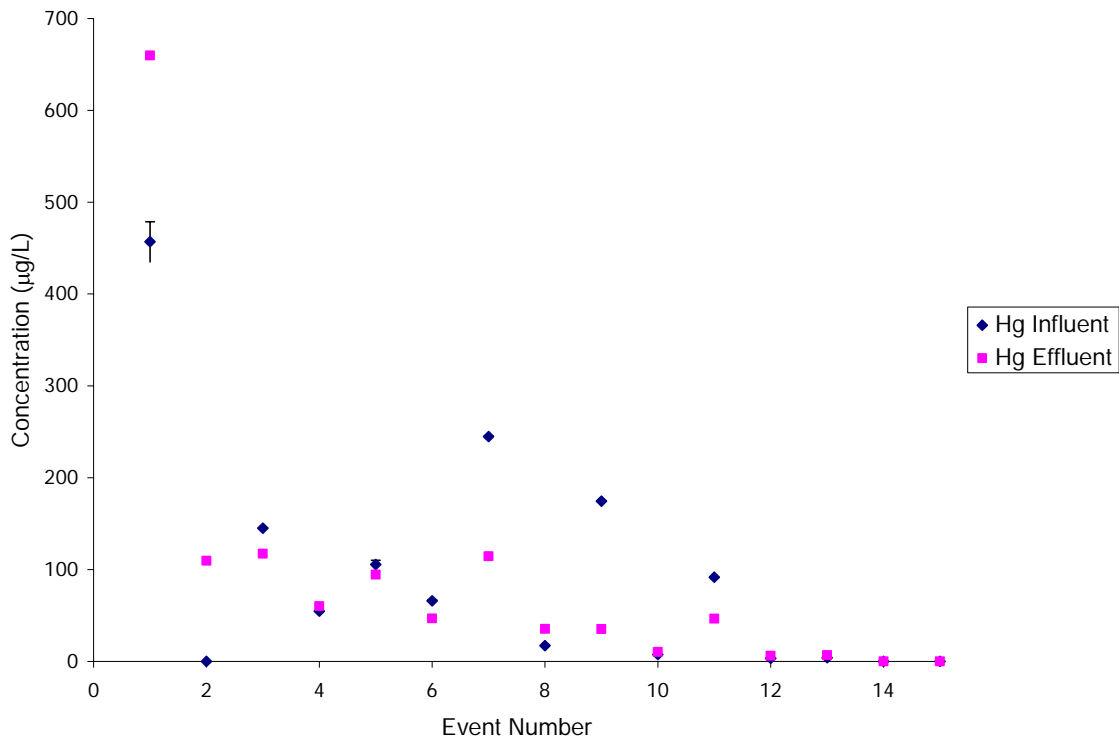
**8. Storm event number, date of event, and mercury concentration values.**

Storm #	Influent ug/L Hg		Effluent ug/L Hg	
	Influent	St. Dev	Hg Effluent	St. Dev.
1	457	22	660	7
2	NS	NS	110	0
3	145	0	117	1
4	55	0	60	1
5	106	5	94	2
6	66	1	47	1
7	245	1	114	0

8	17	0	35	0
9	174	0	35	0
10	7	0	10	0
11	92	0	47	0
12	3	0	6	0
13	4	0	7	0
14	0	0	0	0
15	0	0	0	0
16	0	0	0	0
17	0	0	0	0
18	0	0	0	0

					%
					Removal
Samples 1-15					
Average	97.9	2.2	89.5	0.8	0.09
Std. Dev.	128.1	5.8	163.4	1.8	

					%
					Removal
Samples 16-18					
Average	0.0	0.0	0.0	0.0	#DIV/0!
Std. Dev.	0.0	0.0	0.0	0.0	



9. Storm event number, date of event, and arsenic concentration values.

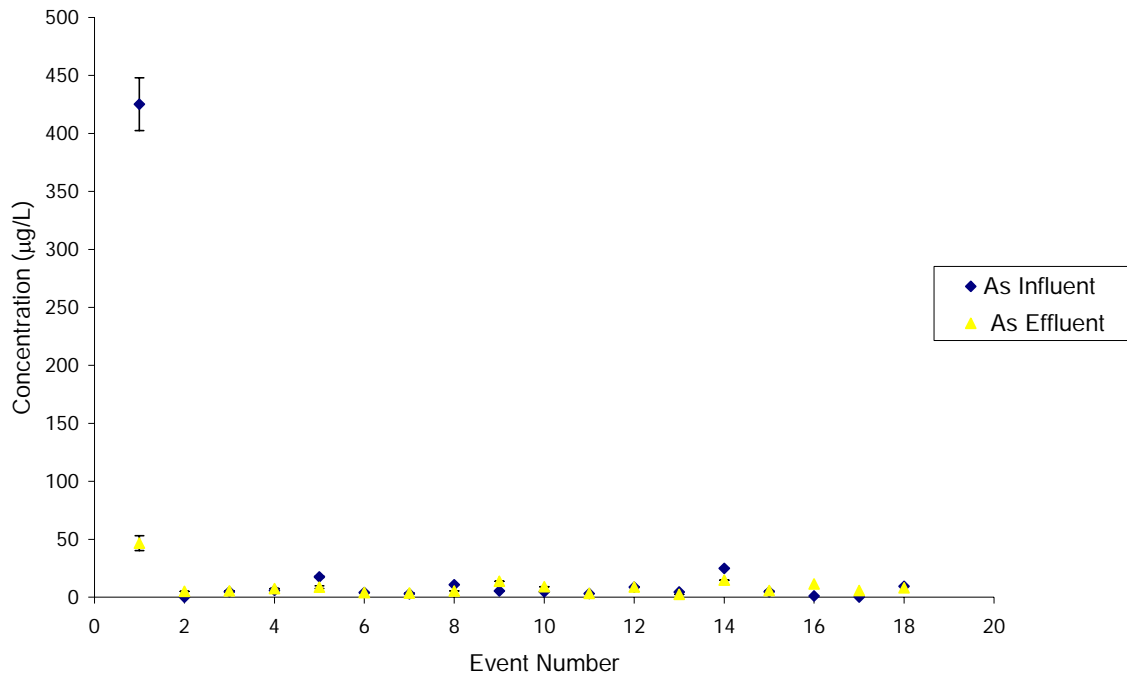
Storm #	As Influent		As Effluent	
	As Influent	St. Dev	As Effluent	St. Dev.
1	425.2	22.8	46.6	6.4
2	NS	NS	5.0	0.0
3	4.7	0.0	5.5	0.0
4	5.9	0.0	7.5	0.1
5	17.6	0.7	8.7	1.3



6	4.0	0.1	4.0	0.0
7	3.0	0.0	3.6	0.0
8	10.8	0.0	5.4	0.0
9	5.3	0.0	13.8	0.0
10	4.6	0.0	9.0	0.0
11	3.2	0.0	3.3	0.0
12	8.7	0.1	8.9	0.1
13	4.5	0.0	2.5	0.0
14	24.9	0.1	14.7	0.0
15	4.8	0.1	5.7	0.1
16	1.0	0.0	11.4	0.0
17	0.1	0.0	5.7	0.1
18	9.4	0.1	8.2	0.1

Samples 1-15					% Removal
Average	37.7	1.7	9.6	0.5	0.74
Std. Dev.	111.7	6.1	10.8	1.6	

Samples 16-18					% Removal
Average	3.5	0.0	8.4	0.1	-1.41
Std. Dev.	5.1	0.0	2.9	0.0	



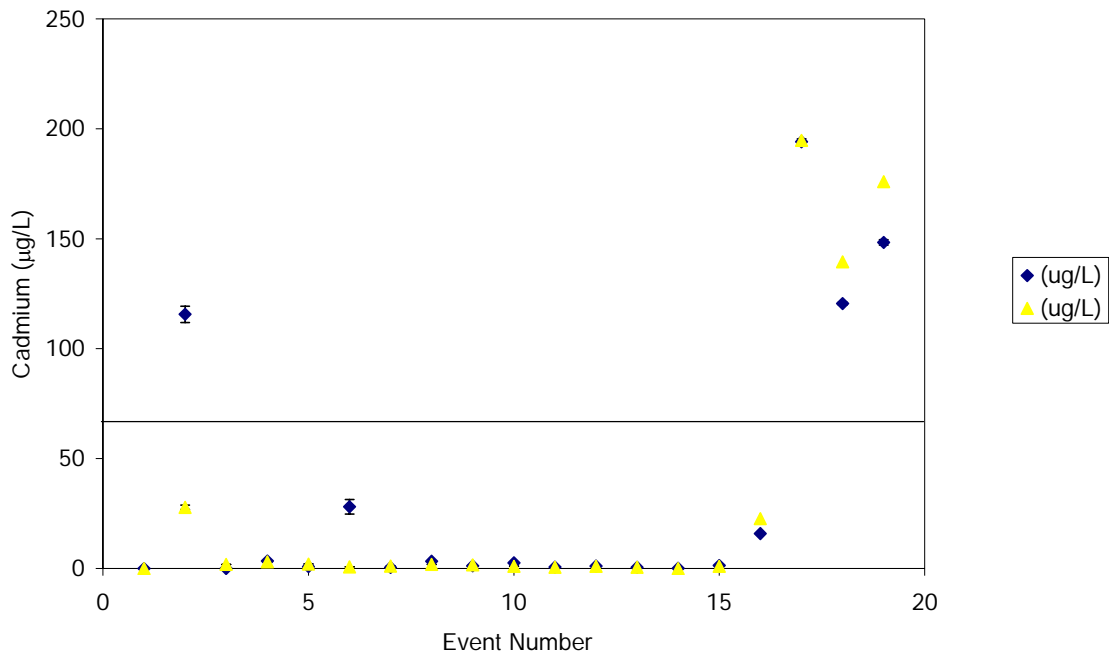
**10. Storm event number, date of event, and cadmium concentration values.**

Storm #	(ug/L) Cd		(ug/L) Cd	
	Influent	St. Dev	Effluent	St. Dev.
1	115.6	3.7	27.9	0.9
2	NS	NS	1.84	0.00
3	3.4	0.0	3.1	0.0

4	0.8	0.0	2.0	0.0
5	28.1	3.3	0.7	0.0
6	0.5	0.0	1.1	0.0
7	3.3	0.0	1.8	0.0
8	1.2	0.0	1.7	0.0
9	2.5	0.0	1.0	0.0
10	0.6	0.0	0.6	0.0
11	1.1	0.0	1.0	0.0
12	0.5	0.0	0.5	0.0
13	0.1	0.0	0.0	0.0
14	1.4	0.0	1.0	0.0
15	15.8	0.0	22.6	0.6
16	194.1	1.3	194.8	1.3
17	120.5	0.6	139.5	0.7
18	148.3	1.2	176.0	3.3

Samples 1-15					% Removal
Average	12	1	4	0	0.64
Std. Dev.	31	1	9	0	

Samples 16-18					% Removal
Average	154	1	170	2	-0.10
Std. Dev.	37	0	28	1	



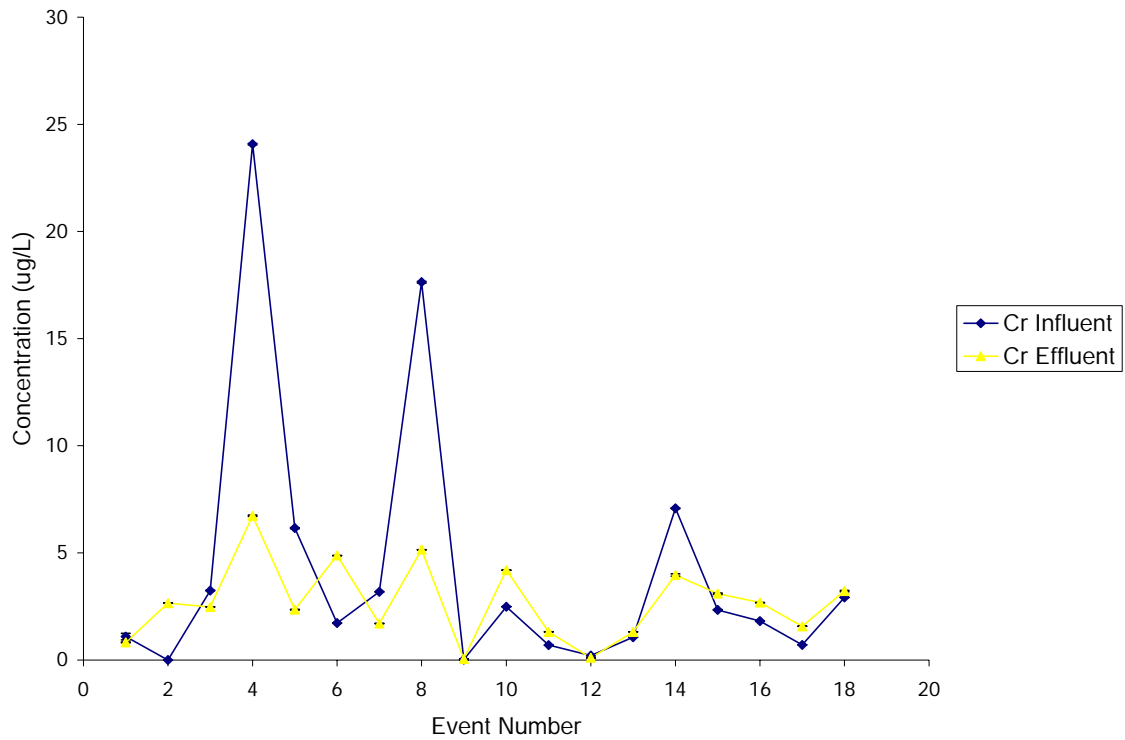
### 11. Storm event number, date of event, and chromium concentration values.

Storm #	(ug/L) Cr Influent	St. Dev	(ug/L) Cr Effluent	St. Dev.
---------	-----------------------	---------	-----------------------	----------

1	1.1	0.2	0.8	0.0
2	NS	NS	2.66	0.00
3	3.2	0.0	2.5	0.0
4	24.1	0.0	6.7	0.0
5	6.2	0.0	2.4	0.0
6	1.7	0.0	4.9	0.0
7	3.2	0.0	1.7	0.0
8	17.6	0.0	5.1	0.0
9	0.0	0.0	0.0	0.0
10	2.5	0.0	4.2	0.0
11	0.7	0.0	1.3	0.0
12	0.2	0.0	0.1	0.0
13	1.1	0.0	1.3	0.0
14	7.1	0.0	4.0	0.1
15	2.3	0.0	3.1	0.0
16	1.8	0.0	2.7	0.0
17	0.7	0.0	1.6	0.0
18	2.9	0.0	3.2	0.0

Samples 1-15					% Removal
Average	5.1	0.0	2.7	0.0	0.46
Std. Dev.	7.1	0.0	2.0	0.0	

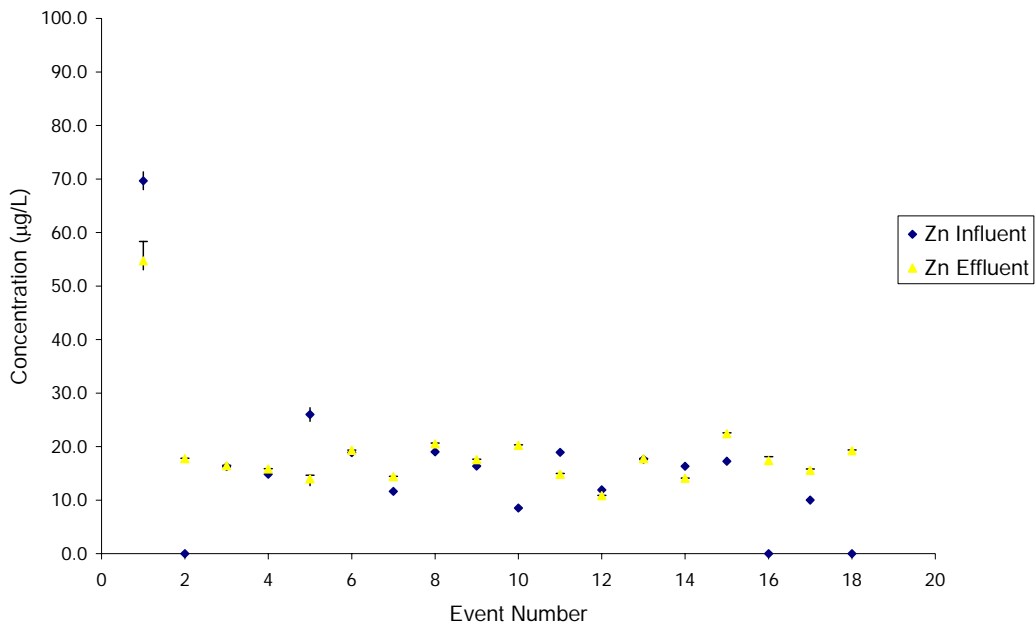
Samples 16-18					% Removal
Average	1.8	0.0	2.5	0.0	-0.37
Std. Dev.	1.1	0.0	0.8	0.0	



12. Storm event number, date of event, and zinc concentration values.

Storm #	Zn Influent		Zn Effluent	
	St. Dev	St. Dev.	St. Dev.	St. Dev.
1	69.7	1.7	54.7	3.6
2	NS	NS	17.8	0.1
3	16.3	0.1	16.4	0.1
4	14.8	0.0	15.8	0.1
5	26.0	1.3	14.0	0.7
6	18.9	0.1	19.3	0.1
7	11.7	0.2	14.4	0.0
8	19.0	0.0	20.5	0.2
9	16.4	0.2	17.6	0.1
10	8.5	0.1	20.2	0.1
11	18.9	0.0	14.8	0.2
12	11.9	0.0	10.9	0.0
13	17.7	0.0	17.7	0.0
14	16.4	0.1	14.1	0.0
15	17.3	0.2	22.4	0.2
16	0.0	0.0	17.4	0.8
17	10.0	0.0	15.6	0.2
18	0.0	0.0	19.2	0.2

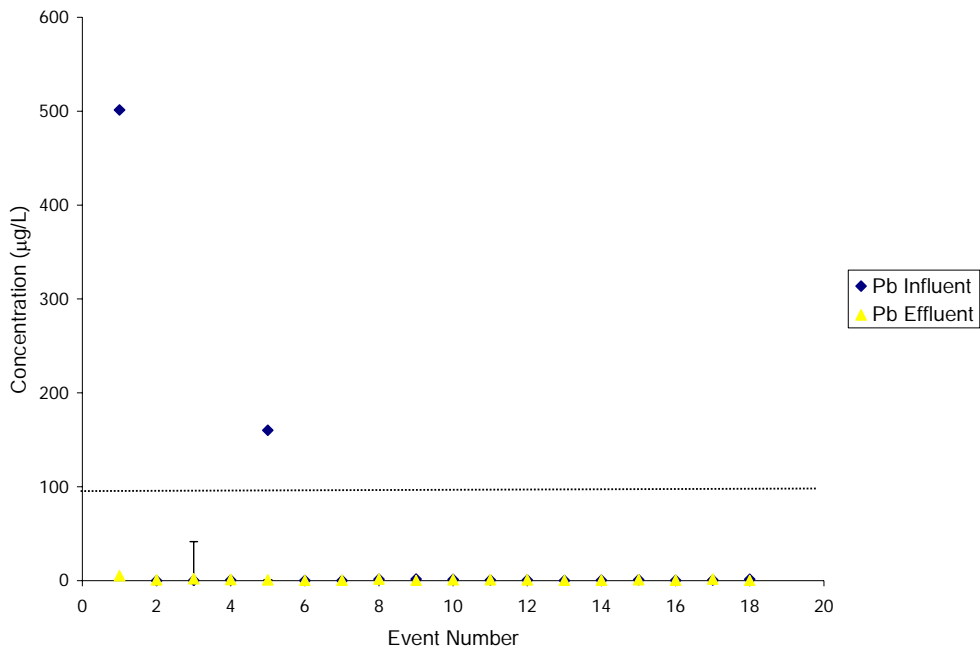
Samples 1-15					% Removal
Average	20	0	19	0	0.04
Std. Dev.	15	1	10	1	
Samples 16-18					% Removal
Average	3	0	17	0	-4.22
Std. Dev.	6	0	2	0	



13. Storm event number, date of event, and lead concentration values.

Storm #	(ug/L) Pb		(ug/L) Pb	
	Influent	St. Dev.	Effluent	St. Dev.
1	501.3	39.5	5.3	0.3
2	NS	NS	1.0	0.0
3	0.5	0.0	2.1	0.0
4	0.7	0.0	1.4	0.0
5	160.2	0.4	0.8	0.0
6	0.2	0.0	0.0	0.0
7	0.1	0.0	0.3	0.0
8	1.5	0.0	1.7	0.0
9	1.8	0.0	0.2	0.0
10	1.4	0.0	1.1	0.0
11	0.8	0.0	1.2	0.0
12	0.7	0.0	0.9	0.0
13	0.3	0.0	0.2	0.0
14	0.5	0.0	0.6	0.0
15	1.2	0.0	1.1	0.1
16	0.4	0.0	0.6	0.0
17	0.7	0.0	1.8	0.0
18	1.4	0.0	0.2	0.0

Samples 1-15					% Removal
Average	47.9	2.9	1.2	0.0	0.97
Std. Dev.	137.2	10.5	1.3	0.1	
Samples 16-18					% Removal
Average	0.8	0.0	0.8	0.0	0.00
Std. Dev.	0.5	0.0	0.8	0.0	



## 14. PAH Measurements

### Compounds Measured for:

- 1 Indeno (1,2,3 - cd)pyrene
- 2 Benzo(ghi)perylene
- 3 Dibenzo(a,h)anthracene
- 4 Benzo(a)Pyrene
- 5 Benzo(k)Flouranthene
- 6 Chrysene
- 7 Benzo(a)Anthracene
- 8 Pyrene
- 9 Flouranthene
- 10 Anthracene
- 11 Phenanthrene
- 12 Acenaphthylene
- 13 Napthalene
- 14 Benzo(b)flouranthene

Events and the Compounds with concentrations above 0.5 ppb in at least one sample

### PAH REPORT (15 Events)

	INLET Conc. (ppb)	OUTLET Conc. (ppb)	Rem. Eff.	EPA Priority Pollutant (ppb)
Naphthalene	0.09	2.90	-3164%	0
Anthracene	1.23	0.43	65%	8,300
Flouranthene	55.67	73.07	-31%	130
Pyrene	93.88	18.77	80%	830
Chrysene	0.58	0.70	-21%	3.8
Benzo(a)anthracene	0.01	1.23	-12192%	3.8
Benzo(b)flouranthene	0.36	0.82	-131%	3.8
Benzo(k)flouranthene	0.38	0.04	90%	3.8
Benzo(a)pyrene	0.39	0.01	97%	3.8
Dibenzo(a,h)anthracene	4.62	2.46	47%	3.8
Benzo(ghi)perylene	3.65	1.67	54%	0
Ideno(1,2,3-cd)pyrene	0.27	0.03	90%	3.8

### Summary of Storm Event # 1 (2/13/2006)

	HPLC conc.	Actual conc. (ppb)
<b>Chrysene</b>		
In average	0.07	0.33
Out average	0.00	0.01
<b>Pyrene</b>		
In average	0.01	0.06
Out average	0.04	0.22
<b>Flouranthene</b>		
In average	10.86	54.32
Out average	0.00	0.00
<b>Anthracene</b>		

In average	0.21	1.04
Out average	0.00	0.00
<b>Napthalene</b>		
In average	0.01	0.03
Out average	0.00	0.00
<b>Benzo(b)flouranthene</b>		
In average	0.06	0.30
Out average	0.08	0.38

Summary of Storm Event # 2 (4/4/2006)

**Flouranthene**

In average	0.00	0.00
Out average	11.97	59.85

**Pyrene**

In average	13.79	68.95
Out average	0.00	0.00

**Benzo(k)flouranthene**

In average	0.00	0.01
Out average	0.00	0.00

**Benzo(a)pyrene**

In average	0.01	0.05
Out average	0.00	0.00

**Dibenzo(a,h)anthracene**

In average	0.01	0.06
Out average	<u>0.00</u>	0.00

Summary of Storm Event # 3 (4/8/2006)

**Chrysene**

In average	0.00	0.01
------------	------	------

**Benzo(b)flouranthene**

In average	0.00	0.00
Out average	0.00	0.01

**Dibenzo(a,h)anthracene**

In average	0.12	0.60
Out average	0.00	0.00

**Benzo(ghi)perylene**

In average	0.67	3.36
Out average	0.00	0.02

**Ideno(1,2,3-cd)pyrene**

In average	0.00	0.01
Out average	0.00	0.00

Summary of Storm Event # 4 (4/22/2006)

**Chrysene**

In average	0.02	0.12
Out average	0.00	0.00

**Benzo(a)anthracene**

In average	0.00	0.00
Out average	0.00	0.01

**Benzo(b)flouranthene**

In average	0.00	0.01
Out average	0.00	0.00
<b><u>Benzo(k)flouranthene</u></b>		
In average	0.00	0.00
Out average	0.00	0.01
<b><u>Dibenzo(a,h)anthracene</u></b>		
In average	0.03	0.17
Out average	0.16	0.80
<b><u>Benzo(ghi)perylene</u></b>		
In average	0.00	0.00
Out average	0.00	0.01

**Summary of Storm Event # 5 (5/8/2006)**

<b>Chrysene</b>		
In average	0.00	0.02
Out average	0.00	0.00
<b><u>Dibenzo(a,h)anthracene</u></b>		
In average	0.27	1.37
Out average	0.31	1.54
<b><u>Benzo(ghi)perylene</u></b>		
In average	0.01	0.06
Out average	0.00	0.00

**Summary of Storm Event # 6 (5/11/2006)**

<b><u>NAPHTHALENE</u></b>		
In average	0.00	0.01
Out average	0.00	0.01
<b><u>Anthracene</u></b>		
In average	0.00	0.01
Out average	0.00	0.00
<b><u>Benzo(b)flouranthene</u></b>		
In average	0.00	0.02
Out average	0.00	0.00
<b><u>Benzo(k)flouranthene</u></b>		
In average	0.03	0.15
Out average	0.00	0.00
<b><u>Benzo(a)pyrene</u></b>		
In average	0.07	0.34
Out average	0.00	0.00
<b><u>Dibenzo(a,h)anthracene</u></b>		
In average	0.13	0.67
Out average	0.00	0.00
<b><u>Benzo(ghi)perylene</u></b>		
In average	0.02	0.10
Out average	0.00	0.00
<b><u>Ideno(1,2,3-cd)pyrene</u></b>		
In average	0.02	0.10
Out average	0.00	0.00

**Summary of Storm Event #7 (5/26/2006)**



<b><u>Anthracene</u></b>		
In average	0.02	0.11
Out average	0.00	0.00
<b><u>Pyrene</u></b>		
In average	1.93	9.63
Out average	0.00	0.00
<b><u>Benzo(b)flouranthene</u></b>		
In average	0.00	0.01
Out average	0.00	0.00
<b><u>Benzo(k)flouranthene</u></b>		
In average	0.00	0.02
Out average	0.00	0.00
<b><u>Dibenzo(a,h)anthracene</u></b>		
In average	0.00	0.00
Out average	0.04	0.10
<b><u>Benzo(ghi)perylene</u></b>		
In average	0.00	0.01
Out average	0.00	0.01
<b><u>Ideno(1,2,3-cd)pyrene</u></b>		
In average	0.00	0.01
Out average	0.01	0.03

**Summary of Storm Event #8 (6/09/2006)**

<b><u>NAPHTHALENE</u></b>		
In average	0.00	0.01
Out average	0.57	2.85
<b><u>Anthracene</u></b>		
In average	0.01	0.04
Out average	0.05	0.25
<b><u>Flouranthene</u></b>		
In average	0.00	0.00
Out average	1.27	6.35
<b><u>Pyrene</u></b>		
In average	0.02	0.11
Out average	0.87	4.35
<b><u>Chrysene</u></b>		
In average	0.00	0.00
Out average	0.04	0.22
<b><u>Benzo(a)anthracene</u></b>		
In average	0.00	0.00
Out average	0.04	0.19
<b><u>Benzo(b)flouranthene</u></b>		
In average	0.00	0.00
Out average	0.02	0.09
<b><u>Dibenzo(a,h)anthracene</u></b>		
In average	0.01	0.04
Out average	0.00	0.01
<b><u>Benzo(ghi)perylene</u></b>		
In average	0.00	0.00
Out average	0.00	0.01

Summary of Storm Event #9 (6/12/2006)

**NAPHTHALENE**

In average	0.00	0.01
Out average	0.00	0.00

**Anthracene**

In average	0.00	0.00
Out average	0.03	0.16

**Flouranthene**

In average	0.01	0.05
Out average	1.37	6.87

**Pyrene**

In average	2.11	10.57
Out average	0.36	1.78

**Benzo(b)flouranthene**

In average	0.00	0.00
Out average	0.06	0.32

**Benzo(k)flouranthene**

In average	0.00	0.00
Out average	0.01	0.03

**Dibenzo(a,h)anthracene**

In average	0.00	0.00
Out average	0.00	0.01

Summary of Storm Event #10 (6/19/2006)

**NAPHTHALENE**

In average	0.00	0.02
Out average	0.00	0.01

**Anthracene**

In average	0.01	0.03
Out average	0.00	0.01

**Flouranthene**

In average	0.26	1.30
Out average	0.00	0.00

**Pyrene**

In average	0.89	4.46
Out average	2.41	12.06

**Chrysene**

In average	0.05	0.23
Out average	0.09	0.47

**Benzo(a)anthracene**

In average	0.00	0.00
Out average	0.21	1.03

**Benzo(b)flouranthene**

In average	0.00	0.01
Out average	0.01	0.03

**Benzo(k)flouranthene**

In average	0.01	0.06
Out average	0.00	0.00

**Dibenzo(a,h)anthracene**

In average	0.21	1.03
Out average	0.00	0.00
<b><u>Benzo(ghi)perylene</u></b>		
In average	0.00	0.02
Out average	0.00	0.00

**Summary of Storm Event # 14 (9/1/2006)**

**NAPHTHALENE**

In average	0.00	0.00
Out average	0.00	0.02

**Pyrene**

In average	0.00	0.00
Out average	0.07	0.36

**Benzo(a)pyrene**

In average	0.00	0.00
Out average	0.00	0.01

**Benzo(ghi)perylene**

In average	0.00	0.00
Out average	0.32	1.62

**Ideno(1,2,3-cd)pyrene**

In average	0.01	0.05
Out average	0.00	0.00

**Summary of Storm Event # 15 (9/14/2006)**

**NAPHTHALENE**

In average	0.00	0.01
Out average	0.00	0.01

**Anthracene**

In average	0.00	0.01
Out average	0.00	0.00

**Benzo(b)flouranthene**

In average	0.00	0.02
Out average	0.00	0.00

**Benzo(k)flouranthene**

In average	0.03	0.15
Out average	0.00	0.00

**Benzo(a)pyrene**

In average	0.07	0.34
Out average	0.00	0.00

**Dibenzo(a,h)anthracene**

In average	0.13	0.67
Out average	0.00	0.00

**Benzo(ghi)perylene**

In average	0.02	0.10
Out average	0.00	0.00

**Ideno(1,2,3-cd)pyrene**

In average	0.02	0.10
Out average	0.00	0.00

**Summary of Storm Event # 16 (10//2006)**

**Benzo(b)flouranthene**

In average	0.00	0.00
Out average	0.01	0.04

Summary of Storm Event # 17 (10/16/2006)

0.00

Summary of Storm Event # 18 (10/27/2006)

0.00

# Conclusions

## Benning Road Bioretention

In this study grab samples of the influent and effluent water for 15 storm events have been monitored for the bioretention site located adjacent to the Benning Road Bridge. This water quality monitoring project is concluded well. The methodology and protocols for the sampling of the storm water at the site reached the point of routine for Dr. Glass and his four students. With confidence we entered the rainy season for the Washington D.C. area with the belief that sampling for this first site would be completed by this month, July 2005. Preparatory work for the second site has neared completion. The housing is in place and we are finalizing the plans for withdrawing the water from the inlet and outlet of the sand filter to be monitored at D.C. Village.

Unfortunately it is the belief of this project team that the Benning Road bioretention site was poorly designed, constructed, maintained, or all of the above. From visual inspection of the catch basins one of the inlets to the bioretention did not operate properly for the length of the project. Only a trickle of storm water reaches the bioretention site from the clogged inlet, the majority of the storm water proceeds directly into the combined sewer system with no diversion to the bioretention cell from one of the two catch basins. This is most likely a maintenance problem.

In addition, this site seems to be too small for the watershed that it is theoretically supposed to be treating. For seven of the fifteen storm events monitored the overflow of the bioretention was reached. This bioretention system seems to overflow for relatively small storms and it is only treating the inflow of one of the two pipes that are connected to it. Pollutants that are dissolved pass through the system with little potential for removal when overflow occurs.

In summary, when evaluating the average values of the parameters in the inlet and outlet from this bioretention, it must be concluded that it is not representative of the capability of this technology when properly designed, built, and maintained. Only total suspended solids and total dissolved solids were removed on a semi-consistent basis from the system, at 86% and 91% removal efficiencies. Most of the dissolved constituents were removed at no better than 50% efficiency. These values are much less than removal percentages of bioretention systems in the literature or the performance of other bioretention systems monitored by this investigator in the past.

## DC Village Sand Filter

In this study 12 storm events were monitored to evaluate the efficiency of a DC Sand Filter on one of the parking lots serving the DC Village facility. The site was equipped with two ISCO Automatic Samplers with a submerged flow monitor, a strainer, and a rain gauge. This site seems to treat the relatively light load of pollutants found in this parking lot very well. The efficiency of solids removal was almost 90% and because

this parking lot was not loaded with heavy metals and oil and greases none of the other parameters was found to be excessive. The system did not remove the low concentrations of nutrients or organic carbon at a high percentage; however they are not designed to remove those pollutants. There were several problems with the use of the samplers.

In the future, Dr. Glass and his students will have to receive training to enter into the sewer system with out the assistance of DC DOE staff so that regular maintenance and upkeep of the subsurface installation can be achieved. In addition, sampling equipment that is left in the open space without security is destined to be vandalized by the public. The sampling equipment was destroyed during the 12<sup>th</sup> event at the site as a result of someone running over the metal conduit that protected the submerged probes electrical wiring and the tube that connected the strainer to the pump in the automatic sampler.

## W Street Parking Facility BaySaver

A BaySaver is designed to remove solids, some suspended solids, and oils and grease from ordinary, normal traffic parking lots. The BaySaver website states that the device should remove 80% of TSS for a 1 inch per hour rainfall event. The storm events for this study were not limited to 1 inch of rainfall, which showed only a 62% removal rate for TSS. There is no readily available information at the BaySaver website, however there is no doubt that the system was not designed to receive the level of pollutant input from the industrial site for the intense storms that we receive here in the D.C. metropolitan area.

When first viewing the two chambers of the BaySaver at the W Street parking facility, it was known that the site needed to be cleaned. Given the contractual nature of the project we could not wait to sample when the system was cleaned, so we began sampling immediately upon determining how we would take the grab samples and transport them to the laboratory. The facility was not designed for proper monitoring with automatic samplers, just as the bioretention at Benning Road had not been. The monitoring revealed that there is very poor removal of the water quality pollutants of interest by the BaySaver. The BaySaver is designed to store oil and grease, solid matter, and floatables until a pump truck can come to empty the chamber. In addition, they are designed to overflow at a given flowrate. It is the belief of this research team that when the BaySaver overflows some of the pollutants that have been stored inside of the device flow out of the system, resulting in pollution and the poor efficiency that was measured throughout this project.

# Assessment of Waterborne Contamination with Human Pathogens in Tributaries of the Anacostia River using the Asiatic Clam (*Corbicula fluminea*)

## Basic Information

<b>Title:</b>	Assessment of Waterborne Contamination with Human Pathogens in Tributaries of the Anacostia River using the Asiatic Clam ( <i>Corbicula fluminea</i> )
<b>Project Number:</b>	2006DC80B
<b>Start Date:</b>	3/1/2006
<b>End Date:</b>	2/28/2007
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	District of Columbia
<b>Research Category:</b>	Biological Sciences
<b>Focus Category:</b>	Water Quality, Non Point Pollution, Solute Transport
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Thaddeus K. Graczyk

## Publication

1. Graczyk, Thaddeus K., Cynthia McOliver, Ellen K. Silbergeld, Leena Tamang, Jennifer D. Roberts, 2007, Risk of Handling as a Route of Exposure to Infectious Waterborne *Cryptosporidium parvum* Oocysts via Atlantic Blue Crabs (*Callinectes sapidus*), *Applied and Environmental Microbiology*, Vol.73 (12), p. 4069-4070.
2. Graczyk, Thaddeus K., Deirdre Sunderland, Ana M. Rule, Alexandre J. da Silva, Iaci N. S. Moura, Leena Tamang, Autumn S. Girouard, Kellogg J. Schwab, Patrick N. Breyse, 2007, Urban Feral Pigeons (*Columba livia*) as a Source for Air-and-Waterborne Contamination with *Enterocytozoon bieneusi* Spores, *Applied and Environmental Microbiology*, published online ahead of print on 4 May 2007.
3. Jedrzejewski, Syzmon, Thaddeus K. Graczyk, Anna Slodkowicz-Kowalska, Leena Tamang, Anna C. Majewska, 2007, Quantitative Assessment of Contamination of Fresh Food Produce of Various Retail Types by Human-Virulent Microsporidian Spores, *Applied and Environmental Microbiology*, Vol. 73 (12), p. 4071-4073.
4. Graczyk, Thaddeus K., Deirdre Sunderland, Leena Tamang, Timothy M. Shields, Frances E. Lucy, Patrick N. Breyse, 2007, A Quantitative Evaluation of the Impact of Bather Density on Levels of Human-Virulent Microsporidian Spores in Recreational Water, *Applied and Environmental Microbiology*, published online ahead of print on 4 May 2007.
5. Graczyk, Thaddeus K., Leena Tamang, Richard Pelz, 2007, the Effect of a Taste Enhancement Process for Cold-Stored Raw Shell-Stock Oysters (*Crassostrea virginica*) on the Spillage of Human Enteropathogens, 2007.



**Award Number:** GF4136F201

**Principal Investigator:** Thaddeus K. Graczyk

**Organization:** Johns Hopkins Bloomberg School of Public Health,  
Department of Environmental Health Sciences,  
615 N. Wolfe St., Rm E6616, Baltimore, MD 21205  
Tel: (410) 614-4984, Fax: (410) 955-0105  
E-mail: tgraczyk@jhsph.edu  
[http://faculty.jhsph.edu/Default.cfm?faculty\\_id=274](http://faculty.jhsph.edu/Default.cfm?faculty_id=274)

**Peer-reviewed publications resulted from the Award Number:** GF4136F201: five (5).  
(Attached)

## Final Report

### Description of Experiments

1. Depuration of *Corbicula fluminea* clams collected from the Anacostia River.
2. Determination of the bioaccumulation rate of human waterborne parasites by *Corbicula fluminea* clams from the Anacostia River and comparison with *Dreissena polymorpha* mussels.

*Corbicula fluminea*, 2.0 to 2.5 cm shell length were obtained from Anacostia River, and *Dreissena polymorpha*, 2.0 - 3.5 cm shell length, were obtained from the St. Lawrence River. Clams and mussels were depurated for 3 weeks (4), and after depuration 30 randomly selected clams and mussels were individually tested for *Cryptosporidium* and *Giardia* (4). Depurated *C. fluminea* clam were tested for *Cryptosporidium*, *Giardia*, and human-virulent microsporidia as described previously (6). Three, 38-l aquaria (approximately 10-gallon), i.e. aquarium A, B, and C, were filled with dechlorinated drinking water filtered by the Filterite 10- $\mu$ m-pore yarn-wound cartridge (Memtec America Corp., Baltimore, Maryland). Each aquarium was equipped with a Fluval filter (model 403) (Askoll, Italy) and two air-stones. Two hundred-twenty specimens of *C. fluminea* or *D. polymorpha* were placed separately in aquarium A and B, respectively, and 110 of each bivalve species were placed in aquarium C. Shellfish in aquaria were maintained as described previously (4).

*Cryptosporidium parvum* oocysts and *G. lamblia* cysts originated from experimental infection of a calf and were purified by CsCl<sub>2</sub> gradient centrifugation (7). Oocysts and cysts were enumerated by flow cytometry (2). Water in each aquarium was spiked daily in the early morning with 106 oocysts and 304 cysts for 31 consecutive days. The inoculum size was calculated to produce the concentration of oocysts and cysts reported from surface water, i.e., 28 oocysts/10 liters, and 304 cysts/10 liters (1).

Thirty bivalves were sampled 7 times at weekly intervals in the late afternoon with the

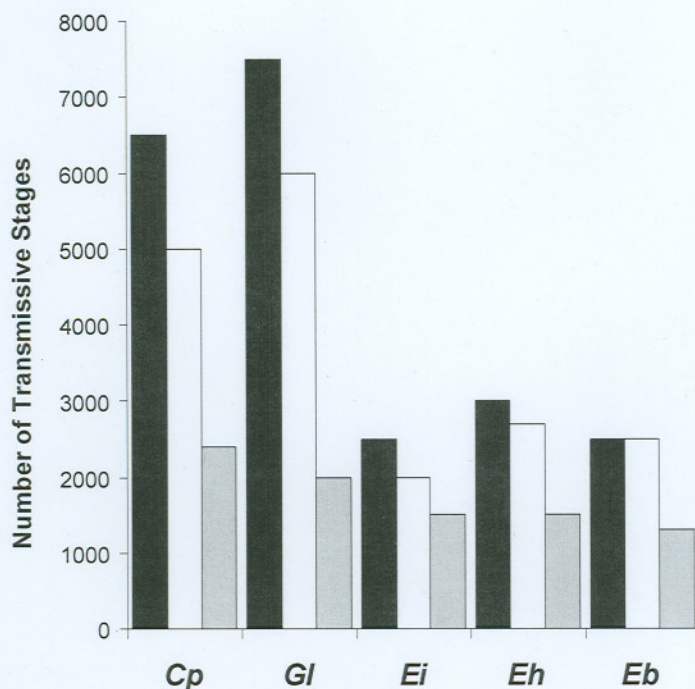
first sampling timepoint, i.e., week 1, on three days after the first water contamination event. The fifth sampling timepoint, i.e., week 5, occurred the day of the last water contamination timepoint. Each time the sampled bivalves included 30 clams (aquarium A), 30 mussels (aquarium B), and 15 of each species (aquarium C). The bivalves were opened (4), the soft tissue and hemolymph from 30 shellfish was pooled, homogenized with a doubled volume (w/v) of phosphate-buffered saline (PBS) (pH 7.4), and the homogenate was sieved, sedimented (5, 8), and purified over CsCl<sub>2</sub> gradient (7). The oocyst and cyst-containing fraction of CsCl<sub>2</sub> was centrifuged (1,000 g; 3 min; 4°C), and the pellet resuspended in 4 ml of deionized water. Approximately 500 µl of resuspension was placed in each of eight wells on an 8-well-chamber tissue culture glass slide (Nalge Nunc International, Naperville, IL, USA). After 3 hr incubation at 20°C, the fluid was aspirated from each well, the plastic dividers were removed, and the slide was air-dried. *Cryptosporidium parvum* oocysts and *G. lamblia* cysts were visualized by immunofluorescent antibody (IFA) of the MERIFLUOR™ test kit (Meridian Diagnostic, Cincinnati, OH) and enumerated (5). The overall numbers of oocysts and cysts were adjusted for the method recovery efficiency, i.e., 51.1% (5). Sediments from all aquaria were tested for *Cryptosporidium* and *Giardia* (4) every time the bivalves were sampled. Efforts were made to collect all sediments. All water from all aquaria was filtered by the cellulose acetate membrane disk; 393-mm diameter, 3.0-µm pore size (Millipore Corp., Bedford, MA) (3) every time the bivalves were sampled. After total aquarium drainage the filtered water was recirculated back to the aquarium. The membranes were processed to detect *C. parvum* and *G. lamblia* (9,10). To confirm the recovery efficiency of this method 5 38-l water samples were processed as described above except that each sample was spiked with 106 *C. parvum* oocysts and 304 *G. lamblia* cysts.

Statistical analysis was carried out with Statistix 4.1 (Analytical Software, St. Paul, Minnesota). The variables were examined by the Runs test to determine conformity to a normal distribution. The degree of linear association between variables was evaluated using Pearson's correlation coefficient (*R*), two-sample *t*-test was used to assess the significance of differences between mean values, and fractions were compared using the *G*-heterogeneity test. Mean values (*x*) were associated with standard deviation (SD). Statistical significance was considered to be *P* < 0.05.

## Results

The numbers of human pathogens identified in *C. fluminea* clams from the Anacostia River are presented in Figure 1.

The numbers of *C. parvum* oocysts and *G. lamblia* cysts identified in shellfish tissue increased progressively through week 5, and both parasites were identified for the first time, i.e., on week 1, in *D. polymorpha* tissue (Fig. 2). There was a significant correlation observed in all three experiments between the cumulative numbers of *C. parvum* oocysts seeded to the water and identified in bivalve tissue (Pearson correlation; *P* = 0.94, *P* < 0.02). This was also the case for *G. lamblia* in two experimental options, i.e., aquarium A and B (Pearson correlation; *P* = 0.96, *P* < 0.01). The parasite levels decreased on the week 6 after cessation of water contamination, but *C. parvum* and *G. lamblia* were still detected in *D. polymorpha*, i.e., aquarium B and C, two



**Figure 1.** Number of *Cryptosporidium parvum* (Cp), *Giardia lamblia* (Gl), *Encephalitozoon intestinalis* (Ei), *Encephalitozoon hellem* (Eh), and *Enterocytozoon bienersi* (Eb) recovered from 30 *Corbicula fluminea* clams from the Anacostia river during first (black), second (white), and third (gray) week of depuration.

weeks after the last water contamination event.

In general, more cystic stages of both parasites were identified in the tissues of *D. polymorpha* (aquarium B) than *C. fluminea* (aquarium A). In aquarium C in which equal numbers of each bivalve species were kept (and sampled), most parasites were identified in the *D. polymorpha* tissue. Based on the data from all three 7-week-long experiments, on average  $48 \pm 24.9$  pathogen cystic stages (both *C. parvum* and *G. lamblia*) were identified in the tissue of 30 *C. fluminea* clams, and  $70 \pm 25.8$  in 30 *D. polymorpha* mussels. Analysis of these results by two-sample *t*-test demonstrated that significantly higher numbers of parasites were identified in *D. polymorpha* than in *C. fluminea* ( $t = 3.03$ ,  $P < 0.05$ ).

On average, from 7% to 32% (mean, 17.8%) of all *C. parvum* oocysts added to the water were identified in the bivalve tissue for the 31 day duration of water contamination (Fig. 3). This level was significantly higher than the level of *G. lamblia* cysts (range: 1 - 5%; mean, 1.7%) (two-sample *t*-test;  $t = 59.2$ ,  $P < 0.01$ ). Overall, for all three 7-week-long experiments 35.0% and 16.3% of the parasite cystic stages seeded into the water were identified in *D. polymorpha* and *C. fluminea*, respectively (*G*-heterogeneity test:  $G = 6.8$ ,  $P < 0.01$ ).

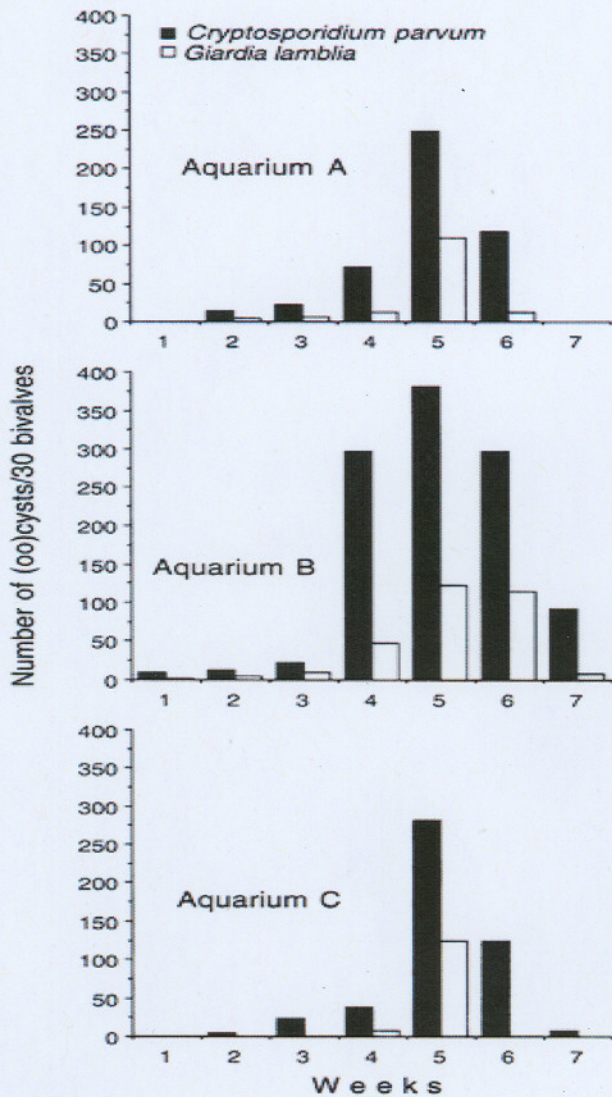
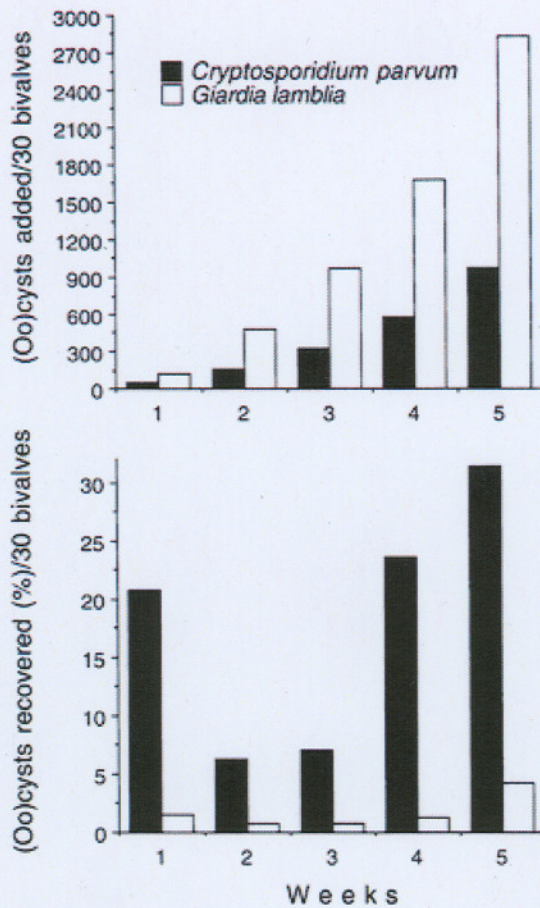


Fig. 2. Identification of *Cryptosporidium parvum* oocysts and *Giardia lamblia* cysts recovered from artificially contaminated water by freshwater bivalve mollusks, *Corbicula fluminea* (aquarium A), *Dreissena polymorpha* (aquarium B); aquarium C contained equal numbers of both bivalve species which were sampled equally. Water in each 38-l aquarium seeded daily for 31 consecutive days, i.e., up to week 5, with 106 oocysts and 304 cysts. Aquarium C; *Cryptosporidium parvum* and *G. lamblia* identified in *D. polymorpha* tissue only. Oocysts and cysts identified by immunofluorescent antibody.



**Fig 3.** *Upper panel* The theoretical cumulative numbers of *Cryptosporidium parvum* oocysts and *Giardia lamblia* cysts seeded to the water in three 38-l aquaria with freshwater mollusks, *Corbicula fluminea* clams and *Dreissena polymorpha* mussels (aquarium A, B, and C, as described in Fig. 1. *Lower panel* The overall mean percentage of oocysts and cysts identified in the tissue of bivalves maintained in aquaria with *Cryptosporidium parvum* and *G. lamblia*-seeded water.

### Conclusions

- *Corbicula fluminea* collected from the Anacostia River are highly contaminated with humans waterborne pathogens such as *Cryptosporidium parvum*, *Giardia lamblia*, *Encephalitozoon intestinalis*, *Encephalitozoon hellem*, and *Enterocytozoon bieneusi*.
- Anacostia River waters is contaminated with human pathogens.

- *Corbicula fluminea* clams are able to bioaccumulate waterborne parasites recovered from contaminated water in proportion to ambient concentrations.
- *Corbicula fluminea* clams can be used as bioindicators for waterborne contamination and for sanitary assessment of water quality.
- *Corbicula* clams have an important role in aquatic habitats because of filtering suspended particles, thereby clarifying the water and improving water quality.
- *Corbicula fluminea* clams are convenient for biomonitoring because they form dense populations, do not have economic value, are easily collected, have a relatively small size, and occur in large numbers that facilitate collection of a large sample.

### References

1. Atherholt TB, LeChevallier MW, Norton WD, Rosen JS. 1998. Effect of rainfall on *Giardia* and *Crypto*. *Journal of American Water Works Association* 90:66-80.
2. Bennett JW, Gauci MR, LeMoenic S, Schaefer FW, Lindquist HD. 1999. A comparison of enumeration techniques for *Cryptosporidium parvum* oocysts. *Journal of Parasitology* 85:1165-1168
3. Fayer R, Lewis EJ, Trout JM, Graczyk TK, Jenkins MC, Higgins J, Xiao L, Lal AA. 1999. *Cryptosporidium parvum* in oysters from commercial harvesting sites in the Chesapeake Bay. *Emerging Infectious Diseases* 5:706-710.
4. Graczyk TK, Fayer R, Cranfield MR, Conn DB. 1998. Recovery of waterborne *Cryptosporidium parvum* oocysts by freshwater benthic clam (*Corbicula fluminea*). *Applied and Environmental Microbiology* 64:427-430.
5. Graczyk TK, Fayer R, Lewis EJ, Trout JM, Farley CA. 1999. *Cryptosporidium* oocysts in Bent mussels (*Ischadium recurvum*) in the Chesapeake Bay. *Parasitology Research* 85:518-521.
6. Graczyk, T. K., F. E. Lucy, L. Tamang, and A. Miraflor. 2007. Human enteropathogen load in activated sewage sludge and corresponding sewage sludge-end products. *Applied and Environmental Microbiology* 73 (6): 2013-2015.
7. Kilani RT, Sekla L. 1987. Purification of *Cryptosporidium* oocysts and sporozoites by cesium chloride percoll gradient. *American Journal of Tropical Medicine and Hygiene* 36:505-508.
8. McMahon RB. 1991. Mollusca: Bivalvia. In: Thorp JH, Covich AP, editors. Ecology and classification of North American freshwater invertebrates. Academic Press, San Diego, California, pp. 315-401.
9. Rodgers MR, Flanigan DJ, Jakubowski W. 1999. Method 1622: *Cryptosporidium* in water by filtration/IMS/FA. U.S. Environmental Protection Agency, Office of Water. EPA/821-R- 99-001, p. 24-27.

10. Rodgers MR, Flanigan DJ, Jakubowski W. 1999. Method 1623: *Cryptosporidium* and *Giardia* in water by filtration/IMS/FA. U.S. Environmental Protection Agency, Office of Water. EPA/821-R-99-006, p. 40.

## **Information Transfer Program**

The Cooperative Extension Service/Water Quality Education Program Extension Agent, Ms. Wellela Hirpassa has had a significant impact on the Institutes information transfer and outreach capacity. Listed are some of her accomplishments in conjunction with the Institute: Prepared and distributed water quality education brochures and fact sheets to DC residents; Conducted workshops on water quality education at various DC Recreation Centers and Public Schools; Visited DC Water and Sewer Authority (DCWASA) Water Quality Division for potential collaboration Periodically visited USDA\CSREES National Water Program to enhance Water Quality Education Program for future collaboration; and Participated on the Mid-Atlantic Regional Water Quality Program Steering Committee

The Institute now has a new website that is regularly updated <http://www.udc.edu/wrri/> And recently distributed it The Institute has electronically disseminated its Water Highlights Newsletter, Summer/Fall 2006 issue [http://www.udc.edu/docs/dc\\_water\\_resources/newsletters/WaterHighlights\\_Volume\\_II\\_Summer\\_Fall\\_2006.pdf](http://www.udc.edu/docs/dc_water_resources/newsletters/WaterHighlights_Volume_II_Summer_Fall_2006.pdf). This document is very informative and highlights current research and educational projects sponsored by the Institute along with interactions among faculty members and their student interns on projects and conferences.

An electronic mailing list of over 150 Water Resources faculty and experts in the consortium of universities in Washington DC is maintained and regularly updated and sent regular information via email on local, region, and nation water issues when received by the Institute. This line of information transfer has enhanced the visibility and credibility of the Institute amongst these stakeholders.



## Student Support

<b>Student Support</b>					
<b>Category</b>	<b>Section 104 Base Grant</b>	<b>Section 104 NCGP Award</b>	<b>NIWR-USGS Internship</b>	<b>Supplemental Awards</b>	<b>Total</b>
<b>Undergraduate</b>	5	0	0	0	5
<b>Masters</b>	5	0	0	0	5
<b>Ph.D.</b>	0	0	0	0	0
<b>Post-Doc.</b>	2	0	0	0	2
<b>Total</b>	12	0	0	0	12

## Notable Awards and Achievements

## Publications from Prior Projects