D.C. Water Resources Research Institute
Annual Technical Report
FY 2016

Introduction

District of Columbia is totally urban and its waterways are impacted due to urban runoff and combined sewer outfalls. Consequently, the designated uses that directly relate to human use of the District's waters are generally not supported, such as swimming and fishing. Moreover, the uses related to the quality of habitat for aquatic life is not supported. It is also noted that the water quality of the District's waterbodies continues to be impaired. The mission of the DC Water Resources Research Institute (WRRI), here on called the Institute is to identify the problems and contribute to their solution through applied research and training funded through the seed grants.

This report is a summary of the research activities of the Institute for the period of March 1, 2016 through February 28, 2017. Hosted by the College of Agriculture, Urban Sustainability and Environmental Sciences (CAUSES) of the University of the District of Columbia, the DC WRRI continued to coordinate water-related research, training and outreach activities in the District of Columbia in order to enhance the management of quality and quantity of DC waterways.

Since 2005, the Institute has provided seed grants for 97 research projects and trained hundreds of graduate and undergraduate students. The seed grants created opportunities for students and new faculty in creating innovative research projects and getting trained in the new water technologies. The seed grant also helped new faculty leverage extramural funding. Through the Institute, the University of the District of Columbia has received about $2 million in financial support to build state-of-the-art research and training laboratories for environmental and water quality testing, as well as modeling and simulation. These laboratories facilitated the establishment of new graduate programs, including water resources management, urban sustainability, and urban agriculture.

In 2016, the Institute funded and implemented eight research projects that address key water issues in the District. The overarching goal of these projects includes identifying city water resources and environmental problems and contributing to their solutions. About 20 graduate and undergraduate students were directly involved in the research projects, but more than 100 students were trained in the water quality testing technologies through lab and field experiences.

Partially funded through the administrative project, the Institute also manages two state-of-the-art laboratories: water and environmental quality testing laboratory, and water and environmental quality modeling and simulation laboratory. The water and environmental quality testing laboratory became accredited by the National Environmental Laboratory Accreditation Program (NELAP) with NELAC standard in October 2015 through the State of New Hampshire Environmental Laboratory Accreditation Program. The lab is now nationally accredited for trace metals, minerals and water hardness in potable and non-potable waters. The lab is now in the process of expanding its NELAP accreditation for pesticides analysis, and pathogens in potable and non-potable waters, and trace metal analysis in soil and biosolids. This NELAP accreditation is the 1st of its kind in the Washington DC metropolitan area and has a significant impact in enhancing the research and training capacity of UDC in preparing future water scientists.

Even if there was no funded information transfer project during the reporting time, the Institute continued conducting successful information transfer projects through training workshops and the regional annual water symposium. The Institute continued building collaboration with other centers within the hosting institution and beyond for conducting information transfer activities. In collaboration with the American Water Resources Association in the National Capitol Region (AWRA-NCR), the Institute organized the 4th Annual Water Symposium on April 8, 2016, at the University of DC. This one-day symposium sought to bring together experts from governmental agencies, academia, the private sector, and non-profits to present and discuss rethinking the value of water: innovations in research, technology, policy, and management. In close collaboration with other land-grant centers in CAUSES, such as the Center for Sustainable Development, the Institute continued in supporting the training workshops in green infrastructure maintenance. The Institute will continue working closely with both internal and external collaborators to build on its current success of information transfer activities.

Research Program Introduction

In FY 2016, the Institute funded eight research projects that address three areas: hydrology and stormwater management, water quality, and green infrastructure. The progress report of Dr. Behera project introduces the model that analyzes the long-term storm event for Washington DC based on different inter-event-time-definition (IETD). In contrast to the current approach that uses only one value that represents a design storm event, the proposed approach provides ranges of value as ideally the stormwater infrastructures are subjected to entire storm events which have several characteristics such as storm volume, storm duration, average intensity, maximum intensity and inter-event time etc.

The progress report of Drs. Nian Zhang and Pradeep Behera investigates the application of a least-squares support vector machine (LS-SVM) model to improve the accuracy of streamflow forecasting. They applied modified k-nearest neighbors (KNN) classifier method and compared its performance with the conventional k-nearest neighbors method. The experimental results show that the proposed enhanced KNN method is better than the conventional method.

The progress report of Drs. Jiajun Xu and Xueqing Song investigates the effectiveness of engineered nanocomposite structure in treating wastewater. The broader goal of this research project is to assist in exploring a new artificial nanocomposite structure that can offer a pathway to the development of engineered materials with novel macroscopic properties for a more feasible and efficient pollutants treatment solution. Based on the preliminary results, this method is promising in water treatment, in particular, the heavy metal removal.

The progress report of Drs. Song and Xu work investigate the application of Nanoparticles (ZnS, Fe_2O_3, and TiO_2) as catalytic degradation materials of glyphosate and its primary metabolite aminomethylphosphonic acid in aqueous samples. Glyphosate is one of the organophosphate herbicides that are produced the largest volume worldwide, and this research will explore a promising solution.

The progress report of Drs. Kamaran Zendehdel, Harris Trobman and Xiaochu Hu introduces the effectiveness of interactive signage at advancing communicating, promoting, and educating the public on green infrastructure projects in public spaces. The result of this research project will enhance the public's understanding of the environmental benefits of green infrastructure practices.

The progress report of Dr. Carol Salomon assess the impact of NH_4^+ on the aquatic biota, including phytoplankton and fish productivity and community composition in the Anacostia River's N-enriched waters by both sampling of the River and conducting bioassay experiments. This project will directly contribute to monitoring the influence of the pre- and postconstruction of green and gray infrastructure on local phytoplankton and fish populations and the resulting impacts on local residents who fish in the Anacostia River.

The progress report of Dr. Arash Massoudieh introduces a new mathematical method that can be applied to the performance evaluation of urban stream restoration technologies using process-based modeling. The preliminary results showed that the proposed model is useful for the performance evaluation of green infrastructure, including rain garden, and bio-retention.

The progress report of Sebhat Tefera and Yacov Assa introduces a new technique that applies to the analysis of perchlorate in drinking water, surface water by AxION Direct sample analysis (DSA) with Time of flight (TOF) Mass Spectrometer. The proposed method will develop a rapid approach for screening as well as quantification of perchlorate.

The progress report of Dr. Jiajun Xu introduces the development of A Novel Stormwater Runoff Collection and Treatment System for Urban Agriculture and Food Security. This project contributes to the current rapid growth of urban agriculture and its impact on the urban waterways.

Listed below are the title and PI of eight grants awarded through 104B grant for the FY 2016:

1. Titile: Measurement and Performance Analysis of UDC Van-Ness Campus Green Roof System with automated sensors, Sasan Haghani, University of the District of Columbia

2. Title: In-Situ Comparison of Extensive and Intensive Greenroof Infiltration, Kamaran Zendehdel, University of the District of Columbia

3. Title: Quantifying the Recharge and Evapotranspiration Rates of the Chesapeake Bay Watershed using Land Surface State Observations, Leila Farhadi, George Washington University.

4. Title: Performance Monitoring of Green Infrastructure Maintenance in the District, Harris Trobman, University of the District of Columbia.

5. Title: Assessing the effectiveness of urban gardens in reducing stormwater pollution, Karen L. Knee, American University

6. Titile: Examining genetic microbial diversity to monitor pathogens and toxins and in the Anacostia River, DC, Caroline Solomon, Gallaudet University

7. Title: Anatomical and Behavioral Outcomes of Toxicant Exposure in the Anacostia River: Building a Zebrafish (Danio rerio) Model of Biological River Health, Victoria P. Connaughton, American University

8. Title: Examination of nutrient and land use patterns in the tidal Anacostia River, Stephen E. MacAvoy, American University

Influence of consistently high levels of ammonium on food web dynamics in the Anacostia River

Basic Information

Title:	Influence of consistently high levels of ammonium on food web dynamics in the Anacostia River
Project Number:	2016DC176B
Start Date:	3/1/2016
End Date:	2/28/2017
Funding Source:	104B
Congressional District:	DC
Research Category:	Water Quality
Focus Categories:	Nutrients, Water Quality, Education
Descriptors:	None
Principal Investigators:	Caroline Solomon

Publications

There are no publications.

Influence of consistently high levels of ammonium on food web dynamics in the Anacostia River: Final Report

GALLAUDET
UNIVERSITY

Caroline Solomon, Ph.D.
Professor, Department of Sciences, Technology and Mathematics, Gallaudet University

April, 2017

1. Executive Summary

The Anacostia River in Washington, D.C. is classified as an impaired river from pollution based on several indicators; however, it is not well known how nutrient pollution and the different nitrogen (N) forms (i.e., NO_3^-, NH_4^+, urea) vary temporally or spatially or which N forms are of greatest concern. Such shifts in N form often influence the physiology of phytoplankton that lead to shifts in algal species and harmful or disruptive algal blooms. Recent literature is starting to suggest that excessive concentrations of NH_4^+ can lead to suppression of phytoplankton growth, which may have implications for migratory anadromous fish species that are filter feeders. Shifts in both phytoplankton community composition and fish communities will impact which fish are present in the Anacostia River for recreational and subsistence fishing.

In order to properly assess N and food web dynamics in the Anacostia River, it is necessary to determine the effects of changing N form and proportions on phytoplankton and fish community composition and productivity. This project aims to assess the impact of NH_4^+ on phytoplankton and fish productivity and community composition in the Anacostia River's N-enriched waters by both sampling of the River and conducting bioassay experiments. Samples will be collected over the course of a year bi-weekly from eleven sampling sites for assessment of nutrients, chlorophyll, and bacteria and phytoplankton community composition. Bioassay experiments done over several days will involve samples from certain sites that will be variably enriched with NH_4^+ and NO_3^-, with and without supplemental additions of phosphate (P) to produce a range of nutrient supply ratios. Data from the two-prong approach will be analyzed along with fish community data from District Department of the Environment to understand the impact on fisheries. Currently, there are regulatory advisories against fishing and thousands of people fish along the river for sustenance. This project will directly contribute to monitoring the influence of the pre- and post-construction of green and gray infrastructure on local phytoplankton and fish populations and the resulting impacts on local residents who fish in the Anacostia River.

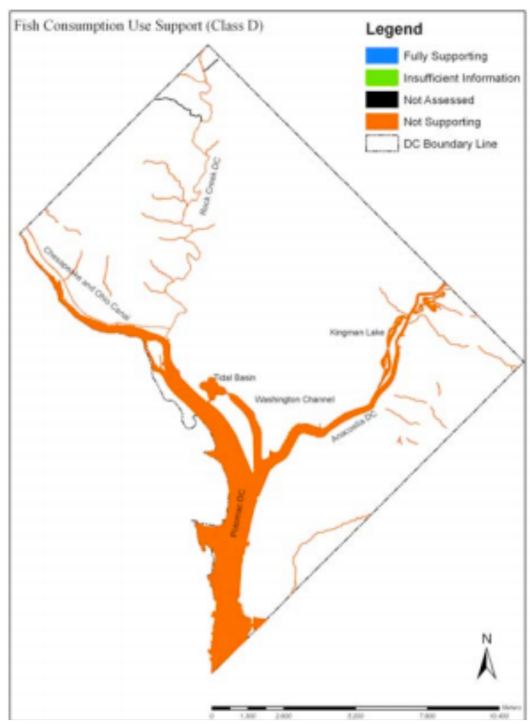

Figure 1: Currently the Anacostia River does not support fish consumption in the District of Columbia (Anacostia 2032 Plan, 2008)

2. Introduction

Of the two rivers that flow through the District of Columbia, the Anacostia River is often called the "forgotten river" as it was neglected for many decades while the neighboring Potomac River has received more attention and is monitored more closely (Wennersten, 2008). The Anacostia River recently received an overall score of F on its report card based on several water quality parameters (Anacostia Watershed Society, 2014).

Fishing on the Anacostia is a recreational activity that provides sustenance for lower social-economical groups that primarily live in southeast Anacostia and tie into the natural resource economics of this region (*Addressing the Risk*, 2012). Unhealthy fish are a community concern because approximately 17,000 community residents, despite warnings from the District Department of Environment and other regulatory agencies since 1989 are consuming fish from the Anacostia (**Fig. 1;** Anacostia 2032 Plan, 2008; Anacostia Watershed Restoration Partnership, 2012; *Addressing the Risk*, 2012; *Sustainable DC Plan*, 2013). Many recreational fish that feed on phytoplankton are migratory anadromous fish such as American and Hickory shad, Blueback herring, Alewife, and Atlantic menhaden (District Department of the Environment, 2014). These fish might be the most exposed to lower availability of phytoplankton due to suppression of algal growth from the potential toxic amounts of NH_4^+ that reach the Anacostia through various means. In San Francisco Bay estuary, changes in fish communities over the past several decades have been shown to be negatively related to increased loading of N and P and the form of N (Glibert et al. 2011).

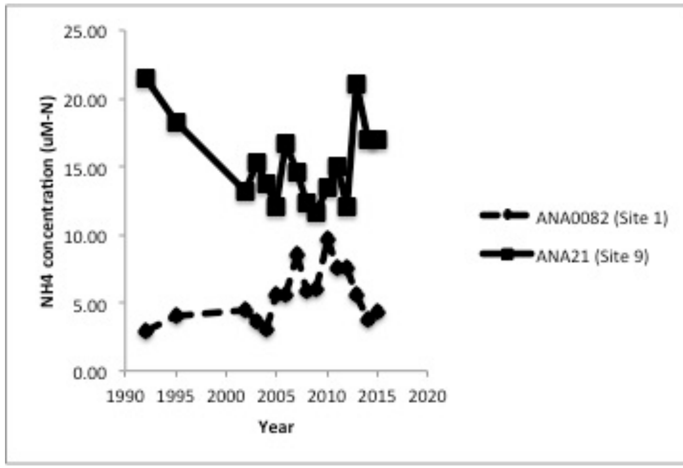

Figure 2: NH_4^+ concentrations at two sites in the Anacostia River from 1992 to 2015 (data from Chesapeake Bay Program and Solomon lab)

Water quality monitoring typically measures only dissolved inorganic nutrients – both nitrogen (DIN; NO_3^-, NH_4^+ and NO_2^-) and phosphorus (DIP) – based on the premise that bacteria and phytoplankton primarily use these sources (reviewed by Mulholland and Lomas, 2008). The levels of NH_4^+ have been consistently high in the Anacostia River, dating back to 1992 (**Fig. 2**). NH_4^+ concentrations increase from the upper watershed to where the Anacostia River meets the Potomac River (**Fig. 3**).

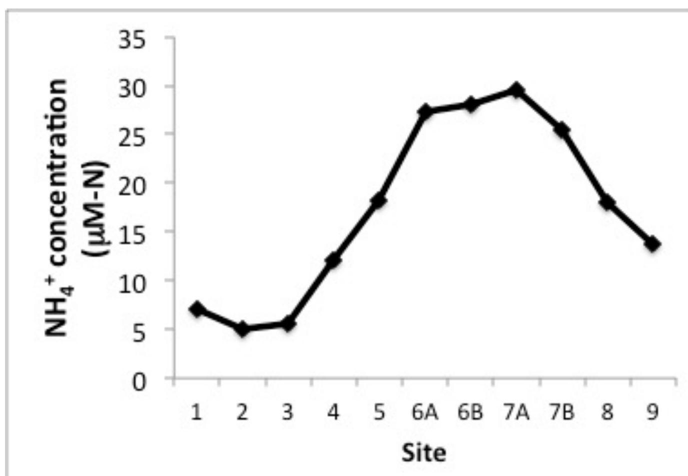

Figure 3: NH_4^+ concentrations along the Anacostia River from Bladensburg, MD to near the Nationals Stadium (Yards Park), DC in August (averaged from 2013 and 2014, Solomon, unpublished)

A large possible source of NH_4^+ to the Anacostia River is sewage overflows and treated effluent. The Anacostia has many combined sewage outfalls (CSO) that occur at 17 sites in DC (Natural Resources Defense Council, 2012; DC Water and Sewer Authority, 2012) that is part of Washington, D.C.'s antiquated sewer system that is over 150 years old. Each year during rain events greater than half an inch to an inch, approximately two to three billion gallons total of untreated sewage are mixed with storm water and released into the river carrying with it coliform bacteria, nutrients, trash and sediments (DC Water and Sewer Authority, 2012). For instance, the three weeks after Tropical Storm Sandy hit the Eastern seaboard in 2012, NH_4^+ concentrations increased nearly four fold (4.72 to 17.2 μM-N), suggesting that NH_4^+ might have entered the River via the CSO (Solomon, preliminary data). The questions are: how do the growth rates of different phytoplankton respond to this excess and potentially toxic level of NH_4^+? Do the increased NH_4^+ levels affect the phytoplankton community composition and in turn influence the fish community that is important for many local citizens who fish for sustenance?

It has been commonly argued that phytoplankton growth on NH_4^+ should be higher than that on NO_3^-, or at a least growth on both substrates should be equal. Several studies have corroborated this hypothesis and shown that some phytoplankton species grown on NH_4^+ or urea have higher growth rates than on NO_3^- (e.g., Herndon and Cochlan 2007; Solomon et al. 2010 and references therein).

However, it is more generally observed that different compositions of phytoplankton species develop under NH_4^+ vs. NO_3^- enrichments (at comparable N-equivalent concentrations). Domingues et al. (2011) showed that enrichment by NH_4^+ in a freshwater tidal estuary favored chlorophytes and cyanobacteria, whereas diatoms were favored under NO_3^- enrichment. Consistent with this research, chlorophytes and accompanying rotifers have been regularly observed in the upper portion of the Anacostia in the late summer for the past three years (Solomon, personal observations). Additionally, reports from field studies have shown dinoflagellates, many of which form harmful algal blooms (HABs), being associated with increased dominance of NH_4^+ than NO_3^- (e.g., Berg et al. 2003; Glibert et al. 2006; Heil et al. 2007; Rothenberger et al. 2009).

While different forms of N may lead to different phytoplankton community composition, it has also been documented that under conditions of highly elevated NH_4^+, that may be 10 to 20-fold higher than typical concentrations, both the total N taken up and overall growth with NH_4^+ enrichment can be suppressed rather than enhanced (e.g., Dasgenais-Bellefueille and Morse 2013 and

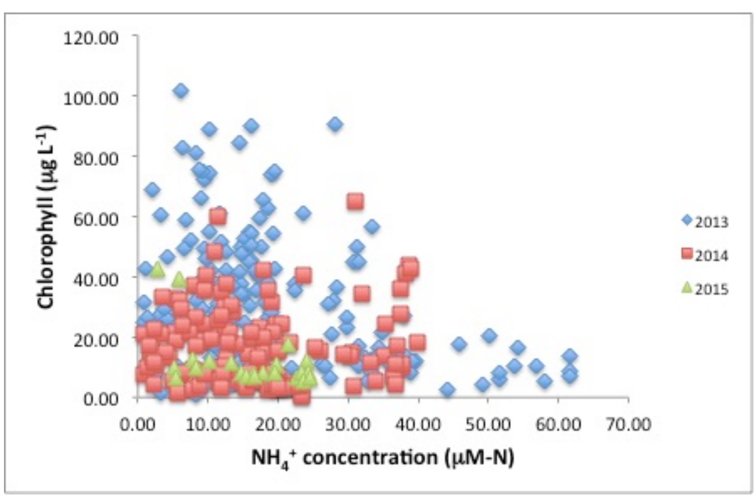

Figure 4: NH_4^+ concentrations vs. chlorophyll levels in the Anacostia River from 2013-2015 (Solomon, unpublished)

references therein, Glibert et al. 2014). This situation may be occurring in the lower Anacostia where blooms have not occurred in the past three years (**Fig. 3**). Also, the relationship between NH_4^+ concentrations and chlorophyll levels in the Anacostia River from 2013-2015 show a negative relationship (**Fig. 4**). Examples of growth suppression by NH_4^+ enrichment are numerous (Dortch 1990, Lomas and Glibert 1999a, Lomas and Glibert 1999b). Total N productivity was found to decrease in the Chesapeake Bay as the proportion of NH_4^+ increased when all samples received the identical total N enrichment, 30 μM and similar observations have been made in experiments conducted in the San Francisco Bay Delta (Glibert et al. 2014). Thus, the conceptual model that NH_4^+ is the preferred N form and that total N uptake and growth on NH_4^+ is the same or exceeds that on NO_3^- is not always true. The growth rates of some species may instead be suppressed by NH_4^+ which in turn causes shifts in the phytoplankton community composition.

Yoshiyama and Sharp (2006) summarized decades of data from the Delaware Bay and observed that the primary productivity rate per unit chlorophyll *a* declined exponentially with increasing NH_4^+ concentrations (most of the change occurring at <10 μM NH_4^+) and classified these systems as High-Nutrient, Low-Growth (HNLG). In the San Francisco Bay Delta it has been suggested that a similar phenomenon of growth suppression is responsible for the lack of spring blooms ever since NH_4^+ loading from sewage effluent increased several decades ago (Wilkerson et al. 2006; Dugdale et al. 2007) which also may be occurring in the Anacostia River. Both the observational and experimental evidence suggest that growth suppression by high concentrations of NH_4^+ may be occurring (e.g., Wilkerson et al. 2006; Parker et al. 2012).

The excess loading of NH_4^+ in the Anacostia may have two effects on this river system. When the concentrations of NH_4^+ are within the tolerable range for the phytoplankton community, it may be shifting the species composition. At “toxic” concentrations, overall phytoplankton growth, or growth of certain species, may be suppressed affecting overall phytoplankton productivity of the river, which would have significant ramifications for the food web, especially for fish populations.

3. Methodologies

Water samples were collected bi-weekly starting in March 2016 until November 2016. Sampling began in March 2014 and this marks the fourth year that data that has collected. Dr. Solomon and/or students collected samples from designated sites on the Anacostia River (Fig. 5) in partnership with the Anacostia Riverkeeper (AK). The Anacostia Watershed Society (AWS) and the DC Department of Environment (DC DOE) also monitor these sites, allowing for comparison with current and historical data. Additional sites were added to monitor certain locations such as near RFK where they are building storage tanks to hold the overflow (began on 8/21/13) and Pennsylvania Avenue Bridge near a CSO (began on 5/29/13).

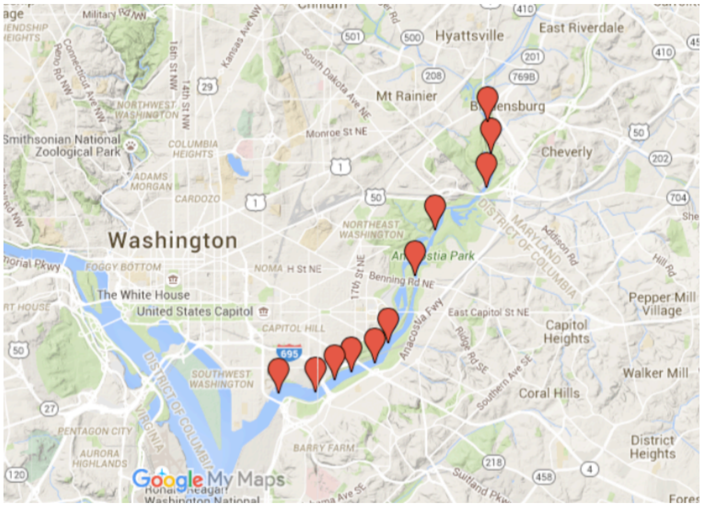

Figure 5: Sampling sites on the Anacostia River (as shown by the red dots)

Bioassay experiments conducted by undergraduate students characterized the phytoplankton community composition of the River with water collected from two highly contrasting sites impacted by high concentrations of NH_4^+. Aliquots of water from each site were variably enriched with NH_4^+ and NO_3^-, with and without supplemental additions of phosphate to produce a range of nutrient supply ratios. Treatments were incubated under natural light and temperature conditions for a period of 4 days, during which phytoplankton community composition, biomass accumulation and productivity were monitored and recorded.

Samples from the River and in bioassay experiments were analyzed for (1) concentrations of nutrients, including NO_3^-, NH_4^+, urea and total phosphorus (TP) (2) chlorophyll and associated pigments (3) nitrogen uptake and enzymatic activity and (4) phytoplankton and bacterial composition. Fish data was obtained from District Department of Environment (DOEE).

(1) Nutrients: NO_3^- was analyzed according to the vanadium (III) reduction method (Miranda et al. 2001, Doane and Horwath. 2003), NH_4^+ by the method of Parsons et al. (1984), urea by the method developed by Revilla et al. (2005), and total phosphorus (TP) by the method of Valerrama (1981).

(2) Chlorophyll and associated pigments: Chlorophyll was measured using a modified protocol of Parsons et al. (1984) on a Turner 10-AU flourometer while pigment samples were sent to the analytical services at University of Maryland's Horn Point Laboratories for analysis via high-performance liquid chromatography (HPLC Model 110 system; van Heukelem et al. 1994, van Heukelem and Thomas, 2001).

(3) Uptake and enzymatic activity: Nitrogen uptake rates of the collected phytoplankton community was analyzed according to Glibert and Capone (1993). Enzymatic activity such as urease (Solomon et al. 2007) was measured to better understand how rapidly these phytoplankton utilize the respective nitrogen sources.

(4) Phytoplankton and bacterial composition: Samples for phytoplankton and bacteria enumeration were collected and preserved with 4% glutaraldehyde or Lugol's solution, stored at 4°C until stained with DAPI (4'-6-Diamidino-2-phenylindole) and counted on an epiflourescent microscope. The phytoplankton and microbial community size structure was determined by flow cytometry by the undergraduate students under the guidance of a doctoral student at University of Maryland. DNA samples were also collected on 7/29/16 and 11/16/16 at sites 1, 5 and 9 for genetic identification of different viral and bacterial species.

(5) Fish population surveys. The District Department of the Environment (DOEE) did surveying and inventory of anadromous fish at one site on the Anacostia River (downstream of Pennsylvania Ave Bridge; near site 7B) in May, July, September and November. Alosine species were caught using a 50" x 38" x8" (width x depth x length) mesh net (1/8 inch mesh) hung on a pivoting tubular metal frame from the bow of the boat and deployed for a ten minute period. Approximately 0.83 miles was covered at a constant speed of 5 mph at each sampling event. All alosine species are collected, enumerated, measured and saved for otolith extraction (DOEE, 2017).

Results and Discussion

a. Physical data:

The year 2016 was a dry year with high total precipitation in May and June (Figs. 6A & B). Average temperatures ranged from 10 to 30.5°C (Fig. 7), while average dissolved oxygen was the lowest during the summer months (June, July and August) and highest in March and early April (Fig. 8). Dissolved oxygen levels were consistently the lowest mid-river (sites 6A and 6B).

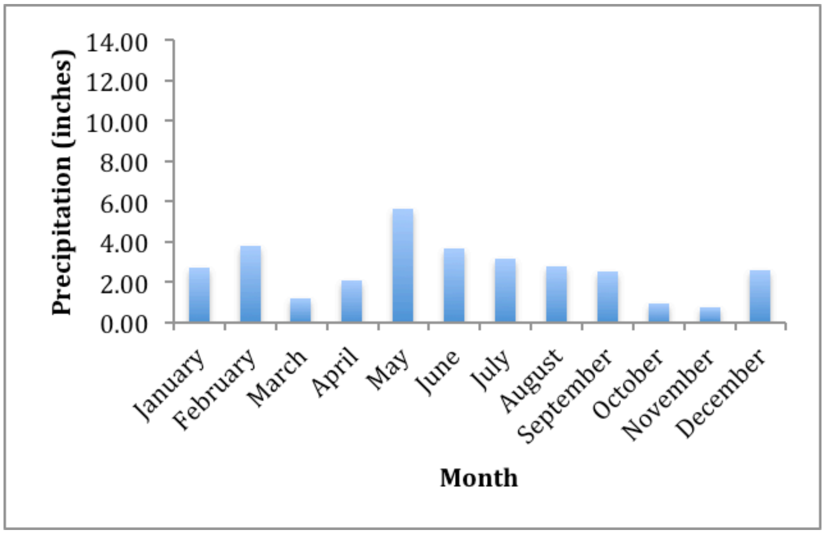

Figure 6A: Monthly precipitation during 2016 (data from the National Weather Service).

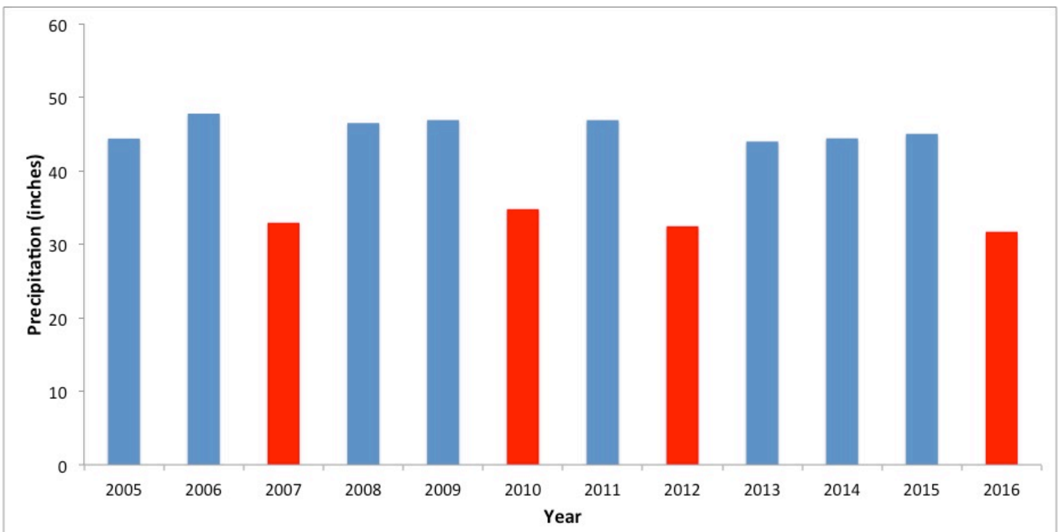

Figure 6B: Yearly precipitation in Washington, D.C. from 2005-2016. The red bars represent total rainfall less than average, while the blue bars represent total rainfall greater than average (data from National Weather Service).

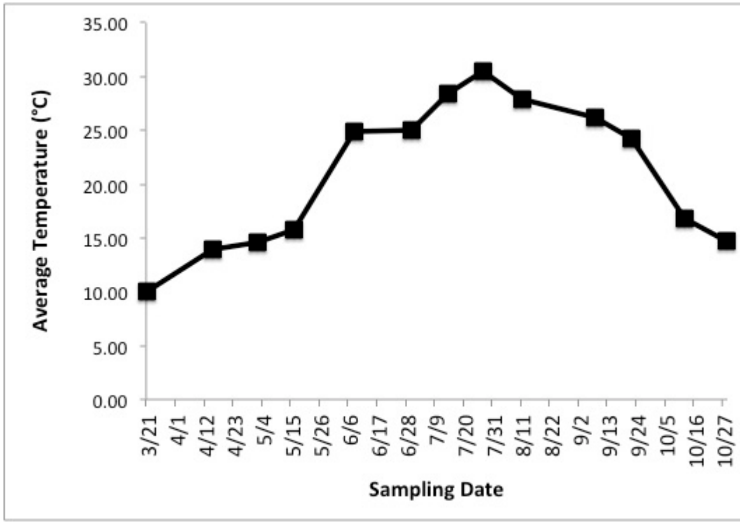

Figure 7: Average temperature of all sites on each sampling date during 2016.

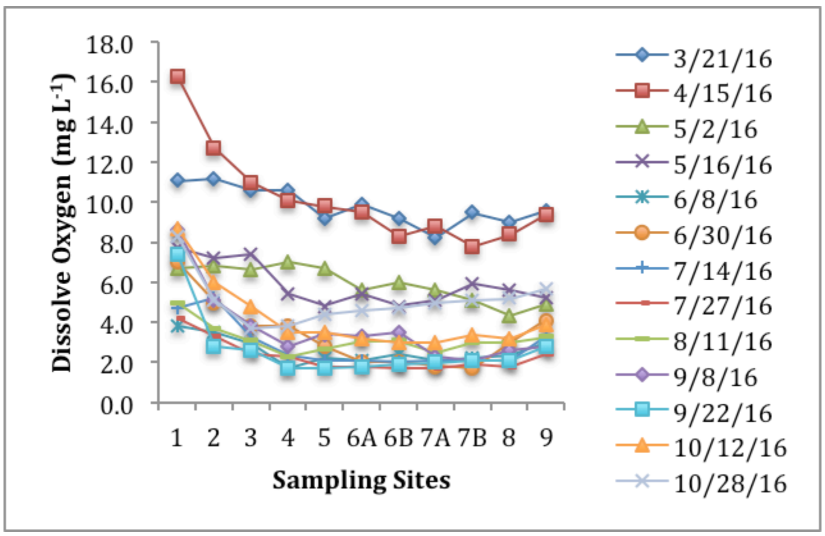

Figure 8: Dissolved oxygen concentrations at each site for each sampling date during 2016.

b. Biological data:

Most of the biological activity occurred during the late summer months in the Anacostia River. Chlorophyll *a* (chl *a*) concentrations increased in late June and remained high until September with the highest level 38.8 μg L^{-1} at site 9 on September 8 (Fig. 9). Chlorophyll concentrations were on average (8.73 μg L^{-1}) lower than previous years (2013 = 31.5 μg L^{-1}, 2014 = 16.6 μg L^{-1}, 2015 = 21.7 μg L^{-1}). Average chl *a* concentrations were 12.2 μg L^{-1} during 2002-2006 with the highest recorded chl *a* concentration of 61.8 μg L^{-1} in August 2002 (Chesapeake Bay Program, 2014) which suggests that 2016, in terms of chl *a* concentrations, was within range.

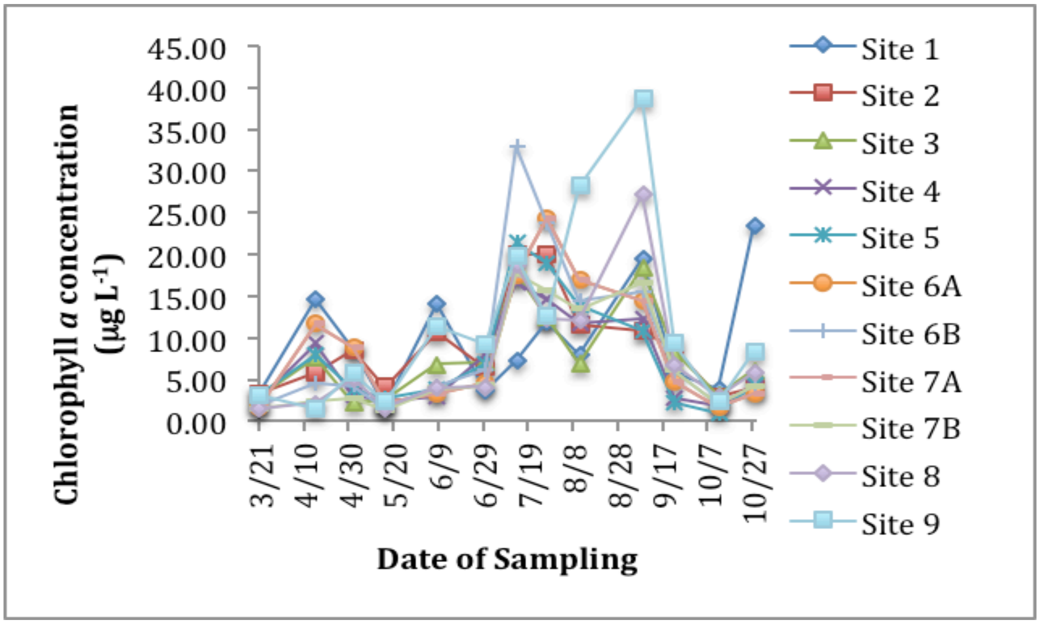

Figure 9: Chlorophyll concentrations in the Anacostia River during 2016.

c. Nutrient concentrations (NO_3^-, NH_4^+, urea, TDP)

Nitrogen concentrations along the river had different trends. NO_3^- concentrations in the upper portion of the river (Sites 1 & 2; 38.92-38.93°N) were higher than the rest of the river, reaching 67.5 μmol L^{-1} in spring (Fig. 10), while NH_4^+ concentrations were higher in the lower river (Sites 8 & 9; 38.87°N), reaching 41.3 μmol L^{-1} in the summer months (Fig. 11). Comparisons with historical NH_4^+ data from 2002-2006 that was available via the Chesapeake Bay Program revealed that the highest concentration was 13 μmol L^{-1} during July 2003. We have historically observed higher NH_4^+ concentrations since we started sampling the river in 2013. We have measured urea concentrations as part of our routine monitoring, and to our knowledge there is no other group measuring this N source to the river. Urea concentrations in 2016 were never higher than 5 μmol L^{-1} (Fig. 12) and were higher in the lower portion of the river with the exception of October.

TDP concentrations during the early months of the year were below 2 μmol L^{-1} (Fig. 13). Bioassay experiments (discussed later) suggest that the Anacostia River is a P-limited system during the summer months.

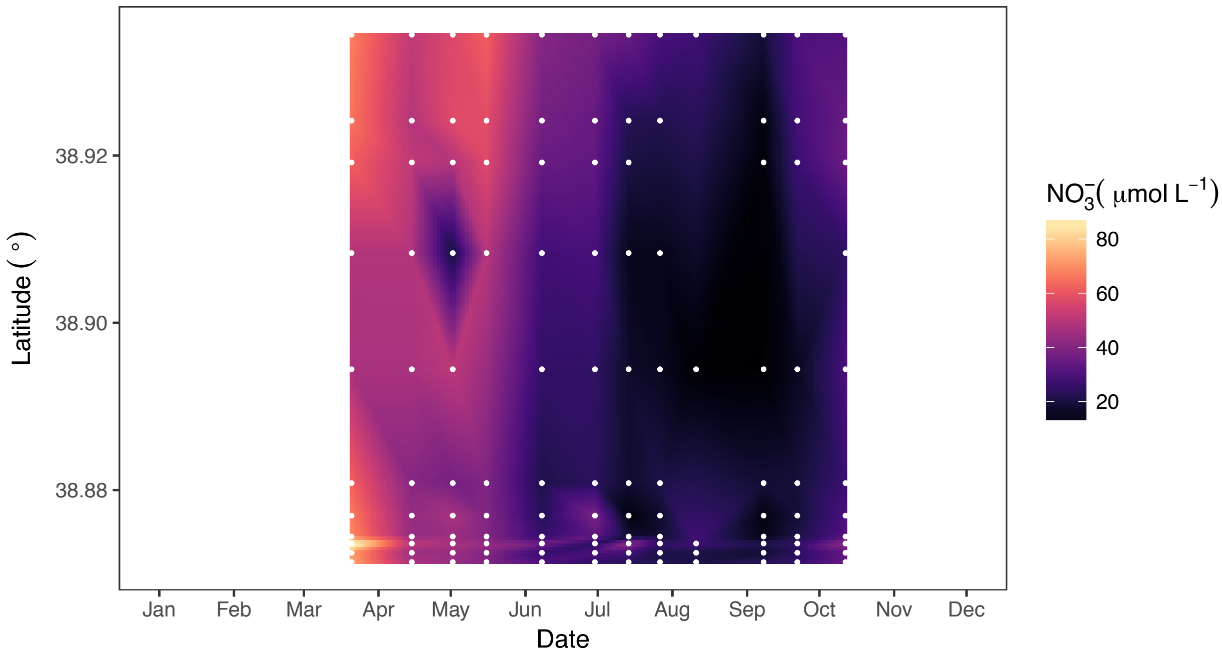

Figure 10: $N0_3^-$ concentrations in the Anacostia River during 2016 (graph by Melanie Jackson).

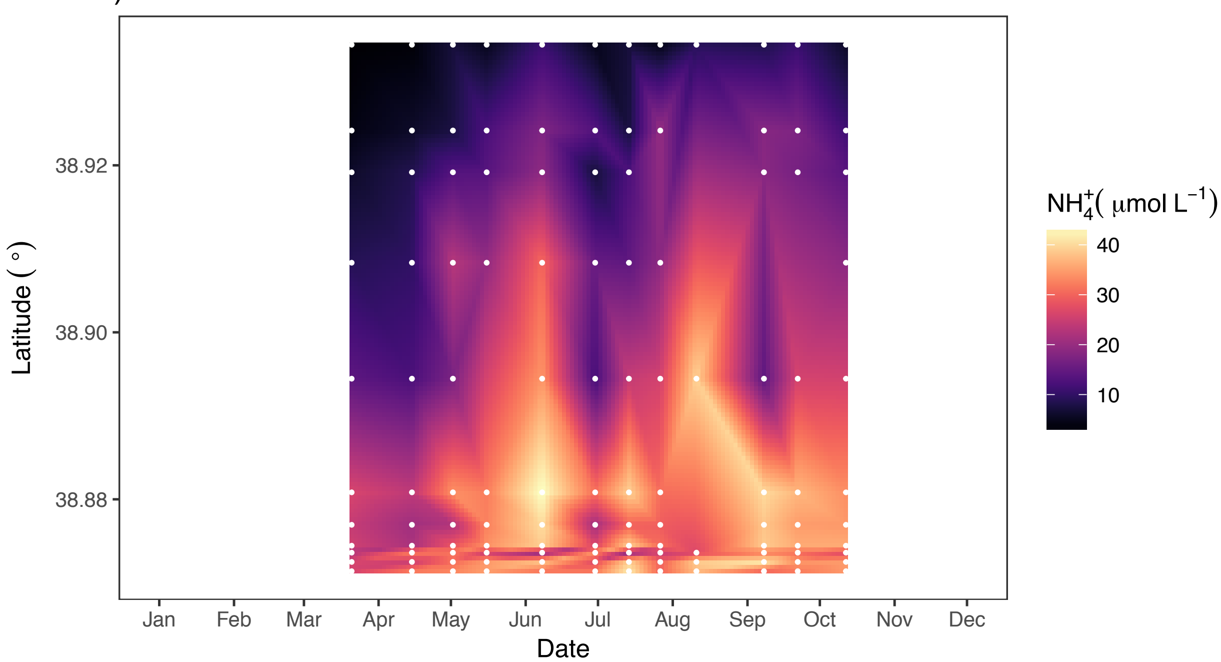

Figure 11: NH_4^+ concentrations in the Anacostia River during 2016 (graph by Melanie Jackson).

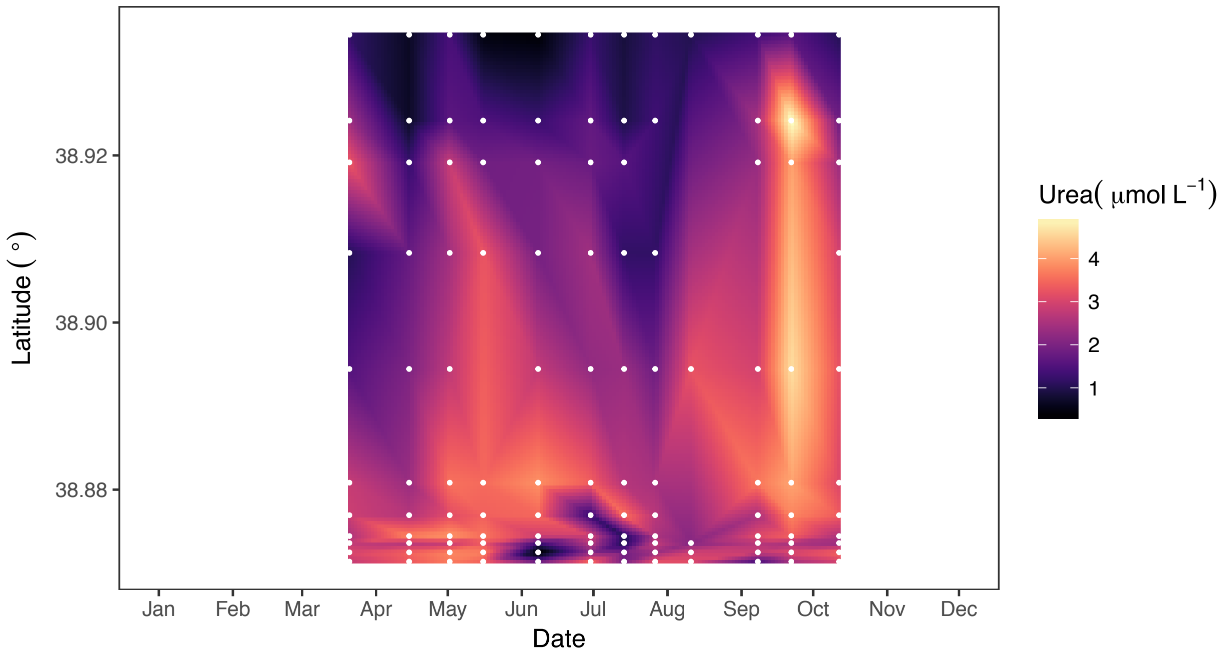

Figure 12: Urea concentrations in the Anacostia River during 2016 (graph by Melanie Jackson)

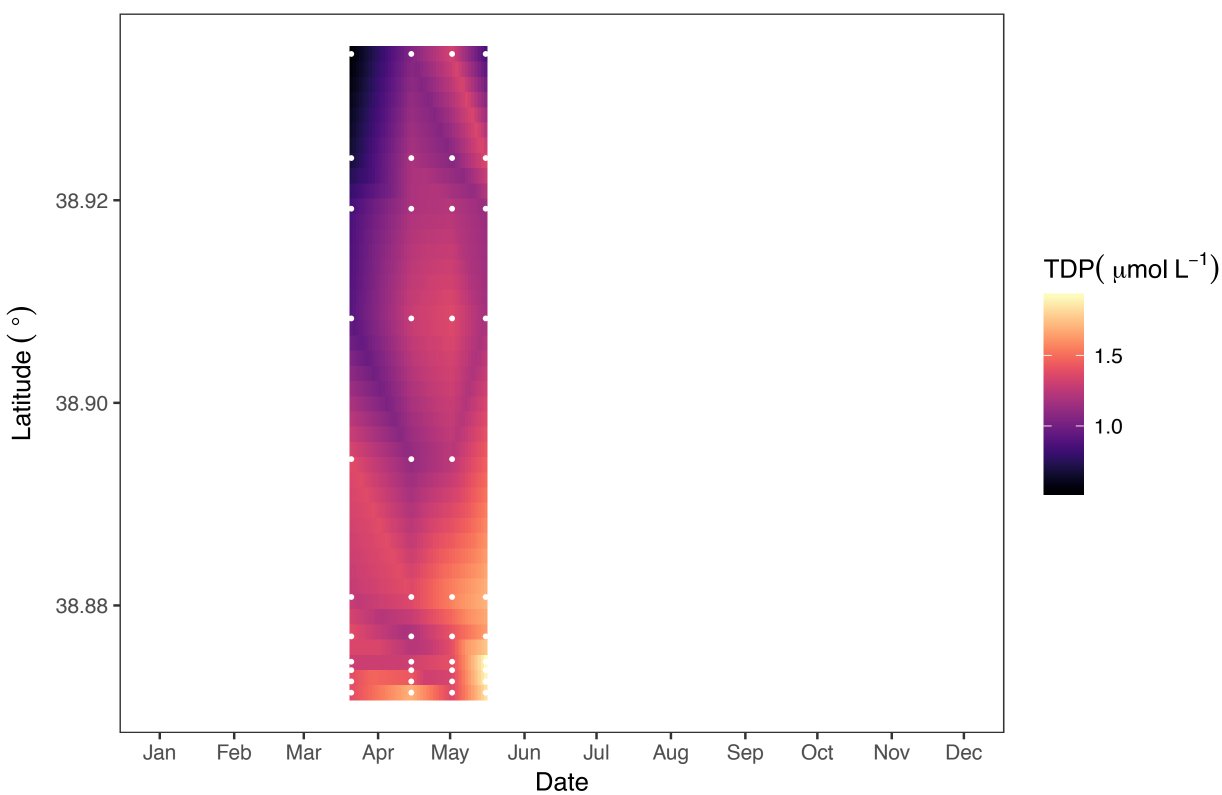

Figure 13: Total dissolved phosphorus (TDP) concentrations in the Anacostia River during early 2016 (graph by Melanie Jackson).

d. Biochemical rates (NH_4^+ uptake and urease activity)

NH_4^+ uptake was only measured at sites 1, 5 and 9. Samples are currently being analyzed by the Glibert lab at University of Maryland Center for Environmental Science, Horn Point Laboratory.

The highest urease activity occurred in late May, with some peaks of activity during the summer (Fig. 13) and were higher in 2016 than previous years (Fig. 14). Urease activity was higher at times in lower portion of the river (e.g. Site 8) when NH_4^+ concentrations were between 25-35 μmol L^{-1} which is surprising because urease activity can be suppressed by high ammonium concentrations (Solomon et al. 2010). Urease activity rates tend to be the highest during the summer months (Solomon, 2006), so rates observed in 2016 are within range with previous observations in the mainstem Chesapeake Bay. Further investigation will find whether those peaks of activity correspond with certain phytoplankton species and NO_3^-:NH_4^+ ratios.

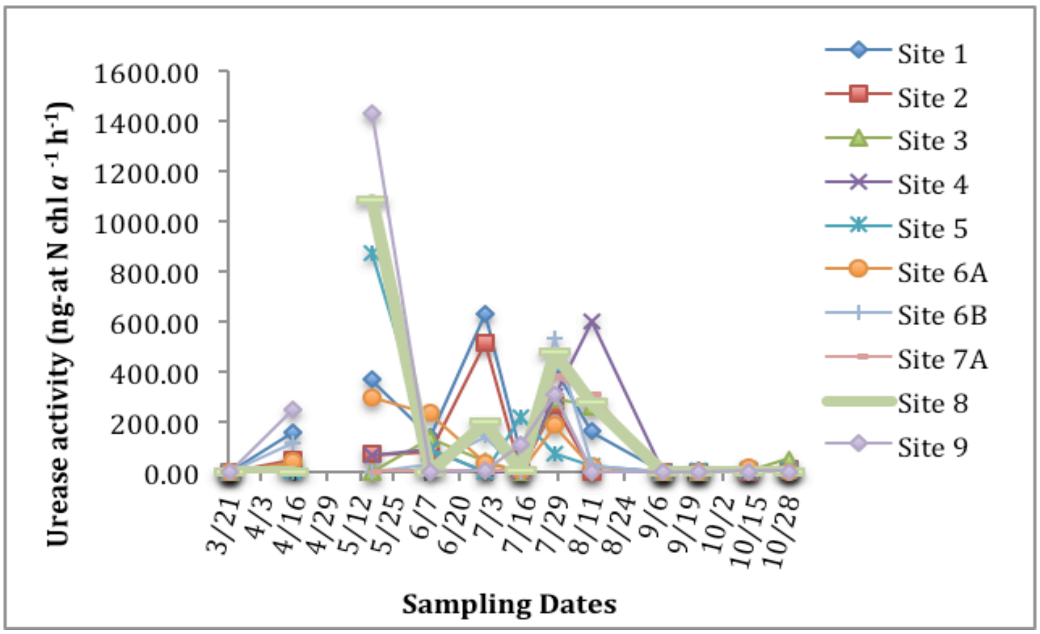

Figure 13: Urease activity rates normalized for chl *a* in the Anacostia River during 2016.

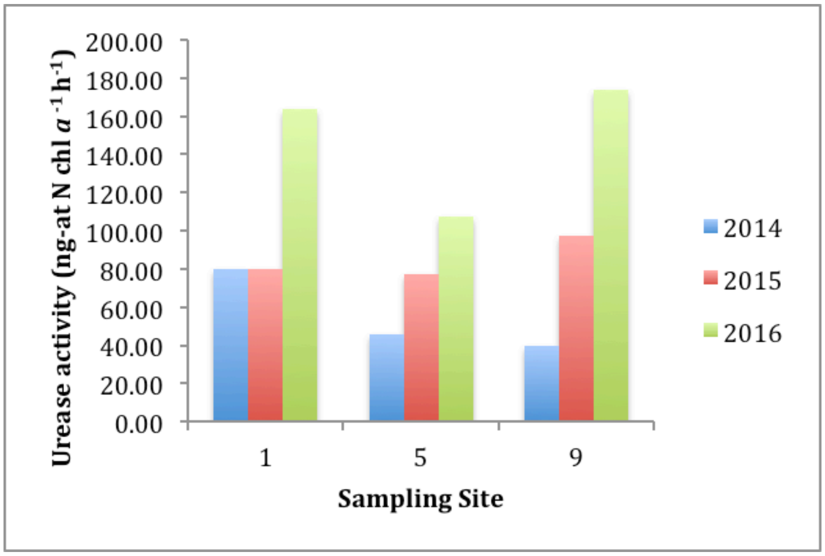

Figure 14: Average urease activity rates at Sites 1, 5, and 9 during three years (2013-2016).

e. <u>Fish data</u> (provided by DOEE)

Fish data was collected by DOEE at only one site on the Anacostia River in 2016 near site 7B which is situated near a CSO. American shad was present at 41.85 fish/1000m^3 which was lower than in 2015 (91.24 fish/1000m^3). The same was true for alewife (4.94 as opposed to 54.48 fish/1000m^3), blueback herring (571.44 as opposed to 1341.1 fish/1000m^3). The Anacostia River had the highest abundance of all three fish among the two rivers that flow through DC.

4. Bioassay experiment

The bioassay experiment was performed during the first week of July 2016. Water was collected on June 30 and then the experiment was started at University of Maryland Center for Environmental Science's Horn Point Laboratory on July 1. There were six nutrient addition treatments (NO_3^-, NO_3^-+P, NH_4^+, NH_4^++P, urea, P) in addition to the control. All nutrients were utilized during the course of the bioassay experiment at both sites with the exception of a few treatments at both sites (Figs. 16-19). There was more utilization of NO_3^- in most treatments on the second and third days of the experiment at Site 1 (which had a high NO_3^-:NH_4^+ratio; 7.52; Fig. 16) while it was much lower at Site 9 (which had a low NO_3^-:NH_4^+ratio, 0.72; Fig. 17). Utilization of NH_4^+ was higher at Site 9 on the second and third days of the experiment (Figs. 17 & 19). Urea was utilized at lower rates at both sites, but was higher at Site 1 after both 24 and 28 hours (Figs 16-19).

The composition of the microbial community was analyzed via changes in chlorophyll *a* concentrations (Fig. 20), flow cytometry analyses (Fig. 21) and pigment analyses (Fig 22 & 23). The highest increase in chlorophyll *a* was in the +P treatments at both sites (Fig. 20), suggesting P-limitation. The +P treatments at Site 1 saw an increase in both picoeukaryotes and nanoplankton which may be primarily cyanobacteria, diatoms and chlorophytes (Figs. 21 & 22). A similar response was seen at Site 9 that also saw an increase in primarily nanoplankton which were diatoms and chlorophytes (Figs. 21 & 23). A previous bioassay experiment conducted in June 2014 that exposed water from the same sites to a gradient of NO_3^- and NH_4^+ additions found that after 48h with NO_3^- additions the percentage of diatoms increased at both sites. The percentage of cyanobacteria increased with NH_4^+ additions at both sites as well (Jackson 2016).

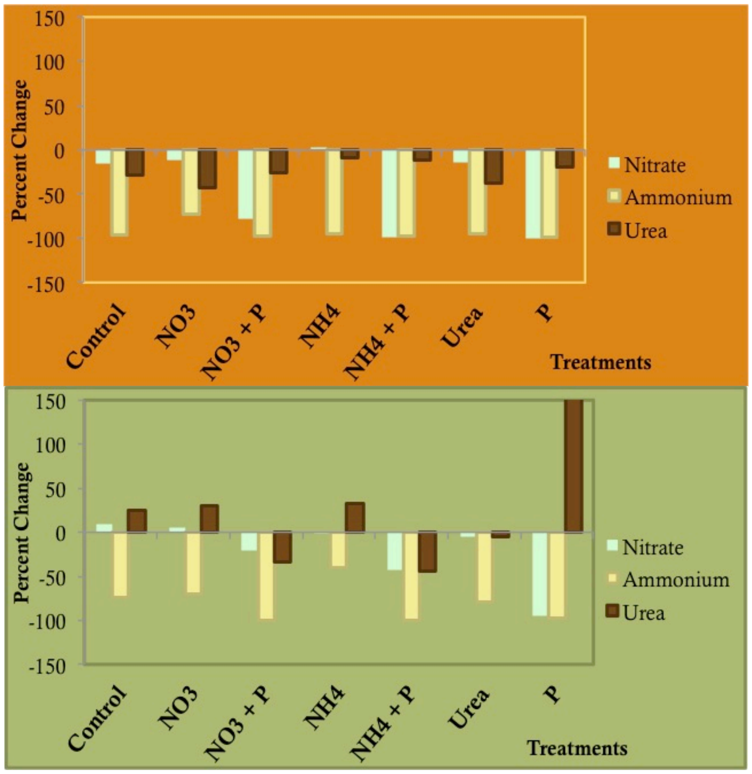

Figure 15: Change in nutrient concentrations (NO_3^-,NH_4^+, urea, TDP) for site 1 (top, orange) and site 9 (bottom, green) during the course of the bioassay experiment (from summer intern Ana Salzar's research poster).

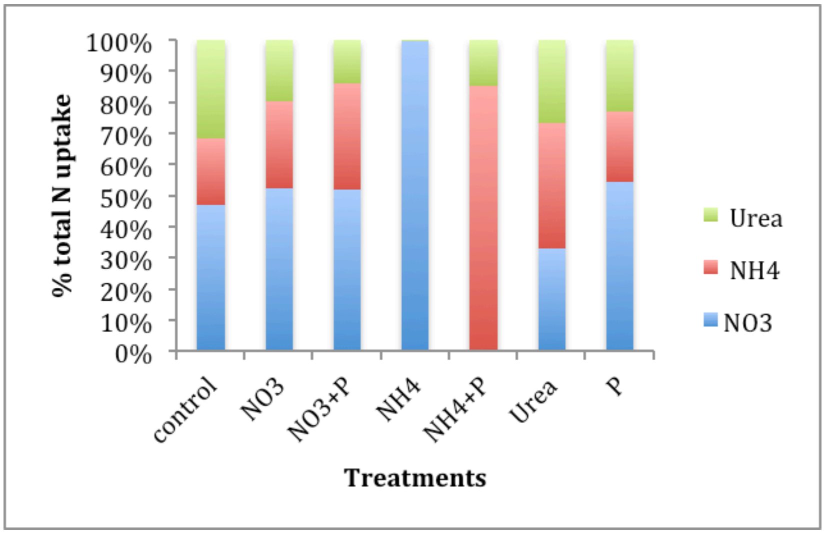

Figure 16: Percentage of N uptake for Site 1 on Day 2 (t_{24})

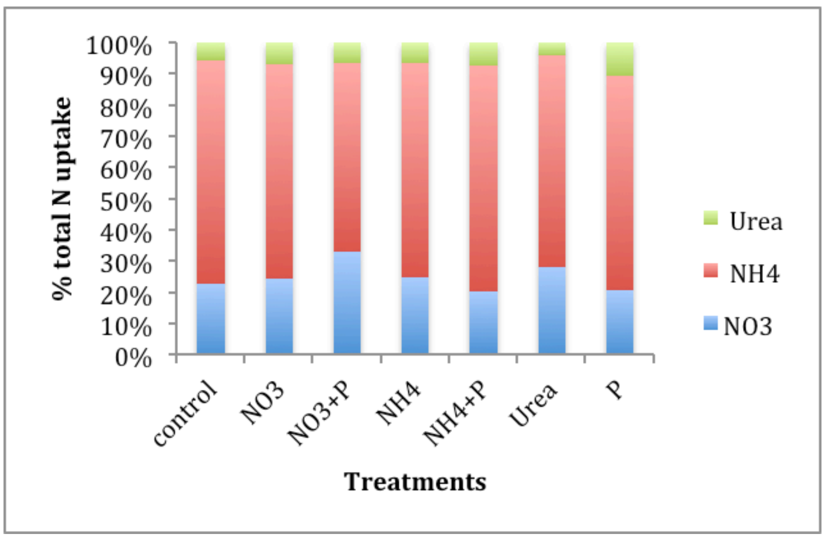

Figure 17: Percentage of N uptake for Site 9 on Day 2 (t_{24})

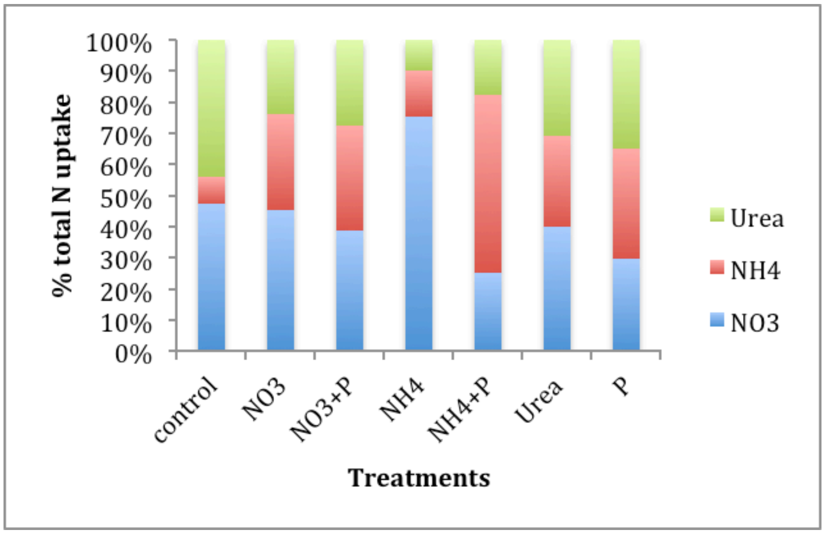

Figure 18: Percentage of N uptake for Site 1 on Day 3 (t_{48})

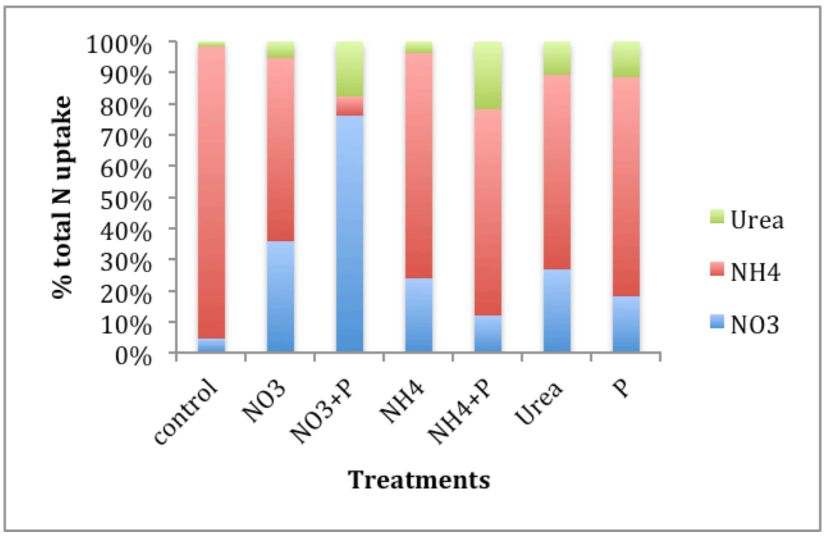

Figure 19: Percentage of N uptake for Site 9 on Day 3 (t_{48})

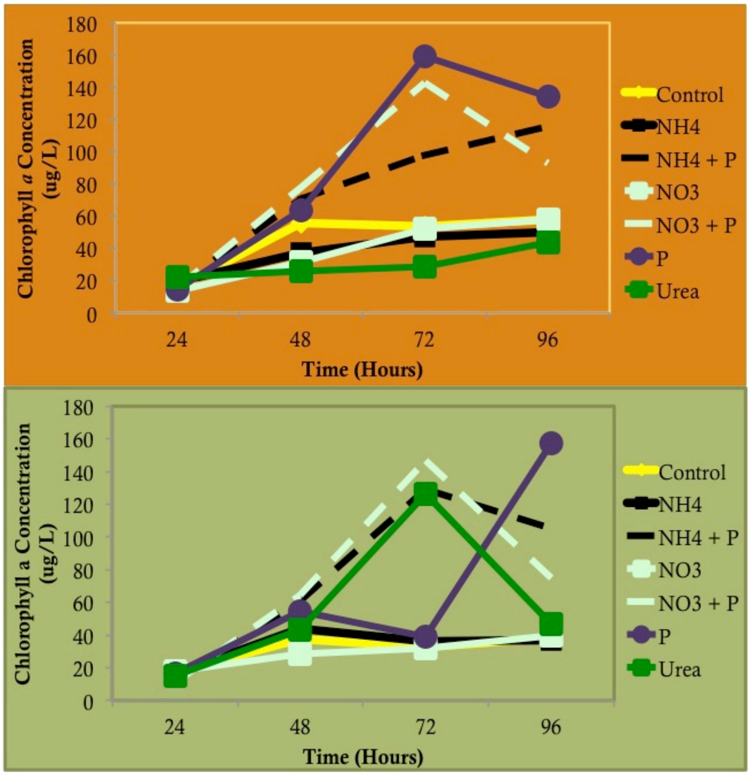

Figure 20: Change in chlorophyll *a* concentrations site 1 (top, orange) and site 9 (bottom, green) during the course of the bioassay experiment (from summer intern Ana Salzar's research poster).

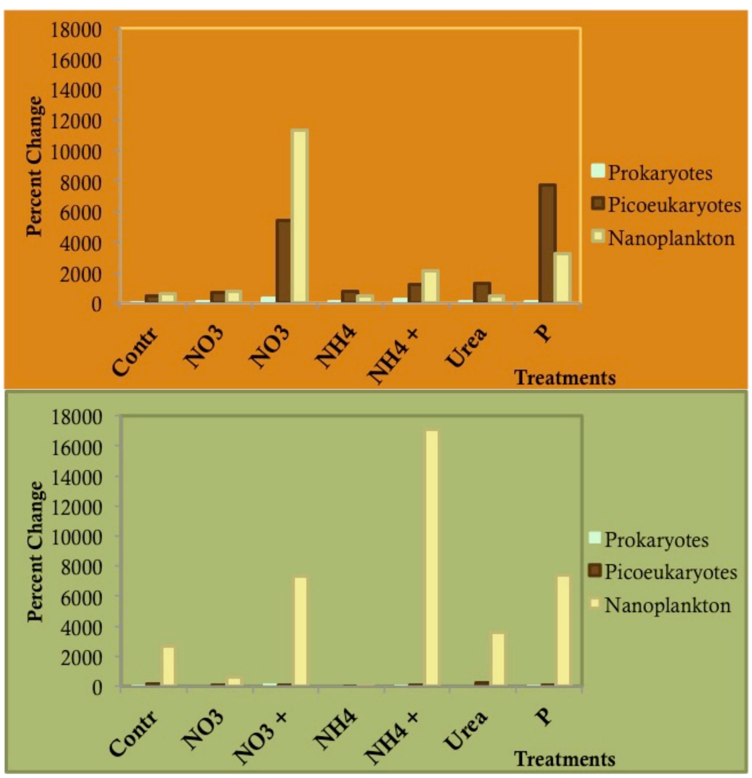

Figure 21: Change in microbial community (top, orange) and site 9 (bottom, green) during the course of the bioassay experiment as determined by flow cytometry (from summer intern Ana Salzar's research poster).

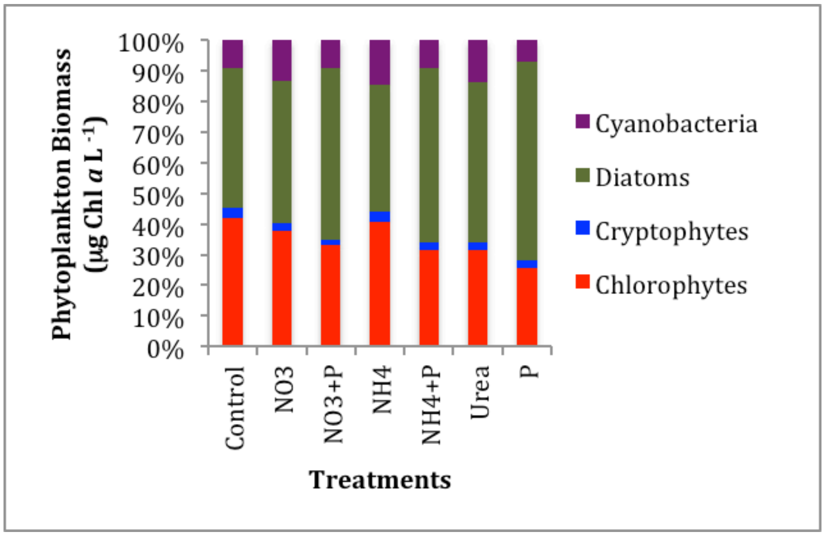

Figure 22: Site 1 phytoplankton biomass and composition on the last day (t_{96}) of the bioassay experiment as determined by HPLC

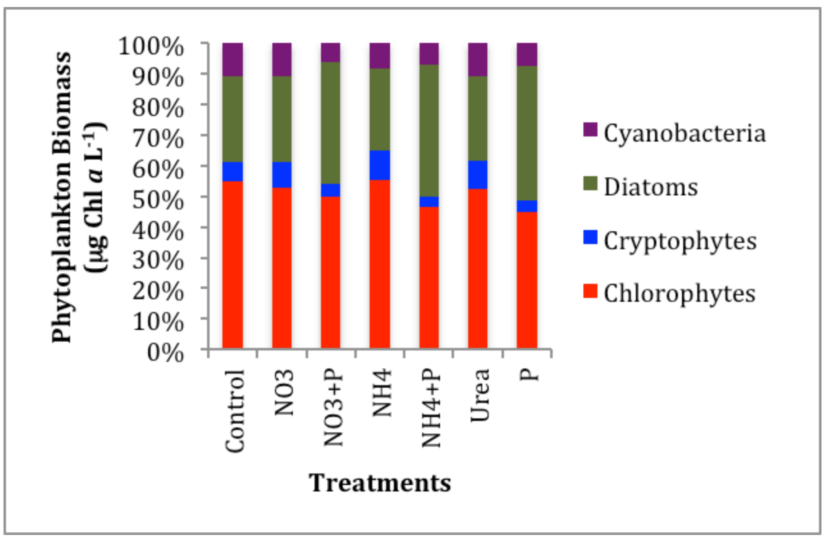

Figure 23: Site 9 phytoplankton biomass and composition on the last day (t_{96}) of the bioassay experiment as determined by HPLC

5. Project outcomes and presentations

a. Collaborations

This project resulted in a successful collaboration with the Anacostia Riverkeeper (AK).

b. Presentations

Summer 2016 interns, Ana Salazar and Kiel Callahan, presented their results to the campus community including several Anacostia River stakeholders (e.g. Anacostia

Riverkeeper) at the end of the summer as part of their internship. They also presented their work at the University of Maryland Baltimore County's Undergraduate Research Symposium in October 2016 in which one of them won first place in their group. Dr. Solomon also traveled during the year to the University of Wyoming (Spring 2016), Tall Timbers Research Station (Tallahassee, Florida; Summer 2016), and Cornell University (Fall 2016) and gave research talks focusing on this project.

c. Weaving the project into the curriculum
Data from the study was used in courses taught by Dr. Solomon to spread awareness among students and the campus community during the Spring 2015, Fall 2016, and Spring 2017 semesters. During the fall 2016 semester, Dr. Solomon taught Ecology in which the two summer interns were also taking at the time so often called on the two students to provide insight on an ecological concept based on their summer research. Other efforts included sharing research results with the Gallaudet University community via the campus research expo (March 2016).

d. Additional funding
Data from the study allowed us to apply for further funding from Maryland Sea Grant (and at the time of this report, we were asked to submit a full proposal) and receive continuous funding from an anonymous donor to continue our work on the Anacostia River.

6. Student support

Two summer undergraduate interns, Ana Salazar and Kiel Callahan, were involved with the project during Summer 2016. They were involved with all sampling trips and all the nutrient analyses.

Melanie Jackson, a MS student at University of Maryland, was involved with the study starting in March 2014, and continued during the time period of this grant. Another graduate student, Yexin Lin, was supported by this grant over the summer months and provided guidance to the undergraduate students on how to conduct the bioassay experiments and run flow cytometry analyses.

7. Conclusion

The year 2016 was different than the other years (2013-2015) sampled due to lower precipitation that resulted in lower NO_3^- concentrations, but higher NH_4^+ concentrations may have been fueled by higher urease activity. Future analysis of this data will include comparisons between those years and how precipitation and nutrient concentrations influence nutrient and phytoplankton dynamics in the Anacostia River.

The bioassay experiment conducted in early July provided a peek into the nutrient and phytoplankton dynamics of the river. The two sites (site 1 and site 9) were chosen because of the contrast in NO_3^-:NH_4^+ ratios. The phytoplankton community composition was initially different but nutrient additions such as NO_3^- promoted more growth of diatoms while NH_4^+ additions promoted more growth of chlorophytes and cyanobacteria. The largest growth occurred when P was added with or without a N source, suggesting the Anacostia River is P-limited during the summer months. NO_3^- is utilized more at Site 1 while NH_4^+ is utilized more at Site 9, and this has implications on understanding controlling N and P inputs to the Anacostia River during the summer months.

8. Acknowledgements

Our work on the Anacostia River was supported by grants from the DC Water Resources Research Institute and an anonymous donor who also supported our project. Our collaboration with the Anacostia Riverkeeper allowed us to go out bi-weekly on their boat. They donated their staff time so that one staff person could accompany us and drive the boat.

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Assessing the effectiveness of interactive signage at advancing communicating, promoting, and educating the public on green infrastructure projects in public spaces

Basic Information

Title:	Assessing the effectiveness of interactive signage at advancing communicating, promoting, and educating the public on green infrastructure projects in public spaces
Project Number:	2016DC177B
Start Date:	3/1/2016
End Date:	2/28/2017
Funding Source:	104B
Congressional District:	DC
Research Category:	Climate and Hydrologic Processes
Focus Categories:	Education, Surface Water, Hydrology
Descriptors:	None
Principal Investigators:	Kamran Zendehdel, Harris Trobman, Xiaochu Hu

Publications

There are no publications.

Cover Page

Assessing the effectiveness of interactive signage at advancing communicating, promoting, and educating the public on green infrastructure projects in public spaces

Progress Report

Kamran Zendehdel, Principal Investigator

College of Agriculture, Urban Sustainability and Environmental Sciences

University of the District of Columbia

April 27th 2017

Executive Summary:

Managing the challenge of urban stormwater runoff is a significant local and global issue. The urbanization of society in line with the climate change issue, lend to the increasing scope of this problem. Using GI to systemically control the stormwater problem is in its early stage. The nature of this research is to evaluate the public perception in public areas where people are exposed to GI projects regularly. In this way, we will have a better understanding of how people are communicating with these projects and how much they know about the environmental benefits of these projects. In addition, we want to evaluate how much installation of an interactive sign can provide a meaningful and comprehensive education to the community and people in UDC's main campus. We hope that the application of this project will enhance people's understanding about the environmental benefits of GI practices.

Introduction

Effective education, training, and communication is among the toughest challenges for achieving widespread adoption of Green infrastructure (GI) practices in the nation as well as in the District of Columbia. Despite significant advancement and strong efforts of organizations in GI applications in the District of Columbia major barriers exist in effective education of public about the environmental benefits of GI practices. Multiple agencies within Washington DC are applying GI practices to minimize the stormwater runoff problem without a clear plan. As a result Washington DC has become a leader in implementing green infrastructure including leading the United States in green roof coverage. Despite this limited results have been transferred to water quality improvements in Anacostia and Potomac rivers.

Lack of a clear understanding of GI practices and their associated environmental benefits has reduced the advancement of GI practices in the District. The advancement of green infrastructure is limited by the public perception and adoption of these practices taking advantages of incentives to implement this on their own private property. The main question in this research is to find the most effective way to educate students about GI and environmental issues, as well as to design the most effective signage to attract, engage, and motivate the students to learn about green infrastructure and to increase awareness environmental issues. New emerging forms of interactive education forms combined with informal education have been shown to pose great potential in behavioral changes within environmental spaces.

Data Collection and Methods

We conducted survey on four groups of UDC undergraduate, non-environmental major students to capture their attitude, knowledge, and behavior in terms of stormwater management, green infrastructure and water protection. Four undergraduate, general education groups each of about 25 students were selected in spring 2017 semester to participate in this data collection. Three of the four groups were be invited to involve in one kind of the following interventions: signage exposure, lecture, and in-person tour experience, then after the intervention, we asked them to fill in the survey. The fourth group were not be given any intervention and the survey collected from them serve as the baseline. More specifically, Group A were be asked to stay in a classroom or open space with environmental signage we design for 20 minutes, and then asked to fill in the survey. Our surveyor/observers took notes on how much time each student spent on reading each of the signs. Group B were be given a 20-minute lecture about green infrastructure information, then asked to fill in the survey. Group C were be given a 20-minute tour around UDC Van Ness campus about green infrastructure and then asked to fill in the survey. Each intervention is designed to be more comprehensive than the previous one (signage exposure being the least comprehensive, and tour being the most comprehensive), and our hypothesis is that more comprehensive intervention has a larger impact and more effective in affecting students' attitude, knowledge, and behavior in terms of stormwater management, green infrastructure and water protection.

The four sets of survey results will be analyzed in statistical software Stata using ANOVA test and multiple regression. In the questionnaire, we also collect students' grade, credit hour in environment-related courses, as well as demographic information, to be controlled in the regression models.

Project outcomes, presentations, publications (book chapter journals or conference proceedings)

The project is in its final stage and we have done many parts of the project as follow:

Completed Tasks (Aug 2016 – April 2017)

- Received a conditional approval from IRB committee in March 2017
- Refined research design and methods
- Designed and produced samples of green infrastructure signage
- Hired and trained a student assistant to collect and input data
- Developed and implemented questionnaires

We also designed a timeline to be able to finish the project by August 2017. We are currently analyzing the data in April – May 2017 and the final report will be produced by June 10, 2017. The next step will be the focus group study and green infrastructure sign design and installation. We are expecting to have the project final report in August 2017.

Students Support

We have been able to hire one student to conduct the surveys and collect data. We are going to hire another student to work on green infrastructure (GI) sign design soon. The project will give these two students to learn about green infrastructure, the educational impact of these GI projects as well as survey design, data collection and data analysis.

Acknowledgement

We would like to express our special thanks to the UDC Water Resources Research Instituted to provide us with funding for this project. We also have our special thanks to Professors Christopher D. Ellis and Kweon Byoung-Suk from University of Maryland for their insightful advice in refining the research design. We also would like to thank Professors Amanda Huron, Andrea Royal, and Naseem Sahibzada at University of the District of Columbia for their help in volunteering students to participate in the study. Last, we thank our UDC student research assistants Gabriela Borowiec, Juan Urey, Tony ** and Helder Arch, who provided excellent support in designing signage, collecting and inputting data.

Conclusion:

We are in the processes of analyzing the collected data and we will have our conclusions within next two months.

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Appendix 1 - Survey Instrument

Dear students,

We need your help. UDC's College of Agriculture, Urban Sustainability and Environmental Science (CAUSES) is conducting a survey about green infrastructure in neighborhoods in Washington, D.C. This study will help us understand how to work with residents to install green infrastructure in neighborhoods in the most efficient way. It is only with the generous help of people like you that we will be able to understand better attitudes and approaches to stormwater management.

Your participation in this research study is voluntary. You may choose not to participate. If you decide to participate in this research survey, you may stop at any time. Your responses will be kept confidential. All data will be stored in a password protected electronic database. The results of this study will be used for scholarly purposes only.

Thank you,

Kamran Zendehdel, Ph.D.

Harris Trobman

Xiaochu Hu, Ph.D.

If you have any question please contact Dr. Zendehdel.

(Tel: (202) 274-7161; Email: kamran.zendehdel@udc.edu)

Center for Sustainable Development and Resilience
College of Agriculture, Urban Sustainability and Environmental Sciences (CAUSES)
University of the District of Columbia

To start with, here are some terms that you may need to know:

- **Stormwater**, also called runoff, is water that originates during precipitation events and snow/ice melt. Stormwater can soak into the soil (infiltrate), be held on the surface and evaporate, or runoff and end up in nearby streams, rivers, or other water bodies (surface water).
- **Green infrastructure practices** such as rain gardens, rain barrels, greenroof, Vegetated swale, stormwater retention and detention ponds and permeable pavements are becoming more popular as a means of reducing stormwater runoff, improving water quality, and in some cases for conserving water. These green infrastructure practices capture rainwater where it lands and help it infiltrate into the ground, often by using soil and plants.
- **Urban Resilience** is the capacity of individuals, communities, institutions, businesses, and systems within a city to survive, adapt, and grow no matter what kinds of chronic stresses and severe shocks such as flooding, economic shocks and inequality they experience.

1. How much of a risk do you feel each of the following poses to your community health and well-being?

	1=No risk at all	2=Minor risk	3=Moderate risk	4=Major risk	5=Don't know
a. Exposure to chemicals, including pesticides, in food and other products	❍	❍	❍	❍	❍
b. Air pollution	❍	❍	❍	❍	❍
c. Extreme heat	❍	❍	❍	❍	❍
d. Severe storms	❍	❍	❍	❍	❍
e. Obesity	❍	❍	❍	❍	❍
f. Polluted drinking water	❍	❍	❍	❍	❍
g. Climate change	❍	❍	❍	❍	❍
h. Flooding	❍	❍	❍	❍	❍
j. Pollution of local streams, rivers, and other water bodies	❍	❍	❍	❍	❍

2. In the last 12 months, have you experienced one or more of the following? (Check ALL that apply)

	Check ONE or MORE
a. Water damage of your home caused by heavy rains or flooding	❍
b. Impassable roads due to flooding or storm damage	❍
c. Sewage overflows after strong rains or storms	❍
d. Septic system failure due to higher groundwater or flooding	❍
e. A storm-related power outage	❍
f. No household water	❍
g. No household heat (when needed)	❍
h. No household air conditioning (when needed)	❍
i. Lack of access to transportation	❍

j. Lack of access to high quality/nutritious food	❍
k. None of the above	❍
l. Other	❍

3. How much is *Urban Resilience* important from your point of view?

- ❍ Extremely important
- ❍ Very important
- ❍ Somewhat important
- ❍ Not very important
- ❍ Not important at all

4. Do you know that DC has a city wide Sustainability Plan (*DC Sustainable Plan*)?

- ❍ Yes
- ❍ No

5. Have you heard about green infrastructure projects that have been implemented under the DC Sustainable Plan?

- ❍ No
- ❍ I heard about them, but I cannot identify them in the city
- ❍ Yes, and I know where they are

6. To what extent do you believe UDC is green?

- ❍ Not green at all
- ❍ Not very green
- ❍ Neutral
- ❍ Fairly green
- ❍ Very green

7. Are you aware of UDC's green infrastructure projects?

- ❍ Never heard of them
- ❍ Heard of them, but I cannot identify them on campus
- ❍ Yes, I know where they are on campus

8. What are the green infrastructure practices that UDC has installed at its Van Ness Campus? (Check all that apply)

- ❍ Cisterns
- ❍ Rain Barrels
- ❍ Rain garden
- ❍ Greenroof
- ❍ Permeable pavers
- ❍ I do not know
- ❍ Other (please specify) ________________________________

9. Please rate your level of agreement about the following statements.

	1=Strongly Disagree	2=Somewhat Disagree	3=Neutral	4=Somewhat Agree	5=Strongly Agree
a. There are many things that I can personally do to help improve the stream/river/pond where I live.	❍	❍	❍	❍	❍
b. I pay attention to the annual water quality report in my area.	❍	❍	❍	❍	❍
c. I can easily identify a green infrastructure on campus and in my community.	❍	❍	❍	❍	❍
d. I believe green infrastructure practices can help reduce flooding and improve quality of water in our streams.	❍	❍	❍	❍	❍
g. I prefer the look of nicely kept grass than a rain garden.	❍	❍	❍	❍	❍
h. It is the government's responsibility to protect the water bodies.	❍	❍	❍	❍	❍
i. there are no benefits to students from UDC green infrastructure projects	❍	❍	❍	❍	❍
j. Green infrastructure projects can help students to learn about their environment	❍	❍	❍	❍	❍

10. What is your age? __________ years

11. What is your gender?

- ❍ Male
- ❍ Female

12. What is your grade at UDC?

- ❍ Freshman
- ❍ Sophomore
- ❍ Junior
- ❍ Senior
- ❍ Graduate or professional degree
- ❍ Non-degree seeking

13. How many credits related to environmental science have you taken at the college level? _________

14. What is your major in college? ___________

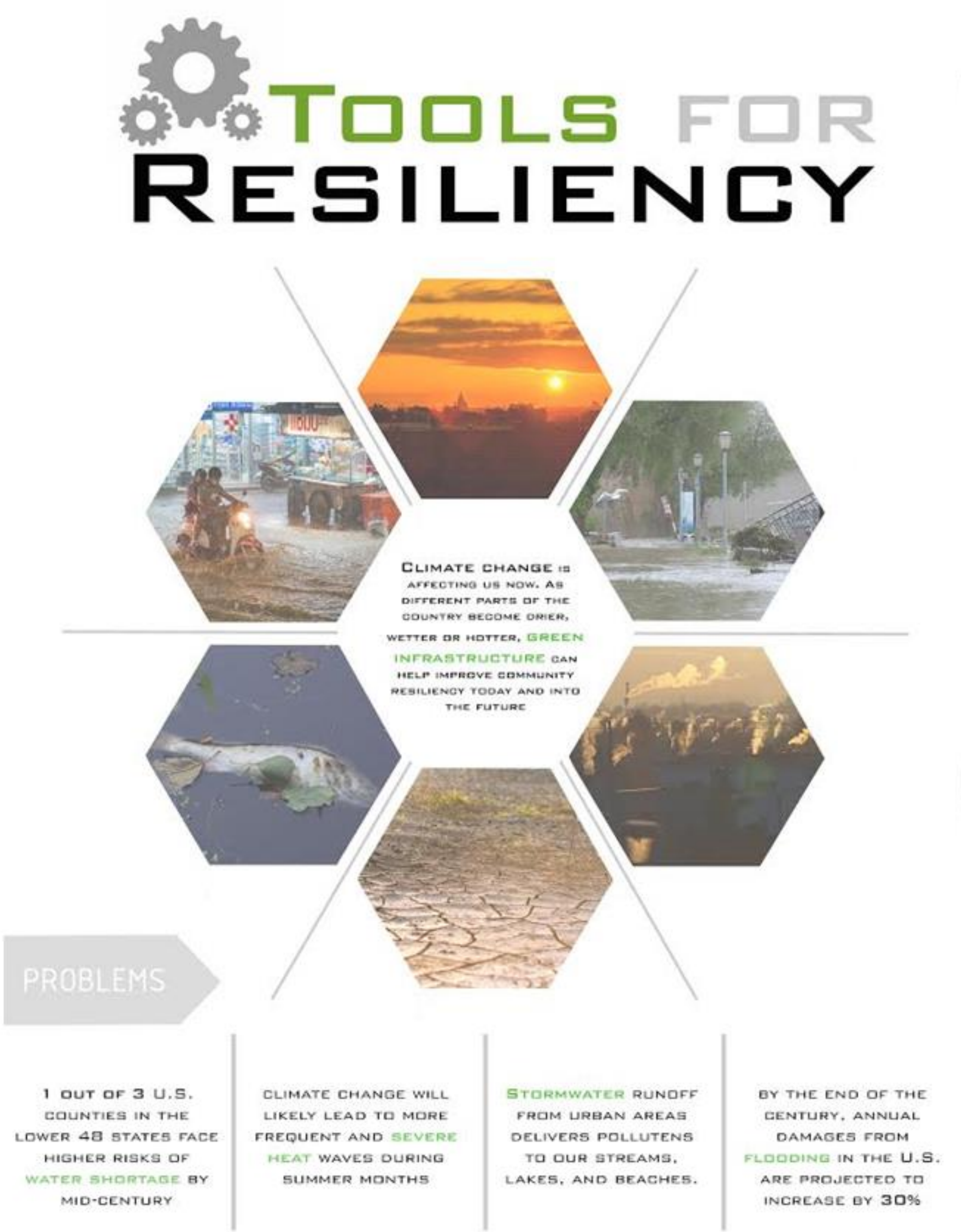
15. Do you consider yourself Hispanic?

- ❍ Yes
- ❍ No

16. Which race category best describes you?

- ❍ American Indian and Alaska Native
- ❍ Asian
- ❍ Black/African American
- ❍ Native Hawaiian and Other Pacific Islander
- ❍ White
- ❍ Some other race

Appendix 2 – Environmental Signage




SOLUTIONS
UNIVERSITY OF THE DISTRICT OF COLUMBIA
COLLEGE OF AGRICULTURE, URBAN SUSTAINABILITY AND ENVIRONMENTAL SCIENCES
GREEN ROOFS
Studies show that green roofs can reduce the energy needed for cooling on the floor below the roof by more than 50%
RAIN GARDENS
A study showed a 93% reduction in runoff volume after the installation of 17 rain gardens in a 5.3 acre neighborhood.
RAIN BARRELS
Capturing rainwater for reuse can help save on water bills for landscape irrigation and other non-potable
PERMEABLE PAVEMENT
Permeable asphalt, concrete, or paver blocks allow water to seep into gravel and soil below. These systems can have significantly lower maintanace costs than traditional pavement, resulting in lower overall life-cycle costs
UDC TOOLS


UDC BLDG 44 GREEN ROOF
UDC STUDENT CENTER RAIN GARDEN
UDC PLAZA STORMWATER CISTERN

Performance evaluation of urban stream restoration using process-based modeling

Basic Information

Title:	Performance evaluation of urban stream restoration using process-based modeling
Project Number:	2016DC178B
Start Date:	3/1/2016
End Date:	2/28/2017
Funding Source:	104B
Congressional District:	DC
Research Category:	Water Quality
Focus Categories:	Surface Water, Hydrology, Surface Water
Descriptors:	None
Principal Investigators:	Arash Massoudieh

Publications

1. Massoudieh, Arash, Sassan Aflaki, and Srinivas Panguluri, 2016, User's manual for green infrastructure fexible model (gifmod), http://gifmod.com/wp-content/uploads/2016/12/GIFMod_User_s_Manual.pdf
2. Massoudieh, Arash, Mahdi Maghrebi, Babak Kamrani, Christopher Nietch, Michael Tryby, Sassan Aflaki, and Srinivas Panguluri, 2017, A flexible modeling framework for hydraulic and water quality performance assessment of stormwater green infrastructure. Environmental Modelling & Software, 92:57-73.

Progress report on Performance evaluation of urban stream restoration using process-based modeling

Arash Massoudieh

May 18, 2017

Contents

1 Summary

Stream restoration projects have been widely used to improve the quality of impaired waters and also to reduce the peak flow entering receiving water bodies. The goal of this project was to evaluate the effect of stream restoration on hydraulics and water quality in a small urban stream in south east Washington, DC. The urban stream. The objectives of the project included performing data analysis on pre- and post-restoration monitoring data of flow, and water quality constituents including: nitrogen species and phosphorus, heavy metals, organic carbon in a small urban watershed in the S.E. portion of the District of Columbia (known as Texas Ave. Corridor), where a stream restoration project is being conducted. The pre- and post-implementation monitoring has been done by DDOE and DDOT and we will use this data for the project and to develop a process-based water quality model and to perform rigorous parameter estimation of various components of the model using the monitored data.

2 Tasks performed

- A model of post-restoration stream has been already developed using the GIFMOD water quality modeling framework (www.gifmod.com) [Massoudieh et al., 2016, 2017].
- The watershed-stream system is modeled as a catchment a stream and the bottom sediments. Dams are assumed to be placed along the stream. The stream is descretized into 20 blocks each connected to the bottom sediments underneath them (Figure 1). This allows modeling hyporheic flow and in particular the effect of dams on diverting flow to the subsurface. In the future we will add a biogeochemical cycling module to the model and the added transit time due to the hyporheic component of the flow can have a significant impact on the biogeochemical transformation and removal of nutrients. The blocks representing bottom sediments are horizontally connected to allow horizontal flow of water due to the hydraulic head difference in the overlying water.
- It is assumed that the water from the catchment enters into the upstream block of the stream. These assumptions will be revised during the course of model calibration. Simulations are performed based on the precipitation data in 2012 (Figure 2). The precipitation data for the Reagan National Airport has been used for the simulation.
- Figure 3 shows the flow at three locations in the channel (upstream, downstream and middle section). The graph clearly shows the flow peak reduction as a result of the dams in the stream.
- Figure 4 shows the vertical hyporheic flow at three locations including upstream, mid-section and downstream of the channel. As expected the hyporheic flow is nearly downward at the upstream and upward at the downstream which clearly shows the effect of dams in diverting the water to the bottom sediments.

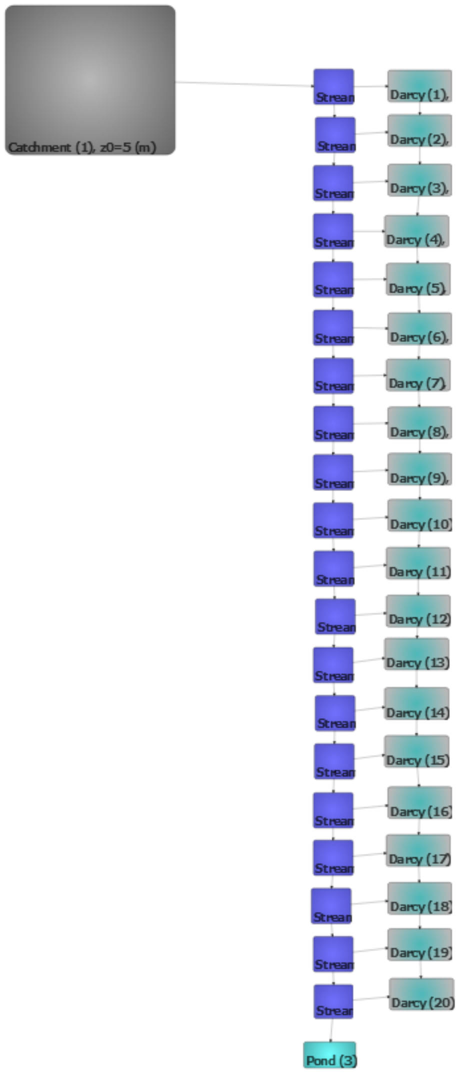


Figure 1: The schematic of conceptual model used to represent the stream-catchment system

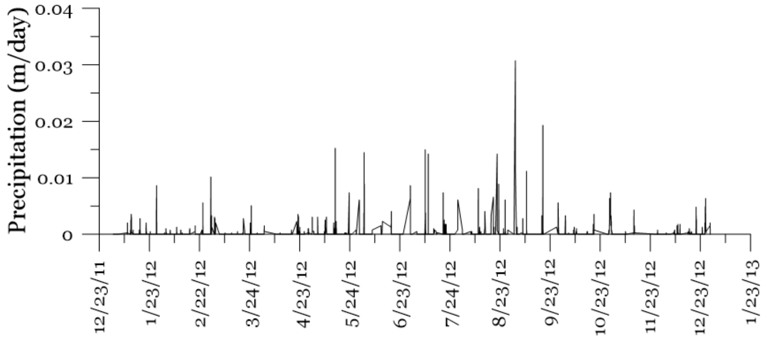


Figure 2: Precipitation record in year 2012

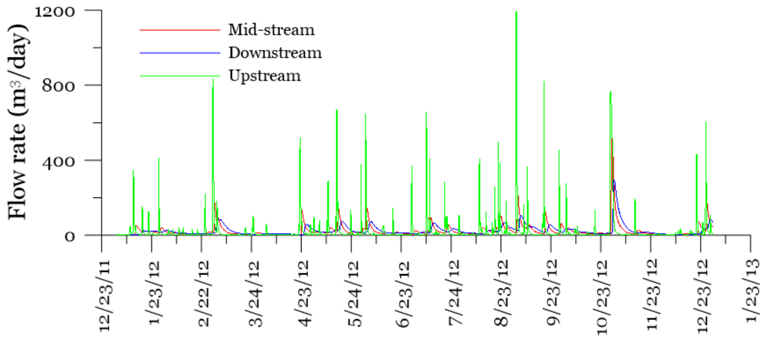


Figure 3: Flow rate in the stream at upstream, mid-section and downstream of the channel

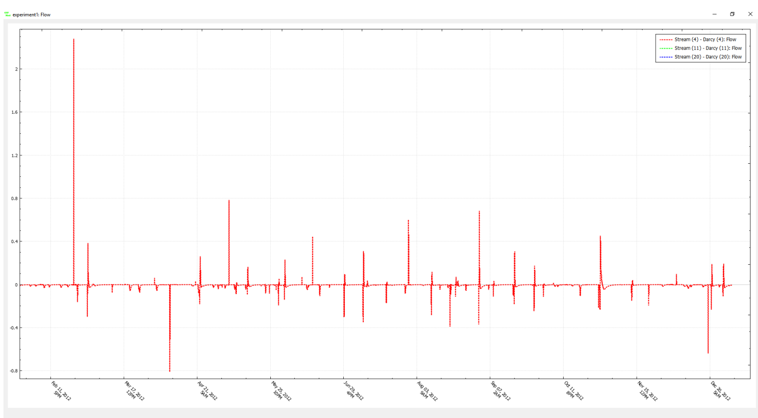


Figure 4: Vertical hypotheic flow at upstream, mid-section and downstream of the channel

3 Remaining tasks

The following tasks will be finished by the end of summer of 2017:

- **Refining model configuration:** We will refine the model configuration and geometrical dimensions of the stream based on real data recieved from DDOE.
- **Water quality:** We will model the fate and transport of nutrients including major nitrogen species (i.e. NO_3, NH_3, Organic nitrogen), Phosphorous, and major constituents affecting the biogeochemical transformation of nutrients such as dissolved oxygen and organic carbon. The transformation of the water quality constituents including carbon mineralization, nitrification and denitrification will be included into the model and the impact of stream restoration on the efficacy of the stream in removing nutrients will be evaluated.
- **Model Calibration:** The model will be calibrated using real monitoring data received from DDOE. In order to do so parameters such as Manning's roughness coefficient for the channel and catchment and hydraulic conductivity of the bottom sediments will be estimated to minimize the difference between model and measured flow at the downstream of the stream.
- We expect the findings of the research to be published in a peer review journal paper.

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Arash Massoudieh, Mahdi Maghrebi, Babak Kamrani, Christopher Nietch, Michael Tryby, Sassan Aflaki, and Srinivas Panguluri. A flexible modeling framework for hydraulic and water quality performance assessment of stormwater green infrastructure. *Environmental Modelling & Software*, 92: 57–73, 2017.

Analysis of perchlorate in drinking water, surface water by AxION Direct sample analysis (DSA) /Time of flight (TOF) Mass Spectrometer

Basic Information

Title:	Analysis of perchlorate in drinking water, surface water by AxION Direct sample analysis (DSA) /Time of flight (TOF) Mass Spectrometer
Project Number:	2016DC179B
Start Date:	3/1/2016
End Date:	2/28/2017
Funding Source:	104B
Congressional District:	DC
Research Category:	Water Quality
Focus Categories:	Toxic Substances, Methods, Nutrients
Descriptors:	None
Principal Investigators:	Sebhat Tefera, Yacov Assa

Publication

1. Tefera, Sebhat, Assa, Yacov, & Deksissa, Tolessa (201). Analysis of Perchlorate in Drinking Water and Surface Water by AxION DSA and Time-of-flight Mass Spectrometry (TOF/MS), NCR-AWRA Annual Water Symposium, April 7, Washington, DC 20008. Poster Presentation.

Analysis of perchlorate in drinking water, surface water by AxION Direct sample analysis (DSA) /Time of flight (TOF) Mass Spectrometer

Progress Report

By

Sebhat Tefera

Project Specialist, Water Resources Research Institute, CAUSES
University of the District of Columbia
stefera@udc.edu; 202-274-7298

May 23, 2017

1. Executive Summary

This study will explore the presence of perchlorate in the public water system. The main objective of this project is to develop a method for fast analysis of perchlorate in water samples using a Direct Sample Analysis (DSA). If the presence of perchlorate is confirmed by DSA, the level of perchlorate will be quantified using Time of Flight and Mass Spectrophotometer (TOF/ MS). Perchlorate is a naturally occurring and manmade chemical that is used to produce rocket fuel, fireworks, flares and explosives that can ultimately contaminate the drinking water system. Environmental regulators and public water system managers are concerned that perchlorate may occur in the public water systems at levels of public health concern. Availability of rapid cost effective screening method is crucial to address this concern. Current methods to analyze the target perchlorate anion in drinking water samples are expensive and time consuming. To our knowledge, fewer investigations have been made in determining perchlorate in potable and non-potable water by AxION Direct sample analysis (DSA) /Time of flight (TOF) Mass Spectrometer(MS). This method can allow for rapid and greatly simplified analysis, helping lead to faster decisions regarding the presence of perchlorate. With the AxION DSA system, it is possible to cut traditional analysis time into few seconds without compromising results. Water samples for analyses will be collected from tap water and surface waters from public and private residences of the District of Columbia. The proposed analytical method will be beneficial to the DC Public in screening the presence of perchlorate not only in public water system, but also in fruit juice and green produces.

Introduction

Recent studies have detected perchlorate in drinking water in major metropolitan areas and ground water associated with the production of solid rocket propellant (Jackson et al., 2000). The discovery of perchlorate in lettuce samples that were irrigated with Colorado River water are some of the recent examples (Seyfferth, & Parker, 2006). These and other recent events have increased the need for the low detection of Perchlorate in matrices such as ground water, saline water, and soil and plant material. This level of concern about perchlorate detection in matrices other than drinking water has motivated instrument manufacturer, academia and commercial laboratories to develop methods for analyzing perchlorate in difficult matrices.

Perchlorate is an environmental contaminant usually associated with the storage, manufacture, and testing of solid rocket motors which use ammonium perchlorate as an oxidizer. One source of perchlorate contamination is the removal and recovery of propellant from solid rocket motors, which can result in wastewater that contains ammonium perchlorate. Another source of contamination is the frequent replacement of old stocks of ammonium perchlorate after its limited useful lifetime for rocket motor usage. Perchlorate infiltrates the watershed through a variety of mechanisms, such as leaching and groundwater recharge (Izbicki et al., 2015). Potential health effects are associated with perchlorate, can interfere with the ability of the thyroid gland to produce thyroid hormones. Therefore, perchlorate has been added to the U.S. Environmental Protection Agency's Candidate Contaminant List (CCL) which is the list from which future regulated drinking water compounds will be selected. For a candidate to be selected for regulation, several requirements must be met. Namely, the contaminant must have sufficient data documenting adverse health effects, it must occur over a sufficiently wide area to qualify for federal interest, and there must be suitable methods to treat such contaminated water. To properly study treatment options, analytical techniques are needed to quantitate perchlorate in drinking water matrixes at suitable concentrations.

Methodologies

DSA-TOF/MS screening allows quick, simple measurement, the need to reach regulatory limits, means that a company must invest twice or, at the very least, send some samples away for testing at an accredited testing lab. As such, technologies that can deliver real-time detection (regulatory limit results) quickly are fast becoming popular. The AxION 2 TOF with a DSA accessory is a classic example, combining chromatography limits of detection with virtually no sample preparation. For water samples perchlorate can be directly ionized without the need to extract or digest any material.

The AxION 2 TOF MS can run in negative ionization mode with flight voltage of 5000 V. The capillary exit voltage can be set set to -120 V for the analysis. Mass spectra can be acquired in a range of m/z 50-700 at an acquisition rate of 5 spectra/s. Total analysis time per sample can be accomplished within 15 seconds. To obtain higher mass accuracy, the AxION 2 TOF instrument can be calibrated by infusing a calibrant solution into the DSA source at 10 µl/min.

2. Task Performed

- Background study related to perchlorate occurrence and analytical techniches was conducted
- Instalation and testing of TOF/MSA with DSA was completd.
- Imporatnt components of standard solutions of perchlore were purchased.

3. Task to be performed

- Method development for TOF/MS with DSA.
- Sampel collection and analysis for confirmation study.

4. Project outcomes, presentations, publications (book chapter journals or conference proceedings).

Poster was presented at the DC Annual Water Symposium, aka NCR-AWRA, on April 7, 2017:

- Tefera, Sebhat, Assa, Yacov, & Deksissa, Tolessa (201). Analysis of Perchlorate in Drinking Water and Surface Water by AxION DSA and Time-of-flight Mass Spectrometry (TOF/MS).

This project helped three MS thesis trained in vitamins and phenolic compound analysis in vegetables as part of their MS thesis:

- Ahdab Hassan Jabi, Gandurah Almalki, and Linah Alqurashi

5. Acknowledgement

Recgnize the funding agency Water Resources Research Institute (WRRI) and personnel contiributed to the success of the project.

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Development of A Novel Stormwater Runoff Collection and Treatment System for Urban Agriculture and Food Security

Basic Information

Title:	Development of A Novel Stormwater Runoff Collection and Treatment System for Urban Agriculture and Food Security
Project Number:	2016DC180B
Start Date:	3/1/2016
End Date:	2/28/2017
Funding Source:	104B
Congressional District:	DC-001
Research Category:	Water Quality
Focus Categories:	Surface Water, Hydrology, Treatment
Descriptors:	None
Principal Investigators:	Jiajun Xu

Publications

1. Vu, Trinh, Robert Stephenson, Tolessa Deksissa, Jiajun Xu, 2017. Design and Development of a Portable Non-point Stormwater Runoff Collection and Treatment System, Journal of Nanotechnology, (submitted)
2. Vu, Trinh, Tolessa Deksissa, Jiajun Xu. 2017. “Nanoparticles Infused Mesoporous Material for Water Treatment Processes”, ASME 2017 International Mechanical Engineering Congress & Exposition (IMECE), Abstarct accepted.
3. Robert Stephenson, Musa Acar, Trinh Vu, Queenie Sarpomah, Michael Kamen,Tolessa Deksissa, Jiajun Xu, 2017. “MCM Based Hybrid Mesoporous Materials for Water Treatment” 2016 National Capital Region Water Resources Symposium, April 8th, 2017. Poster Presentation.
4. Trinh Vu, Robert Stephenson, Musa Acar, Erika Spangler, Tolessa Deksissa, Jiajun Xu. 2017. “Design and Development of a Portable Non-point Stormwater Runoff Collection and Treatment System”, ASEE Mid-Atlantic Region Spring Conference, Morgan State University, Baltimore, MD April 7-8, 2017, Poster Presentation.
5. Robert Stephenson, Musa Acar, Trinh Vu, Queenie Sarpomah, Michael Kamen,Tolessa Deksissa, Jiajun Xu, 2017. “A Portable Stormwater Runoff Collection and Treatment System for Urban Agriculture and Food Security” 2017 Summer Specialty Conference on Climate Change Solutions: Collaborative Science, Policy and Planning for Sustainable Water Management, June 25-28, 2017. Poster Presentation.

Cover Page

Development of A Novel Stormwater Runoff Collection and Treatment System for Urban Agriculture and Food Security

UNIVERSITY OF THE DISTRICT OF COLUMBIA 1851

Principal Investigator

Jiajun Xu

Department of Mechanical Engineering, University of the District of Columbia

April 21, 2017

1. Executive Summary

With the fast increase of urban population, vast quantities of energy and water are being consumed whilst harmful quantities of wastewater and stormwater runoff are generated through the creation of massive impervious areas. In addition, rising oil prices, unreliable rainfall and natural disasters have all contributed to a rise in global food prices. Food security is becoming an increasingly important issue, especially urban residents here in US. There is an urgent need of developing effective and economical feasible solution for the best management practices to minimize storm water runoff, reduce soil erosion, maintain groundwater recharge, and minimize surface water and groundwater contamination from combined sewer overflows[1]. In the last decade, researchers from universities and nongovernment organizations, as well as industry consultants, have proposed new techniques and methodologies to remedy wastewater which include using micro/nanostructured membrane/filtration, nanoparticle catalytic, and chemical reaction etc[1-12]. However, these methods often times are inapplicable for urban agriculture farm or household, because the cost of the system and requirement of post processing are usually time-consuming and expensive [4, 5, 12]. This proposed project will address this issue by the design and development of a novel stormwater collection and treatment system which can harvest and store stormwater from densely populated urban areas and use it to produce food at relatively low costs. This will reduces food miles (carbon emissions) and virtual water consumption and serves to highlight the need for more sustainable land-use planning. The broader goal is to assist in exploring an efficient and cost-effective way to improve regional and global food security, create local capacity and improve social, economic and environmental condition of people and organizations in the District of Columbia through integrating research, teaching and community service in this project.

The proposal project is accomplished through two tasks: 1. Storm water Treatment Material preparations; and 2. Storm water collection and treatment system design and development. The efficiency of the system will be evaluated at the EPA-Certified Environmental Quality Testing Lab at the UDC Van Ness Campus. To broaden the impact of the project, the results have been disseminated through the following approaches: 1. Live demonstration of the stormwater collection and treatment system at UDC; 2. Presentation and tour program at Discover Science Day and Engineering Discovery Day at UDC to local middle and high school students and visitors, 4. conference poster/presentation and journal publications. The result has shown a promising solution for stormwater collection and treatment, in particular the heavy metal removal. It is very much useful for the District of Columbia because it can help improve the efficiency and reduce the cost of wastewater treatment to meet the increasing volume of wastewater, especially in metropolitan area.

2. Introduction

Urbanization increases the variety and amount of pollutants carried into our nation's waters. In urban and suburban areas, much of the land surface is covered by buildings, pavement and compacted landscapes with impaired drainage. These surfaces do not allow rain and snow melt to soak into the ground which greatly increases the volume and velocity of stormwater runoff. As the runoff flows over the land or impervious surfaces (paved streets, parking lots, and building rooftops), it accumulates debris, chemicals, sediment or other pollutants that could adversely affect water quality if the runoff is discharged untreated. These pollutants can harm fish and wildlife populations, kill native vegetation, foul drinking water, and make recreational areas unsafe and unpleasant[1-4]. The porous and varied terrain of natural landscapes like forests, wetlands and grasslands traps rainwater and snowmelt and allows them to filter slowly into the ground. In contrast, impervious (nonporous) surfaces like roads, parking lots and rooftops prevent rain and snowmelt from infiltrating, or soaking, into the ground. Most of the rainfall and snowmelt remains above the surface, where it runs off rapidly in unnaturally large amounts. Storm sewer systems concentrate runoff into smooth, straight conduits. This runoff gathers speed and erosional power as it travels underground. When this runoff leaves the storm drains and empties into a stream, its excessive volume and power blast out streambanks, damaging streamside vegetation and wiping out aquatic habitat. These increased storm flows carry sediment loads from construction sites and other denuded surfaces and eroded streambanks. They often carry higher water temperatures from streets, roof tops and parking lots, which are harmful to the health and reproduction of aquatic life. The loss of infiltration from urbanization may also cause profound groundwater changes.

Although urbanization leads to great increases in flooding during and immediately after wet weather, in many instances it results in lower stream flows during dry weather. Many native fish and other aquatic life cannot survive when these conditions prevail. Urbanization increases the variety and amount of pollutants carried into streams, rivers and lakes. These pollutants can harm fish and wildlife populations, kill native vegetation, foul drinking water supplies, and make recreational areas unsafe and unpleasant. Thus, how to effectively manage the stormwater runoff is a serious problem for urban area, especially the Washington metropolitan area. In District of Columbia (DC), stormwater entering storm sewers does not receive any treatment before it enters the Potomac and Anacostia Rivers and Rock [5, 6]. The cumulative effects of stormwater runoff on water bodies are evident in both the Potomac and Anacostia Rivers, which regularly receive untreated stormwater, now suffer from poor water quality. If not properly managed, the volume of stormwater can flood and damage homes and businesses, flood septic system drainfields, erode stream channels, and damage or destroy fish and wildlife habitat. Because less water soaks into the ground, drinking water supplies are not replenished and streams and wetlands are not recharged. This can lead to clean water shortages and increased food price for more serious food security crisis. All these will require better urban runoff water management solution.

In addition to that, a distributed optimal technology networks (DOT-NET) has been proposed by scientists as an alternative to the 'huge centralized' water treatment plant[7]. The DOT-NET concept is predicated upon the 'distribution and strategic placement of relatively small and highly efficient treatment systems at specific locations' in existing water supply networks[8]. Such satellite water treatment systems would process relatively low flow rates and would use 'off-the-shelf' treatment technologies of the most advanced nature to meet the water needs of population clusters such as housing subdivisions, apartment complexes and commercial districts. The US Environmental Protection Agency (EPA) is also evaluating the use of many decentralized water treatment concepts as 'small system compliance technology'[3, 9, 10]. These include package treatment plants (i.e., factory assembled compact and ready to use water treatment systems), point-of-entry (POE) and point-of-use (POU) treatment units designed to process small amounts of water entering a given unit (e.g., building, office, household, etc.) or a specific tap/ faucet within the unit. The protection of water treatment systems against potential chemical and biological terrorist acts is also becoming a critical issue in water resources planning. Advances in nanoscale science and engineering are providing unprecedented opportunities to develop more cost effective and environmentally acceptable water purification processes.

There is an urgent need of developing effective and economical feasible solution for the best management practices to minimize storm water runoff, reduce soil erosion, maintain groundwater recharge, and minimize surface water and groundwater contamination from combined sewer overflows[9]. In the last decade, researchers from universities and nongovernment organizations, as well as industry consultants, have proposed new techniques and methodologies to remedy wastewater which include using micro/nanostructured membrane/filtration, nanoparticle catalytic, and chemical reaction etc[1, 3, 8, 9, 11-18]. However, these methods often times are inapplicable for urban agriculture farm or household, because the cost of the system and requirement of post processing are usually time-consuming and expensive [8, 11, 12]. To address the above issues, an innovative approach to design and develop a novel stormwater collection and treatment system which can harvest and store stormwater from densely populated urban areas and use it to produce food at relatively low costs is urgently needed. This will reduces food miles (carbon emissions) and virtual water consumption and serves to highlight the need for more sustainable land-use planning. It not only provides an efficient alternative approach to removing pollutants at a low cost, but also eliminates the risk of nanoparticles contamination and the hassle of post processing. Furthermore, the processed stormwater runoff can be reused to irrigate the plants in backyard and home gardens to save on precious water resources and help protect the environment.

In this study, MCM-48-TiO_2 NP is synthesized by hydrothermal technique. Three different sizes of TiO_2 NP (15 nm, 50 nm, and 300 nm) are used for the synthesis with MCM-48, and then tested for their adsorptions of heavy metals. DI water is contaminated with trace metals and filtered through MCM-48-TiO_2NP material. After that, the filtrates are analyzed in order to determine the adsorptions.

The first objective of this study is to synthesize MCM-48-TiO_2NP. The second objective is to determine and compare the adsorption for heavy metals in water between three TiO_2 NP sizes 15 nm, 50nm, and 300 nm.

3. Methodologies

Stormwater Collection and Treatment System

Residential housing uses standard gutter and down spout system to control roof rainwater runoff. The current design features a plug and play system that required little alteration to the standing runoff system. In addition, a “snap on” fitting for the gutter down spout that functions as a leaf and small debris filter was incorporated into the design. Most importantly, a new type mesoporous material (MCM-48) based hybrid material with embedded metallic oxide nanoparticles was synthesized and used as the filter media between the down spout filter and the storage unit[1-6].

To estimate the size of the container needed to store the stormwater, DC rain water statistics was used to construct the model for calculation and average the amount of water a typical household would use was calculated and tabulated in Table 1.

Table 1. Typical water usage at home in DC

Typical water usage at home	
Bath	A full tub is about 36 gallons.
Shower	2-2.5 gallons per minute. Old shower heads use as much as 4 gallons per minute.
Teeth brushing	<1 gallon, especially if water is turned off while brushing. Newer bath faucets use about 1 gallon per minute, whereas older models use over 2 gallons.
Hands/face washing	1 gallon
Face/leg shaving	1 gallon
Dishwasher	20 gallons/load, depending of efficiency of dishwasher
Dishwashing by hand:	4 gallons/minute for old faucets. Newer kitchen faucets use about 1-2 gallons per minutes.
Clothes washer	25 gallons/load for newer washers. Older models use about 40 gallons per load.
Toilet flush	3 gallons for older models. Most all new toilets use 1.2-1.6 gallons per flush.
Glasses of water drunk	8 oz. per glass
Outdoor watering	2 gallons per minute

A sample of houses from a surrounding neighborhood to determine best configuration of down spout filter as the selected samples are listed below in Figure 1.

Figure 1. Sample down sprout configurations used in DC

It can be seen from the Figure 1 above that the downspout location varies from location. Either it is at grade, or is raised with an extension attachment. The user may need to alter their downspout to attach any device. One goal of this device aims to create a solution that does not require alteration for downspouts at grade. Another observation is the location of downspouts. The tight placement of housing in DC means not everyone will have adequate space to place a fix volume of storage unit.

Hybrid Mesoporous Materials for Water Treatment

Mesoporous materials have pore size from 2 – 50 nm. They are used as adsorbents for environmental contaminants [2, 4-8]. In 1992, Mobil Oil's scientists discovered a family of mesoporous siliceous materials – M41S. Typical members of M41S family are MCM-41, MCM-48, and MCM-50. MCM-41 has one dimensional hexagonal structure, resembling a honeycomb network. MCM-48 has three dimensional cubic symmetry structure, and the structure of MCM-50 is two dimensional stabilized lamellar. Because of large surface area, highly ordered and uniformly porous structure, MCM material is a good adsorbent and a catalyst for acid catalyzed reactions and petroleum refining process. MCM can be used to break down organic matters such as oxidation of cyclohexene with H_2O_2, photocatalytic reduction of CO_2 and H_2O, peroxidative oxidation of methyl methacrylate and styrene. MCM-41 has been studied since 1992, therefore, this experiment focuses on MCM-48 because MCM-48 has three-dimensional channel system which is expected to have more applications than one dimensional hexagonal MCM-41 and two dimensional lamellar MCM-50. Cubic MCM-48 has a three-dimensional network of pores that increases the surface area, leading to more adsorption of molecules. This type of network also minimizes pore clogging and enhances catalytic reactions. A study for Arsenic (As) removal from water using diamino-functionalized MCM-41 and MCM-48 containing different transition metals Fe, Co, Ni, and Cu shows that the adsorption capacity of MCM-48 for As is greater than MCM-41. MCM-48 is selected as the host substrate in this study. Previous studies have shown that MCM can adsorb Arsenic (As) and Chromium (Cr) from water.

TiO_2 nanoparticle (NP) is used widely for its photocatalytic activity in oxidation/reduction reactions. TiO_2 NP can degrade some organic compounds such as benzene, phenolic compounds, and pesticides. It can also disinfect bacteria like E.coli and remove methylene blue and methyl orange dyes. TiO_2 is also a good removal material for heavy metals, especially chromium (Cr), arsenic (As), cadmium (Cd), copper (Cu) and lead (Pb). The ability to remove toxic compounds of TiO_2 NP together with the ability to adsorb on large surface area and uniform pores of MCM-48 can be combined to make a great material for water purification. Previous studies have shown that MCM-41-TiO_2 can remove Cr and MCM-48 has been studied to remove As in drinking water[9, 10].

In this study, MCM-48 infused with TiO_2 NP is synthesized by a modified hydrothermal technique. TiO_2 NP (300 nm) are used for the synthesis with MCM-48, and then tested for their adsorptions of heavy metals and organic components. The analysis was done using Inductively Couple Plasma – Mass Spectrometer (ICP-MS) from PerkinElmer Pure Plus – NexIon 300D model.

4. Results and Discussion

Stormwater Collection and Treatment System Diagram

In total our system is composed of three main parts: the downspout prefilter, the downspout filter, and the storage unit. Below is a breakdown and explanation of each part.

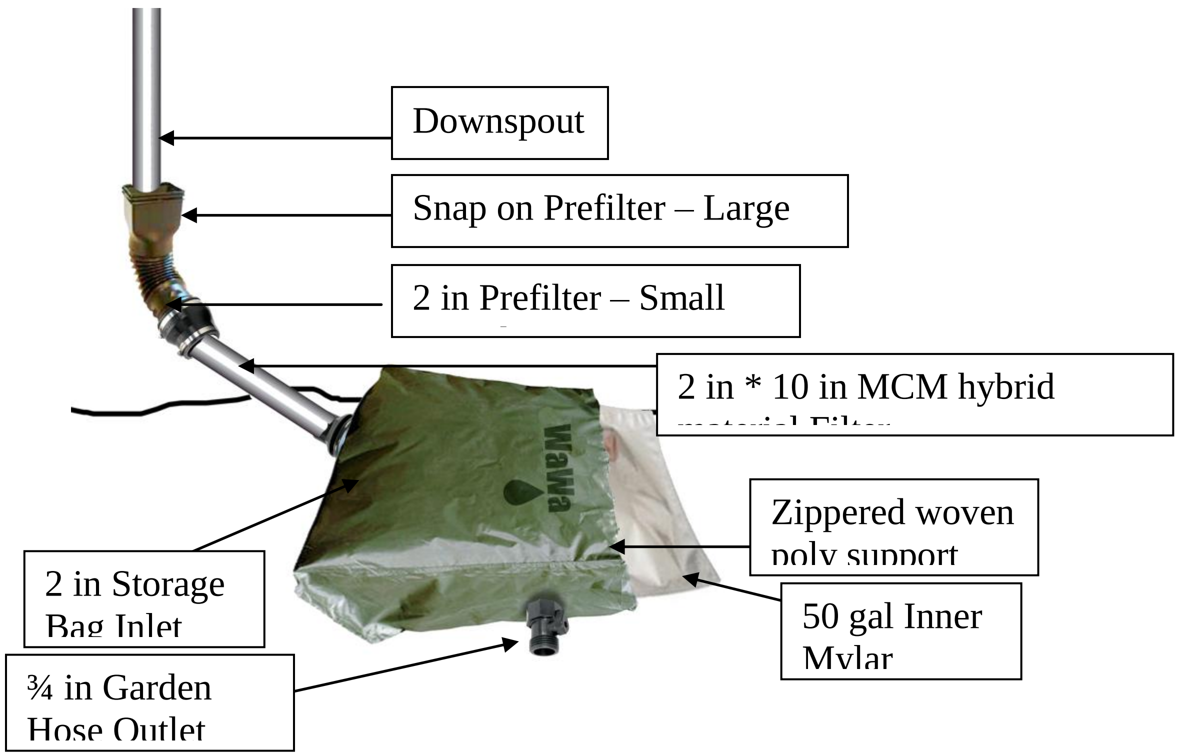

Figure 2. Stormwater collection and treatment system diagram

Each part is explained as following:

1. Drainage area – average DC home rooftop
2. Collection and conveyance system (i.e. gutter and downspouts) – DC home gutter system with front and back spouts ending with an angled end piece at ground level.

3. Pre-screening and first flush diverters – fitted prescreen to spout end piece at inlet and outlet to storage.
4. Storage tank (foil inlay bag with woven Polypropylene outside) – expandable liquid barrier lined material laying at undetermined elevation with fittings for liquid transfer, dark coating to decrease light infiltration discouraging microbe growth and sealed discouraging insect and rodent frequency. Main feature is collapsible for fitting into small spaces, and fitting onto at grade spouts.
5. Water quality treatment – hybrid material compartment
6. Distribution system – spout with hose attachments.
7. The storage bad was equipped with a zipper for easy access. Leak proof rubber striping was added to the front opening of the Mylar bag to prevent small leaks. Sealing the Mylar bag with a outside clamp that screws down onto the Mylar but does not penetrate the bag. This keeps the system intact with and easy to maintain.

Design conditions

The capture system above is compiled from parts that can be purchased from the hardware store. The storage system is compiled from parts that are premade as well.

1. Start with a downspout filter for the large particulate funneling the water to a second filter screen for small particulate.
2. The filter screen also acts as a mosquito barrier to the inside of the tank. A reducer coupling housing the filer screen and reduces from the 4” down spout filter opening to a 2 “opening.
3. A 2 inch hose connects to the reducer and out to the tank.
4. The storage unit is a 50 gallon Mylar lined woven polyethylene bag. The Mylar bag is used as a moisture barrier, and the woven ploy is used to house the Mylar bag and support the pressure and weight of the water. The Mylar bag will be heat sealed and then place inside the woven poly bag.

a. Design the poly bag smaller than the Mylar bag in order to decrease the possibility of over expansion of the inner Mylar bag which has a lower strength then the poly bag. This will remove the need to glue the Mylar bag to the poly bag.
b. Heat seal the Mylar bag while also folding the opening 5 times to create a tighter seal. The folding pushes the Mylar material together and creates a seal that can be mechanically closed for future reopening.

5. Attach the 2 inch inlet, outgas/over fill, and garden hose attachment to a PVC plates that will be glued to the inside of the bag and put through holes that exposes it to the outside. The plate will cover a larger glued surface area reducing the possibility of a leak.

System Test

The complete system was attached to the down spout of a typical DC house. The installation took 20 minutes and did not include difficult alteration. The hardest portion of installation involved removing the bottom section of the downspout in order to slide the prefilter fitting into place.

The system fit into the confined space, and did not collect unwanted bugs or rodents. About 4 gallons of water was collected during a rain fall and filter almost 90% of all large and small particles with prefiltration. The dissolved solids filter is still in test phase. The images below show the large and small particulate filters capacity to keep out material that could potential make the water unusable. Lastly, the system can be rolled up for easy transport and storage.

Figure 3. Stormwater collection and treatment system attached to a downspout

Characterization for Organic Dye Removal

Dye solution: it was prepared by dissolving 1 drop of blue dye into 100 mL of DI water. 14 mL of the dyed solution were filtered through MT15, MT50, and MT300. Color of filtrates were collected and compared with the initial solution. The dye removal efficiency, $\%R$, was expressed as a percentage as follows:

$$(\%)R = \frac{C - C_i}{C_i} \times 100 \quad (1)$$

where C_i and C are the initial and final dye concentrations, respectively.

The results of three hybrid samples for dye solution removal are shown below. Figure 4 shows a comparison of the dye solution before and after one filtration using the hybrid MCM sample and it can be seen clearly that the concentration of dye has been significantly reduced after the first filtration.

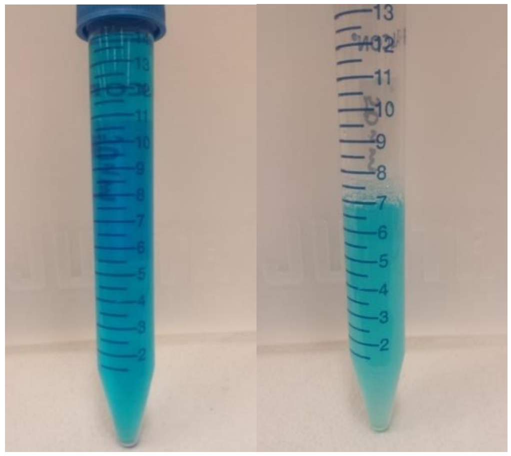

Figure 4. Comparison of dye solution: (a) initial solution, and (b) after one filtration, respectively

The efficiency of the hybrid MCM-48 with TiO_2 sample is compared and summarized in Figure 5 below. It can be seen here that: with the hybrid MCM sample, it can achieve over 80% absorption rate for the blue dye, and the peak absorption efficiency occurs at the fifth filtration with an efficiency near 90%.

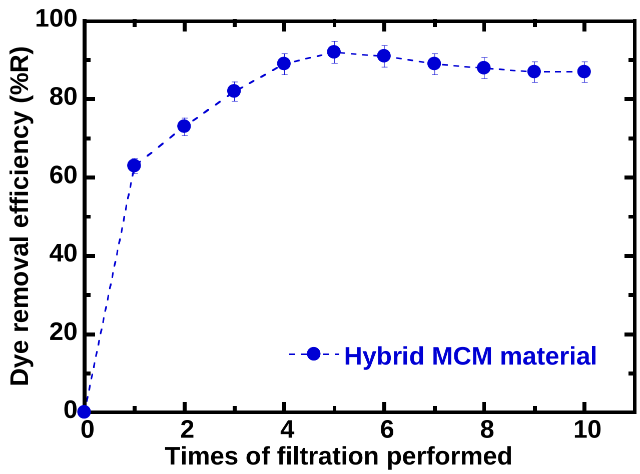

Figure 5: Dye removal efficiency (%R) with time of filtration test for three hybrid samples

Characterization for Heavy Metals Removal

Trace metals: 0.5 mL of 100 mg/L Instrumental Calibration Standard 2 (trace metals and minerals) was added into 497 mL of DI water. They are purchased from PerkinElmer Pure Plus. For each synthesized material, 90 mL of the solution was filtered slowly through 6 g of the hybrid sample and collected in six 15 mL tubes. The collected filtrates were then analyzed for trace metals with ICP-MS. The trace metal removal efficiency, $\% M_X$, was expressed as a percentage as follows:

$$(\%)M_X = \frac{X - X_i}{X_i} \times 100 \quad (2)$$

where X_i and X are the initial and final concentrations of trace metal X, respectively.

Following the procedures listed before, the results of three hybrid samples for trace metals removal were obtained using ICP-MS, and the results are shown below in Table 2. For the hybrid sample, 6 tubes of filtered solution were collected and the sum of absorption date from the 6 tubes gives the total adsorption rate of each sample regarding that trace metal. The results have been complied in Figure 6 below, in which the removal efficiency for each trace metal using the three hybrid samples have been calculated using the Eq. 2 and included as well.

Table 2. Adsorption data of hybrid MCM-48 with TiO_2

Material	No. tubes collected	Amount Adsorbed by MCM-48-TiO_2 (ppb)				
		As	**Cd**	**Cr**	**Cu**	**Pb**
MCM-48 with TiO_2	1	44.90	50.85	18.40	50.25	17.50
	2	78.25	71.70	13.65	106.75	88.25
	3	86.20	77.45	14.65	107.30	92.90
	4	85.40	72.70	10.35	70.80	88.80
	5	79.65	64.75	14.65	75.25	87.90
	6	52.10	34.25	13.85	86.20	50.90

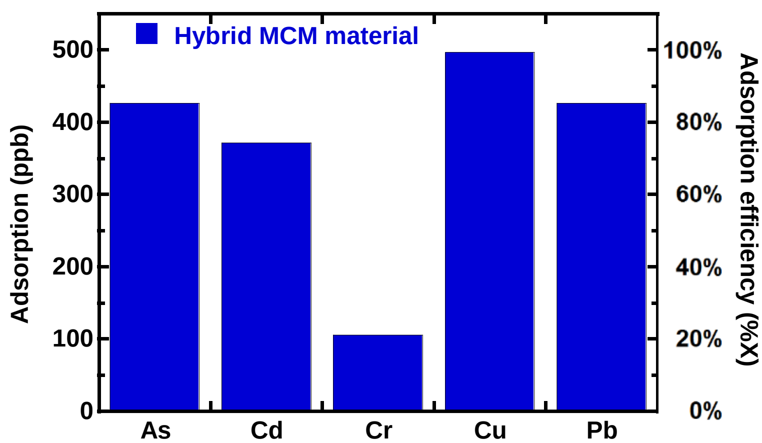

Figure 6. Total adsorption and adsorption efficiency of heavy metals on hybrid MCM-48-TiO_2

It can be seen here that the hybrid sample has shown higher adsorption for As, Cu, Cd and Pb compared to Cr, in which over 80% efficiency can be achieved for As, Cu, Cd and Pb. The maximum amount of heavy metals that each hybrid sample can adsorb cannot be determined at this moment as none of them has reached its maximum rate. The maximum adsorption of the material for certain metal can be determined based on whether there is negative value and there is no negative value has been observed under current test conditions.

5. Project outcomes, presentations, publications (book chapter journals or conference proceedings)

Technical Presentation:

Robert Stephenson, Musa Acar, Trinh Vu, Queenie Sarpomah, Michael Kamen,Tolessa Deksissa, Jiajun Xu, “MCM Based Hybrid Mesoporous Materials for Water Treatment” 2016 National Capital Region Water Resources Symposium, April 8th, 2017

Trinh Vu, Robert Stephenson, Musa Acar, Erika Spangler, Tolessa Deksissa, Jiajun Xu, “Design and Development of a Portable Non-point Stormwater Runoff Collection and Treatment System”, ASEE Mid-Atlantic Region Spring Conference, Morgan State University, Baltimore, MD April 7-8, 2017

Robert Stephenson, Musa Acar, Trinh Vu, Queenie Sarpomah, Michael Kamen,Tolessa Deksissa, Jiajun Xu, “A Portable Stormwater Runoff Collection and Treatment System for Urban Agriculture and Food Security” 2017 Summer Specialty Conference on Climate Change Solutions: Collaborative Science, Policy and Planning for Sustainable Water Management, June 25-28, 2017

Journal publication:

Trinh Vu, Robert Stephenson, Tolessa Deksissa, Jiajun Xu, “Design and Development of a Portable Non-point Stormwater Runoff Collection and Treatment System”, Journal of Nanotechnology, Manuscript submitted and under review

Conference proceedings:

Vu, Trinh, Tolessa Deksissa, Jiajun Xu, “Nanoparticles Infused Mesoporous Material for Water Treatment Processes”, ASME 2017 International Mechanical Engineering Congress & Exposition (IMECE), Abstarct accepted

6. Student supports

It has provided an excellent opportunity for training undergraduate students, researchers and water resources professionals. Six undergraduate students have been involved in the project. Through working on the project the students become familiar with the aspects of wastewater management, nanotechnology, material synthesis and characterization theory and its application to pollutant treatment. The students were also given opportunities to present their work at professional conferences.

7. Extramural funding

The PI has received NIFA funding after receiving this WRRI grant to support his research.

8. Conclusion

Through this research, it has been found that cost of storage, installation onto downspouts, and size of storage are three main barriers to the adoption of rainwater capture systems in urban environments. The design components were addressed by design for ease of installation, low cost, minimal maintenance, space maximization, safely, and easy transport. This solution is expandable system that has flexible slip fittings that lock onto down spout. This design makes transportation of entire system cheaper, storage in small spaces easier, installation on down spouts simpler, and affordable for a wide spectrum of socio economic groups. Only 5 custom processes are needed in this process that is not labor intensive. In addition, a novel hybrid mesoporous material with embedded nanoparticles has been incorporated to treat the collected stormwater and the results have shown that this material can removal organic dye and heavy metal contaminants. This would provide an effective way to removal toxic pollutants for water treatment while maintain versatile and compact. Overall, this portable stormwater collection and treatment system provides an effective and economical affordable solution to process non-point pollutions, especially the stormwater runoff for urban residents.

In addition, undergraduate students have been actively involved in the research, technical presentation and publication at regional and national conferences, in which an increase of participation and awareness of pre-university students have been achieved.

9. Acknowledgement

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A Comparative Study of Nearest-Neighbor Method (NNM) and Extended Nearest-Neighbor (ENN) Method for Annual Streamflow Prediction

Basic Information

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End Date:	2/28/2017
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Congressional District:	DC-001
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Focus Categories:	Water Quantity, Methods, Models
Descriptors:	None
Principal Investigators:	Nian Zhang, Pradeep K. Behera

Publications

1. Zhang, Nian and Devdas Shetty (2016). An Effective LS-SVM Based Approach for Surface Roughness Prediction in Machined Surfaces. Neurocomputing, 198, 35-39.
2. Ramirez, Juan F. Rochac and Nian Zhang, 2016, "Feature Extraction in Hyperspectral Imaging Using Adaptive Feature Selection Approach," in The Eighth International Conference on Advanced Computational Intelligence (ICACI2016), Chiang Mai, Thailand, pp. 36-40.
3. Rochac, Juan F., Nian Zhang, and Pradeep Behera, 2016, "Design of Adaptive Feature Extraction Algorithm Based on Fuzzy Classifier in Hyperspectral Imagery Classification for Big Data Analysis," in The 12th World Congress on Intelligent Control and Automation (WCICA 2016), Guilin, China, pp. 1046 – 1051.
4. Zhang, Nian, 2016, "Cost-Sensitive Spectral Clustering for Photo-Thermal Infrared Imaging Data," in 2016 Sixth International Conference on Information Science and Technology (ICIST), Dalian, China pp. 358 – 361.

A Comparative Study of Nearest-Neighbor Method (NNM) and Extended Nearest-Neighbor (ENN) Method for Annual Streamflow Prediction

Progress Report

Nian Zhang, Ph.D.
Department of Electrical and Computer Engineering
Pradeep K. Behera, Ph.D., P.E., D. WRE
Department of Civil Engineering

Submitted to DC Water Resources Research Institute,
University of the District of Columbia

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1. Executive Summary

The PIs and the students have successfully created modified k-nearest neighbors (KNN) classifier method and compared its performance with the conventional k-nearest neighbors method. Two students participated in this project and was trained by the PI. Several projects have been accepted by conference proceedings or presented and published.

Traditional k-nearest neighbor methods couldn't be able to correctly classify objects when their k nearest neighbors are dominated by other classes. This project formulates a two-class classification problem, and applies a modified k-nearest neighbors (KNN) classifier algorithm based on maximal coherence, validity ratings, and k-fold cross validation to classify the test samples. We build a validity score for the pairs of sample and their surroundings according to their labels. The k nearest neighbors (including the unknown test object) of each sample in the training set as well as the unknown test object itself will be determined. The unknown test object will be tentatively assigned to a class membership. Then we use the validity scores to quantify the degree to which a pre-determined group of samples resemble their k nearest neighbors. A classifier is designed which take into account the coherence and validity ratings. A numerical example demonstrates the effectiveness of the algorithm in detail. The enhanced KNN method is compared with the conventional KNN and the modified KNN method on both real world wine data and photo-thermal infrared imaging spectroscopy (PT-IRIS) data for up to 20 different k values. Classification accuracy of KNN method and our method in terms of various combinations of k-value and k-fold cross validation are compared. The experimental results show that the proposed enhanced KNN method outperforms the conventional KNN and the modified KNN method on both real world wine data and PT-IRIS data. In addition, the classification accuracy of both the conventional KNN and our method increase drastically when k = 5. The average classification accuracy of our method on the PT-IRIS data featuring small sample size and high overlap is 97.87%.

2. Introduction

In regard to stormwater runoff, how urbanized a watershed is or how developed a watershed is can be characterized by the degree of imperviousness found in the watershed [1]. A more urbanized watershed will have a greater percentage of area covered by impervious structures, i.e., roadways, rooftops, sidewalks, parking lots, etc. The effects of these impervious areas create higher peak flows and lower base flows in the watershed tributaries. These effects are most evident in the higher frequency rain/flood events, and they diminish as the range of magnitudes increases, i.e. the initial abstractions (infiltration, interception, and surface storage) become less significant when measured against rainfall for a large event, e.g. a 100-year rainfall event.

Potomac River was determined to be one of the most polluted water bodies in the nation mainly due to the CSOs and stormwater discharges and wastewater treatment plant discharges. This highly urbanized Potomac River watershed suffers from serious water quantity problems including flooding and stream bank erosion. Of approximately 10,000 stream miles assessed in the watershed, more than 3,800 miles were deemed "threatened" or "impaired". The middle

Potomac sub-watershed, including Washington, DC, contains both the greatest percent impervious area and the greatest population density, which is home to 3.72 million or about 70% of the watershed's population. In the next 20 years, the population of the Potomac watershed is expected to grow 10% each decade, adding 1 million inhabitants to reach a population of 6.25 million.

In this regard, it is imperative to provide a reliable streamflow forecasting tool at various locations on the middle Potomac sub-watershed. Engineers, water resources professionals, and regulatory authorities need this streamflow information for planning, analysis, design, and operation & maintenance of water resources systems (e.g., water supply systems, dams, and hydraulic structures). Currently USGS provides the streamflow data at various locations in the form of gage height and discharge volume at specific locations, and we used this input to design a reliable prediction model.

Fix and Hodges proposed the k-nearest neighbors algorithm (i.e. KNN) in 1951 where the classification rules do not depend on the underlying distributions [2]. The non-parametric methods meet the needs when the data distributions of are either unknown or unavailable in many real world applications. The inputs contain k closest training data, while the output of the classifier is a class membership. A test sample is assigned to the same class as the majority of the labels of its k nearest neighbors. Various modified KNN have been proposed to improve the accuracy rate of KNN. Wang and Neskovic presented an adaptive distance measure to significantly improve the performance of the KNN rules [3]. Tang and He proposed an extended k-NN method (i.e. ENN), which not only finds those who are the nearest neighbors of the test sample, but also those who identify the test sample to be their nearest neighbor [4]. Parvin et al generated some kinds of similarities among the training data, and added this additional information to the weight of each neighbor [5]. Taneja et al proposed a fuzzy logic based KNN algorithm where fuzzy clusters are obtained at pre-processing step while the class membership of the training data is computed in reference with the centroid of the clusters [6].

Although these methods demonstrated that the classification accuracy performs better than the conventional KNN, their performance is unknown when the sample sizes are small or the data are highly overlapped. In addition, to date, there have been insignificant efforts to analyze the photo-thermal infrared (IR) imaging spectroscopy (PT-IRIS) data using computational intelligence and data mining techniques [7].

Therefore, it's important to develop an advanced KNN method to further improve the accuracy and compare with the previous variations. We propose an enhanced KNN variation method by exploring the performance on not only the same datasets (i.e. wine dataset) used by other researchers for the purpose of comparison, but also the PT-IRIS datasets, which has small sample size versus much larger feature size [8]. Unlike the conventional KNN method where only the nearest neighbors are used to determine the class of the test object, we also include the test object to the training dataset to maximize the intra-class coherence and then make a classification decision.

3. The Enhanced K-Nearest Neighbor Method

Unlike the conventional KNN method, the idea of the enhanced KNN method is to find out the k nearest neighbors (including the unknown test object) of each sample in the training dataset, as well as the unknown test object. Then we use a concept of validity rating to quantify the degree to which a pre-determined group of samples resemble their k nearest neighbors. Finally, a classifier will assign the unknown test object to a class membership based on the validity ratings.

In a highly overlapped dataset, it is extremely difficult to classify the data with high accuracy. Part of the reasons is that data belonging to different classes mix with each other or a single data is surrounded by large groups of data with different classes. Fig. 1 shows the above situations which would pose several great challenges for classification. First of all, not only X1 is overlapped with Y2, but also X3 is overlapped with Y3; second, a green unknown test object, P to be classified is closest to X1 (Class 1), but it is closer to Y1 and Y2 (Class 2) on the top left than X2 and X3 (Class 1) on the bottom right.

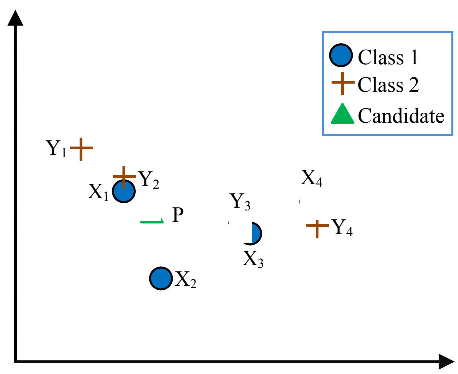

Fig. 1 A two-class classification example. Not only X1 is overlapped with Y2, but also X3 is overlapped with Y3; second, a green unknown test object, P to be classified is closest to X1 (Class 1), but it is closer to Y1 and Y2 (Class 2) on the top left than X2 and X3 (Class 1) on the bottom right.

Let T = {X1, X2, …, Xm, Y1, Y2, …, Yn} be the training data, where {X1, X2, …, Xm} has a given class label, C1, and {Y1, Y2, …, Yn} has a given class label, C2. P is an unknown test candidate data that we want to classify.

A concept of validity rating is used to measure how similar a training data looks to its k nearest neighbors. The validity of a training data is computed based on the label of the data and the labels of its k nearest neighbors, as defined in (1). The validity for data x, V(x) counts the number of nearest neighbors that have the same labels as x.

$$V(x) = \frac{1}{k}\sum_{i=1}^{k} S(label(x), label(NN_i(x, \mathrm{T}))) \qquad (1)$$

Where k is a pre-defined number of nearest neighbors. label(x) is the class membership of data x. is the class membership of the ith nearest neighbor of x. NNi(x, T) stands for the ith nearest neighbor of x inside T. S is a function representing the similarity between x and its ith nearest neighbor. The function S is defined in (2).

$$S(i, j) = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases} \qquad (2)$$

After adding a validity attribute to the training samples, we are able to obtain a score for each training sample based on the labels of the object and its surroundings. Then the k nearest neighbors (including the unknown test object itself) of each sample in the training set as well as the unknown test object will be determined. The unknown test object will be tentatively assigned to a class membership based on some criteria, and form a group. Then we calculate the validity ratings to quantify the degree to which the aforementioned group of samples resembles their k nearest neighbors, as shown in (3).

$$M_i^j(x) = \frac{1}{N+k}\sum_{x\in C}\sum_{i=1}^{k} S(label(x), label(NN_i(x, \mathrm{T}))) \tag{3}$$

Where N is the size of samples determined by criteria, C. k is a pre-defined number of nearest neighbors. The criteria, C are defined in (4):

$$C = \begin{cases} \{\text{Samples in Class}_i\} \cup \{\text{P}\}, \text{ when i = j} \\ \{\text{Samples in Class}_i\}, \quad \text{when i} \neq \text{j} \end{cases} \tag{4}$$

P is the unknown test sample. label(x) is the class membership of data x. is the class membership of the ith nearest neighbor of x. NNi(x, T) stands for the ith nearest neighbor of x inside T. S is a function representing the similarity between x and its ith nearest neighbor. The function S is defined in (2).

A classifier will take into account the coherence and validity ratings, and assign the class label associated to the maximum coherence to the unknown test sample, as defined in (5).

$$Classifier = \underset{j\in 1,2}{\arg\max}\sum_{i=1}^{2} M_i^j(x) \tag{5}$$

4. Numerical Example

In this section, we provide a numerical example corresponding to the enhanced KNN method described in Section 2 and demonstrate the effectiveness of the method.

First we find out the k nearest neighbors (including the unknown test object) of each sample in the training dataset, as well as the unknown test object, as shown in (6). In the training dataset T, {X1, X2, …, Xm} has a given class label, C1, and {Y1, Y2, …, Yn} has a given class label, C2. P is an unknown test object that we want to classify.

$$\begin{array}{ll} NN_{1,2,3}(X_1) = [Y_2, P, Y_1] & NN_{1,2,3}(Y_1) = [Y_2, X_1, P] \\ NN_{1,2,3}(X_2) = [P, X_3, Y_3] & NN_{1,2,3}(Y_2) = [X_1, P, Y_1] \\ NN_{1,2,3}(X_3) = [Y_3, X_4, Y_4] & NN_{1,2,3}(Y_3) = [X_3, X_4, Y_4] \\ NN_{1,2,3}(X_4) = [Y_4, X_3, Y_3] & NN_{1,2,3}(Y_4) = [X_4, X_3, Y_3] \\ NN_{1,2,3}(P) = [X_1, Y_2, X_2] & \end{array} \tag{6}$$

Then the unknown test object will be tentatively assigned to a class membership based on criteria C, and then get involved in the intra-class correlation computation. First we assume , and then solve for and , respectively.

Solve for M_1^1 : Given $P \in C_1$, i=1, j=1, $NN_i(x, \mathrm{T}) = C_1 \cup C_2 \cup \{P\}$, $C = C_1 \cup P = \{X_1, X_2, X_3, X_4, P\}$, $N = 5$, k = 3

According to (3), $M_i^j(x) = \frac{1}{N+k}\sum_{x \in C}\sum_{i=1}^{k} S(label(x), label(NN_i(x, \mathrm{T})))$. The validity ratings can be calculated using (1), (2), and (6). Thus,

$$M_1^1 = \frac{1}{5+3}\sum_{x \in (X_1, X_2, X_3, X_4, P)}\sum_{i=1}^{3} S(label(x), label(NN_i(x, \mathrm{T})))$$

$$= \frac{1}{8} \times \begin{bmatrix} S_1(X_1, Y_2) + S_2(X_1, P) + S_3(X_1, Y_1) + \\ S_1(X_2, P) + S_2(X_2, X_3) + S_3(X_2, Y_3) + \\ S_1(X_3, Y_3) + S_2(X_3, X_4) + S_3(X_3, Y_4) + \\ S_1(X_4, Y_4) + S_2(X_4, X_3) + S_3(X_4, Y_3) + \\ S_1(P, X_1) + S_2(P, Y_2) + S_3(P, X_2) \end{bmatrix} = 0.875$$

Solve for M_2^1 : Given $P \in C_1$, i=2, j=1, $NN_i(x, \mathrm{T}) = C_1 \cup C_2 \cup \{P\}$, $C = C_2 = \{Y_1, Y_2, Y_3, Y_4\}$, $N = 4$, k = 3

According to (3), $M_i^j(x) = \frac{1}{N+k}\sum_{x \in C}\sum_{i=1}^{k} S(label(x), label(NN_i(x, \mathrm{T})))$. The validity ratings can be calculated using (1), (2), and (6). Thus,

$$M_2^1 = \frac{1}{4+3}\sum_{x \in (Y_1, Y_2, Y_3, Y_4)}\sum_{i=1}^{3} S(label(x), label(NN_i(x, \mathrm{T}))$$

$$= \frac{1}{7} \begin{bmatrix} S_1(Y_1, Y_2) + S_2(Y_1, X_1) + S_3(Y_1, P) + \\ S_1(Y_2, X_1) + S_2(Y_2, P) + S_3(Y_2, Y_1) + \\ S_1(Y_3, X_3) + S_2(Y_3, X_4) + S_3(Y_3, Y_4) + \\ S_1(Y_4, X_4) + S_2(Y_4, X_3) + S_3(Y_4, Y_3) \end{bmatrix} = 0.571$$

Next we assume $\mathrm{P} \in \mathrm{C}_2$, and then solve for M_1^2 and M_2^2, respectively.

Solve for M_1^2 : Given $P \in C_2$, i=1, j=2, $NN_i(x, \mathrm{T}) = C_1 \cup C_2 \cup \{P\}$, $C = C_1 = \{X_1, X_2, X_3, X_4\}$, $N = 4$, k = 3

According to (3), $M_i^j(x) = \frac{1}{N+k}\sum_{x\in C}\sum_{i=1}^{k} S(label(x), label(NN_i(x,\mathrm{T})))$. The validity ratings can be calculated using (1), (2), and (6). Thus,

$$M_1^2 = \frac{1}{4+3}\sum_{x\in(X_1,X_2,X_3,X_4)}\sum_{i=1}^{3} S(label(x), label(NN_i(x,\mathrm{T})))$$

$$= \frac{1}{7}\begin{bmatrix} S_1(X_1,Y_2)+S_2(X_1,P)+S_3(X_1,Y_1)+ \\ S_1(X_2,P)+S_2(X_2,X_3)+S_3(X_2,Y_3)+ \\ S_1(X_3,Y_3)+S_2(X_3,X_4)+S_3(X_3,Y_4)+ \\ S_1(X_4,Y_4)+S_2(X_4,X_3)+S_3(X_4,Y_3) \end{bmatrix} = 0.429$$

Solve for M_2^2: Given $P\in C_2$, i=2, j=2, $NN_i(x,\mathrm{T}) = C_1\cup C_2\cup\{P\}$, $C = C_2\cup P = \{Y_1,Y_2,Y_3,Y_4,P\}$, $N=5$, k = 3

According to (3), $M_i^j(x) = \frac{1}{N+k}\sum_{x\in C}\sum_{i=1}^{k} S(label(x), label(NN_i(x,\mathrm{T})))$. The validity ratings can be calculated using (1), (2), and (6). Thus,

$$M_2^2 = \frac{1}{5+3}\sum_{x\in(Y_1,Y_2,Y_3,Y_4,P)}\sum_{i=1}^{3} S(label(x), label(NN_i(x,\mathrm{T})))$$

$$= \frac{1}{8}\times\begin{bmatrix} S_1(Y_1,Y_2)+S_2(Y_1,X_1)+S_3(Y_1,P)+ \\ S_1(Y_2,X_1)+S_2(Y_2,P)+S_3(Y_2,Y_1)+ \\ S_1(Y_3,X_3)+S_2(Y_3,X_4)+S_3(Y_3,Y_4)+ \\ S_1(Y_4,X_4)+S_2(Y_4,X_3)+S_3(Y_4,Y_3)+ \\ S_1(P,X_1)+S_2(P,Y_2)+S_3(P,X_2) \end{bmatrix} = 0.875$$

The classifier will take into account the coherence and validity ratings, and assign the class label associated to the maximum coherence to the unknown test sample.

$$Classifier = \underset{j\in 1,2}{\arg\max}\sum_{i=1}^{2} M_i^j(x) \quad \begin{aligned} &= \arg\max\{M_1^1 + \mathrm{M}_2^1, M_1^2 + \mathrm{M}_2^2\} = \arg\max\{0.875+0.571, 0.429+0.875\} \\ &= \{1.446, 1.304\} \end{aligned}$$

Therefore, we assign *P* to Class 1.

5. Experimental Results

The synthetic data set is ideal to test the proposed enhanced ENN method, as it features small sample size and much larger feature size (i.e. 428 vs. 728). Each data has 728 features representing the temperature increase for the laser pulse [9]. The labels for all explosive materials are +1, while the non-explosives are set to -1.

First we compare our algorithm to the conventional KNN and the modified KNN [5] on the wine data. We increase the k value from 3 to 7, and observe the classification accuracy of the three algorithms. The result is shown in Fig. 2. The left blue column represents the conventional KNN, the middle green column represents the MKNN, and the right yellow column represents our method. The result shows that our algorithm outperforms both of the conventional KNN and the modified KNN.

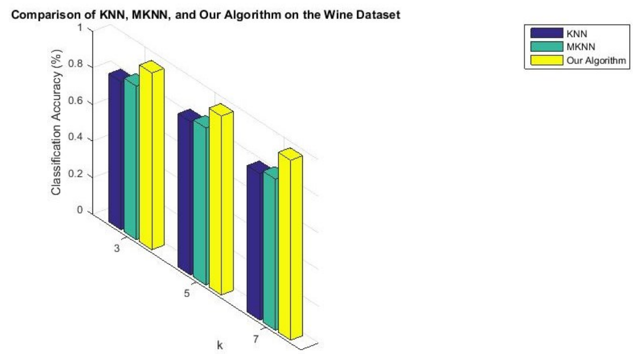

Fig. 2 Comparison of the conventional KNN method, modified KNN method, and our algorithm on the wine data in terms of different *k* values.

We then applied the proposed method on the PT-IRIS data. We compare the classification accuracy of our algorithm to the ENN method. The k value increases from 1 to 20. The result is shown in Fig. 3. The red curve represents the conventional KNN, and the blue curve represents our method. It shows that our method has higher classification accuracy than the conventional KNN except when k = 3. In addition, the classification accuracy of both methods increase drastically when k = 5. At k = 5, the classification accuracy of our method is 97.87%. Moreover, when k is greater than 5, our method keeps high classification accuracy with small scale fluctuation. However, the KNN method dropped twice at k = 6 and k = 11, respectively. Furthermore, both methods have shown a declining trend when k = 20.

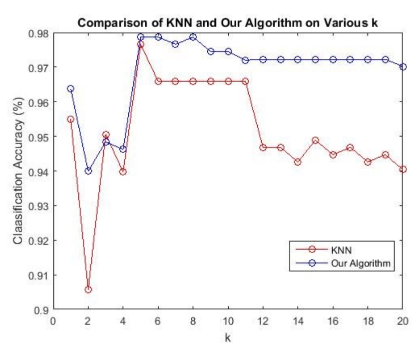

Fig. 3 Comparison of KNN method and our algorithm on various k values from 1 to 20.

We further study the classification performance of the proposed method on the PT-IRIS data in terms of different combination of k values and k-fold values. We use k-fold cross-validation method instead of using the conventional validation method (i.e. dividing the dataset into three sets of 70% for training, 15% for validation, and 15% for testing) because the dataset has small sample size which results in insufficient data to be partitioned into separate training, validation, and testing sets without losing significant modeling competence. We also compare the result with the conventional KNN method. The classification accuracy of KNN and our algorithm are shown in Fig. 4 and Fig. 5, respectively. X-axis represents the number of k value, y-axis represents the number of folds, and the z-axis represents the classification accuracy. Each ribbon corresponds to the classification accuracy at a specific fold value. There are totally 19 folds (i.e. 2nd – 20th fold), so there are 19 ribbons. In addition, on each ribbon, we can observe the classification accuracy on various k values (i.e. k = 1 to 20). From Fig. 4, we can observe that the KNN method has the highest classification accuracy when k =11 for all folds. From Fig. 5, we find that when k = 5 and fold = 17, our method reaches the peak of classification accuracy and remain at peak values when k increases.

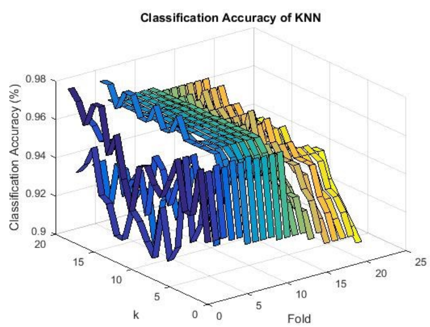

Fig. 4 Classification accuracy of KNN method in terms of various combination of k values and fold values.

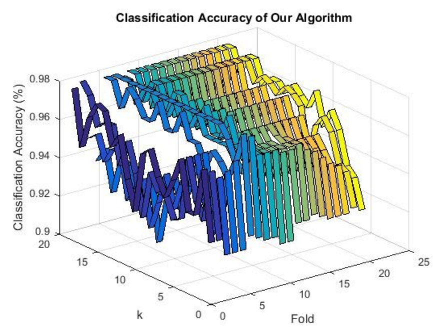

Fig. 5 Classification accuracy of our method in terms of various combination of k values and fold values.

6. Conclusions

This paper formulates a two-class classification problem, and proposes an enhanced k-nearest neighbors (KNN) method based on maximal coherence, validity ratings, and k-fold cross validation. Unlike the conventional KNN method, our method finds out the k nearest neighbors (including the unknown test object) of each sample in the training dataset, as well as the unknown test object. Then we use a concept of validity rating to quantify the degree to which a pre-determined group of samples resemble their k nearest neighbors. Finally, a classifier will be designed to assign the unknown test object to a class membership based on the coherence and the validity ratings. We compare the results of our method to the conventional KNN and the modified KNN method on different combination of k values and fold values. The experimental results demonstrate that our method has significantly higher classification accuracy than the conventional KNN and the modified KNN method on both wine dataset and PT-IRIS dataset.

7. References

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[9] Ramirez Rochac, J. F., Zhang, N.: Reference Clusters Based Feature Extraction Approach for Mixed Spectral Signatures with Dimensionality Disparity. In: 10th Annual IEEE International Systems Conference (IEEE SysCon 2016), Orlando, Florida (2016)

Appendix

1. Student Support

Category	Number of Students Supported
Undergraduate	2
Master	0
Ph.D.	0
Post Doc.	0
Total	1

2.. List of publications (APA format)

- Peer reviewed journal article
    - **Nian Zhang** and Devdas Shetty, "An Effective LS-SVM Based Approach for Surface Roughness Prediction in Machined Surfaces," vol. 198, pp. 35-39, *Neurocomputing*, July 2016.

- Conference proceeding
    - **Nian Zhang**, Jiang Xiong, Jing Zhong, Lara Thompson and Hong Ying, "An Enhanced K-Nearest Neighbor Classification Method Based on Maximal Coherence and Validity Ratings," *14th International Symposium on Neural Networks (ISNN 2017)*, Sapporo, Hokkaido, Japan, June 21-26, 2017.
    - **Nian Zhang** and Lara A. Thompson, "An Intelligent Clustering Algorithm for High Dimensional and Highly Overlapped Photo-Thermal Infrared Imaging Data," *Fall 2016 ASEE Mid-Atlantic Regional Conference*, Hofstra University, Hempstead, NY, October 21-22, 2016.
    - Juan F. Ramirez Rochac, **Nian Zhang**, and Pradeep Behera, "Design of Adaptive Feature Extraction Algorithm Based on Fuzzy Classifier in Hyperspectral Imagery Classification for Big Data Analysis," *The 12th World Congress on Intelligent Control and Automation (WCICA 2016)*, Guilin, China, June 12-15, 2016.
    - **Nian Zhang**, "Cost-Sensitive Spectral Clustering for Photo-Thermal Infrared Imaging Data," *2016 Sixth International Conference on Information Science and Technology (ICIST)*, Dalian, May 6-8, China, 2016.
    - Juan F. Ramirez Rochac and **Nian Zhang**, "Reference Clusters Based Feature Extraction Approach for Mixed Spectral Signatures with Dimensionality Disparity," *10th Annual IEEE International Systems Conference (IEEE SysCon 2016)*, Orlando, Florida, April 18-21, 2016.
    - Juan F. Ramirez Rochac and **Nian Zhang**, "Feature Extraction in Hyperspectral Imaging Using Adaptive Feature Selection Approach," *The Eighth International Conference on Advanced Computational Intelligence (ICACI2016)*, Chiang Mai, Thailand, pp. 36-40, 2016.

- Poster presentation (attach poster): Title, Author, and title of the symposium or conference
    - **Nian Zhang,** Tilaye Alemayehu, and Sasan Haghani, "Development of A Nearest-Neighbor Method (NNM) Method for Annual Streamflow Prediction," *ASEE Zone 2 conference*, San Juan, Puerto Rico, March 2-5, 2017.
    - Tilaye Alemayehu and **Nian Zhang**, "Unmixing-Based Feature Extraction and Classifier for Hyperspectral Image," *2017 Emerging Researchers National (ERN) Conference in STEM*, Washington, D.C., March 2-4, 2017.
    - Tam Le, **Nian Zhang**, and Sasan Haghani, "Analyzing Data Set Classification for Machine Learning Based on ENN Classification Method," *2017 Emerging Researchers National (ERN) Conference in STEM*, Washington, D.C., March 2-4, 2017.
    - Tilaye Alemayehu, Omar Abbas, **Nian Zhang**, and Pradeep K. Behera, "A Nearest-Neighbor Method (NNM) for Annual Streamflow Prediction," *National Capital Region Water Resources Symposium*, Washington D. C., April 8, 2016.
    - Tilaye Alemayehu and **Nian Zhang**, "Optimization-Based Extreme Learning Machine with Multi-kernel Learning Approach for Classification," *The 73rd Joint Annual Meeting BKX and NIS*, Hampton, Virginia, April 6-9, 2016, 2016.
    - Tilaye Alemayehu, **Nian Zhang**, and Sasan Haghani, "Application of Weighted Extreme Learning Machine for Imbalanced Data classification," *2016 Emerging Researchers National (ERN) Conference in STEM*, Washington, D.C., February 25-27, 2016.

Analysis of External and Internal Storm Event Characteristics for Washington DC based on different IETDs

Basic Information

Title:	Analysis of External and Internal Storm Event Characteristics for Washington DC based on different IETDs
Project Number:	2016DC182B
Start Date:	3/1/2016
End Date:	2/28/2017
Funding Source:	104B
Congressional District:	DC-001
Research Category:	Climate and Hydrologic Processes
Focus Categories:	Hydrology, Education, Methods
Descriptors:	None
Principal Investigators:	Pradeep K. Behera

Publication

1. Behera, Pradeep K., and Brahim Sidi Mhamed, 2016. Analysis of External and Internal Storm Event Characteristics for Mid-Atlantic Region, World Environmental & Water Resources Congress, 2016, West Palm Beach, FL, May 22-26, 2016.

Analysis of External and Internal Storm Event Characteristics for Washington DC based on different IETDs

Progress Report

Dr. Pradeep K Behera, PE
Department of Civil Engineering

Submitted to DC Water Resources Research Institute, University of the District of Columbia

April 21, 2017

1. Executive Summary

The planning, analysis, design, operation and maintenance of urban storm water management (SWM) systems is primarily governed by local meteorology which is random in nature. The local input meteorology is represented by measurable parameter, precipitation and its associated frequency. The design of different elements of SWM systems requires utilization of different precipitation characteristics such as conveyance of stormwater (transportation elements) is a function of rainfall intensity whereas storage of stormwater volumes is a function of rainfall volume. In order to better understand the local precipitation, this research presents an analysis of external and internal storm event characteristics for Washington DC. The long-term hourly data from a number of stations within and nearby stations will be collected and a storm event analysis will be conducted at each of the stations. The storm event analysis will be conducted based on the inter-event time definition (IETD). The time series of storm events for different IETDs will be analyzed to obtain (i) characteristics of storm events with high and low rainfall volumes, (ii) characteristics of storm events with large durations, (iii) characteristics of consecutive storm events, (iv) internal characteristics of large storm events, (v) relationships between event volume magnitudes and theirs frequencies. The results of such analysis are very useful for planners and engineers in understanding the local meteorology and provide insights to design the new SWM systems and to manage the existing SWM systems efficiently. The understanding of external and internal storm events characteristics is specifically critical for highly urbanized areas such as Washington DC where small storm events becomes runoff events because of high imperviousness.

2. Introduction

Long-term weather and climate play significant roles in the planning, design, construction, operation, maintenance of the water related urban infrastructures that include urban stormwater management systems, bridges and culverts of transportation systems, water and wastewater treatment plants. These urban infrastructures including existing and future, often planed, designed and operated based on the local precipitation input (rain and snow) primarily based on frequency- magnitude basis. The rational is that long-term climate remains constant and structures will be adequate over the service life time. However, it has been recognized that climate is changing and potentially impacting the precipitation pattern. The potential climate change can have significant impacts on our water resources and related sectors such as water availability, flooding, urban infrastructures, water quality, ecosystems, coastal areas navigation, hydropower, economy and other energy (USGS, 2009). For example, within last few years, the Hurricane Sandy (2012) and Hurricane Patricia (2015) have significantly impacted the east coast.

The current design of urban stormwater management systems generally based on Intensity-Duration- Frequency (IDF) curves examples include NOAA Atlas 14 for Washington DC Region. This curve provide one value for the given duration and frequency (i.e., precipitation volume for a 24-hour, 25 year storm). The IDF curves do not provide any details of the actual storm event characteristics. The use of one value that represents a design storm event is convenient and easy to use. Ideally the stormwater infrastructures are subjected to entire storm events which has several characteristics such as storm volume, storm duration, average intensity, maximum intensity and inter-event time etc. These characteristics play a vital role in evaluating the performance of infrastructure. This research is proposed to analyze the long-term storm event for Washington DC based on different inter-event-time-definition (IETD).

Since the publication of Intergovernmental Panel on Climate Change (IPCC) Report in 2007, many federal, state and local agencies have been developing guidelines for planning, design, operation of transportation systems that include the potential impacts of climate change on the system in a short-term and long-term basis. The primary urban waterways of the DC include Potomac River, Anacostia River and Rock Creek and their tributaries. There are a number of hydraulic structures in the form of culverts to bridges are located within the waterways which facilitate the transportation. Typically, transportation infrastructure has been designed based on event scenarios occurring with short return-period or developed under the assumption that climate and weather patterns remain constant through its service life. With growing climate change impacts and changing land use composition, a better understanding of these changes and impacts is needed such as: climate projections and uncertainties in these projections; vulnerabilities of transportation infrastructure; and strategies needed to adapt the infrastructure to address these changes. DC Water is implementing the long-term control plan by constructing the underground storages to control the combined sewer overflows and stormwater runoff during the wet weather events being discharged into DC's receiving waters. Operation and maintenance of such large infrastructures requires understanding of local storm events and their characteristics.

3. Methodology

The Rainfall Event Definition

A chronological rainfall record may be split up into two distinct groups of time periods: rainfall events, and the intervening times between rainfall events. Here, a rainfall event is characterized by some measurable precipitation. 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. The intensity parameter is a calculated value given by: $i = v/t$.

Once one has defined an event delimiter (in this case an IETD), each event can be scrutinized to determine the following additional characteristics:

1) the volume of precipitation recorded for the event,
2) the duration of the event, and
3) the intensity of the event (volume per unit time).

Thus, each rainfall event that is found within the record may be described by these four parameters (volume v, duration t, average intensity i, interevent time b). The following Figure 1 helps to depict the role of the IETD in determining the boundary between events and the time between the events:

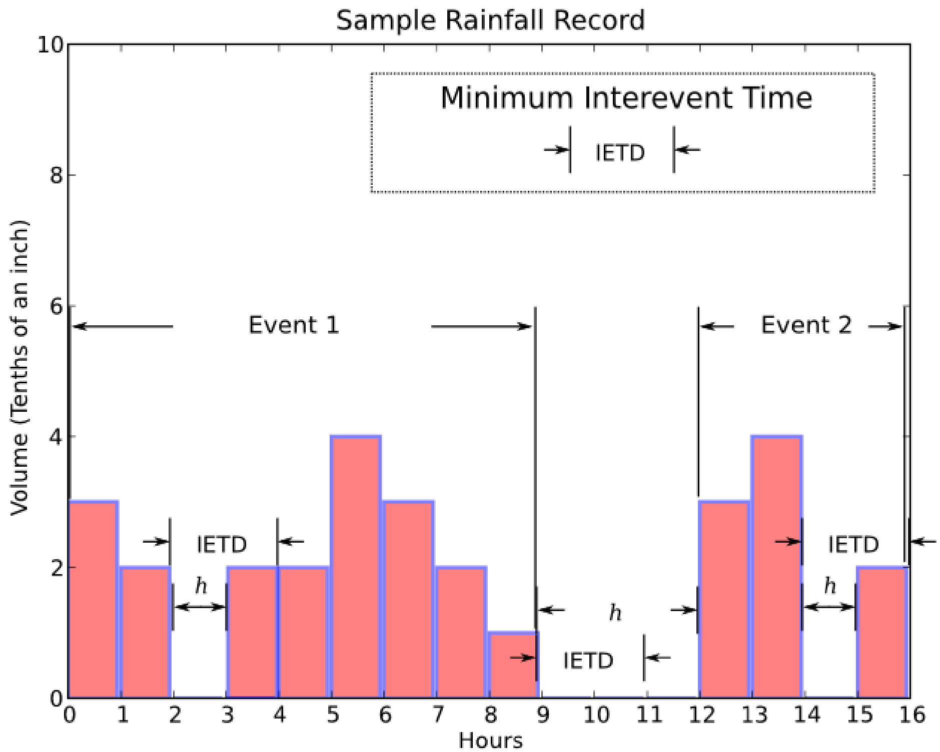

Figure 1: Delineation of Long-term Rainfall Records through IETD

In this example, the rainfall record granularity was given in one-hour intervals, and the volume measurements were given in tenths of inches. The IETD was defined to be two hours. The volume and duration parameters are simply the sum of the volume of rain recorded during the event, and the number of hours that the event lasted respectively. The intensity parameter is therefore given by volume divided by duration of the event.

Following presents the storm event tables based on two different IETDS:

IETD 6 - Top Max- Volume/Duration:

Event #	Start Time	End Time	Duration (hr)	Volume (in)	Intensity (in/hr)	IET (hr)	Max. Volume	IETD 6	Volume	Duration
1	5/1/48 3:00 PM	5/1/48 5:00 PM	2.00	0.03	0.02	0	9.55	Average	0.40	7.22
2	5/2/48 2:00 PM	5/2/48 6:00 PM	4.00	0.17	0.04	21	7.30	Maximum	9.55	110
3	5/3/48 1:00 AM	5/3/48 4:00 AM	3.00	0.50	0.17	7	7.21			
4	5/4/48 8:00 PM	5/5/48 3:00 AM	7.00	0.82	0.12	40	6.60			
5	5/7/48 12:00 AM	5/7/48 8:00 AM	8.00	0.69	0.09	45	6.13			
6	5/7/48 2:00 PM	5/7/48 7:00 PM	5.00	0.09	0.02	6	5.06			
7	5/12/48 9:00 PM	5/13/48 9:00 PM	24.00	2.62	0.11	122	5.04			
8	5/14/48 1:00 PM	5/14/48 3:00 PM	2.00	0.16	0.08	16	4.98			
9	5/16/48 12:00 PM	5/17/48 2:00 AM	14.00	1.25	0.09	45	4.92			
10	5/17/48 3:00 PM	5/17/48 4:00 PM	1.00	0.01	0.01	13	4.86			
11	5/30/48 1:00 PM	5/30/48 10:00 PM	9.00	1.60	0.18	309	4.84			
12	5/31/48 7:00 AM	5/31/48 8:00 AM	1.00	0.01	0.01	9	4.69			
13	6/3/48 7:00 PM	6/4/48 10:00 AM	15.00	0.11	0.01	83	4.57			
14	6/7/48 1:00 AM	6/7/48 3:00 AM	2.00	0.11	0.05	63	4.40			
15	6/7/48 1:00 PM	6/7/48 3:00 PM	2.00	0.93	0.46	10	4.30			

IETD 24 - Top Max Volumes/Duration

Event #	Start Time	End Time	Duration (hr)	Volume (in)	Intensity (in/hr)	IET (hr)	Max. Volume	IETD 24	Volume	Duration
1	5/1/48 3:00 PM	5/3/48 4:00 AM	37.00	0.70	0.02	0	11.37	Average	0.56	15.47
2	5/4/48 8:00 PM	5/5/48 3:00 AM	7.00	0.82	0.12	40	9.08	Maximum	11.37	162
3	5/7/48 12:00 AM	5/7/48 7:00 PM	19.00	0.78	0.04	45	8.16			
4	5/12/48 9:00 PM	5/14/48 3:00 PM	42.00	2.78	0.07	122	7.34			
5	5/16/48 12:00 PM	5/17/48 4:00 PM	28.00	1.26	0.04	45	6.93			
6	5/30/48 1:00 PM	5/31/48 8:00 AM	19.00	1.61	0.08	309	6.60			
7	6/3/48 7:00 PM	6/4/48 10:00 AM	15.00	0.11	0.01	83	6.28			
8	6/7/48 1:00 AM	6/7/48 3:00 PM	14.00	1.04	0.07	63	6.18			
9	6/16/48 2:00 AM	6/16/48 3:00 PM	13.00	1.07	0.08	203	5.83			
10	6/18/48 6:00 PM	6/20/48 2:00 AM	32.00	2.62	0.08	51	5.77			
11	6/24/48 5:00 PM	6/24/48 6:00 PM	1.00	0.10	0.10	111	5.68			
12	6/29/48 7:00 PM	7/1/48 1:00 AM	30.00	0.53	0.02	121	5.13			
13	7/6/48 4:00 PM	7/6/48 6:00 PM	2.00	0.12	0.06	135	5.04			
14	7/13/48 3:00 PM	7/15/48 1:00 AM	34.00	1.66	0.05	165	5.00			
15	7/17/48 4:00 AM	7/17/48 6:00 AM	2.00	0.05	0.02	51	4.99			

4. Results and Discussion

This research project follows basically three major steps:

1- Hourly Precipitation Data was collected from NOAA Websites for Different Stations in the Mid-Atlantic Region. We focused on 13 stations in the Washington, DC metropolitan area, Virginia, and Maryland.

2- A Representative Station in DC area (Ronald Reagan National Airport),To perform the **Analysis**.

3- Replicate the same analysis for the remaining stations.

Using the IETD analysis, the focus of the research was:

a- External Characteristics Analysis:

1- Characterization by Volume:

We divided the volume of rainfall event into different segment of length .5 in ([0,.5[,…,[a,a+.5[/ a<=max<a+.5). Then, we computed the number of events belonging to each range. Finally, we plot a percentile diagram that illustrates the characterization of the event by volume.

2- Characterization by Duration:

We separated the events by duration from 1hr, 2hr… 24hr. Then, we numerated the event belonging to each group represented by certain duration. Finally, we plot a percentile graph representing each category.

b- Internal Characteristics Analysis:

1- Shape of Events with Large Duration:

First, we isolated the events with the largest durations to perform our analysis. The top six events with the largest duration in the DC region were selected. Quartile and Median analysis were performed to come up with trends in the event characteristic shapes. We looked at the trend increase in volume-duration, with IETD and the max Volume for a given large event, which used to be a combination of minor events.

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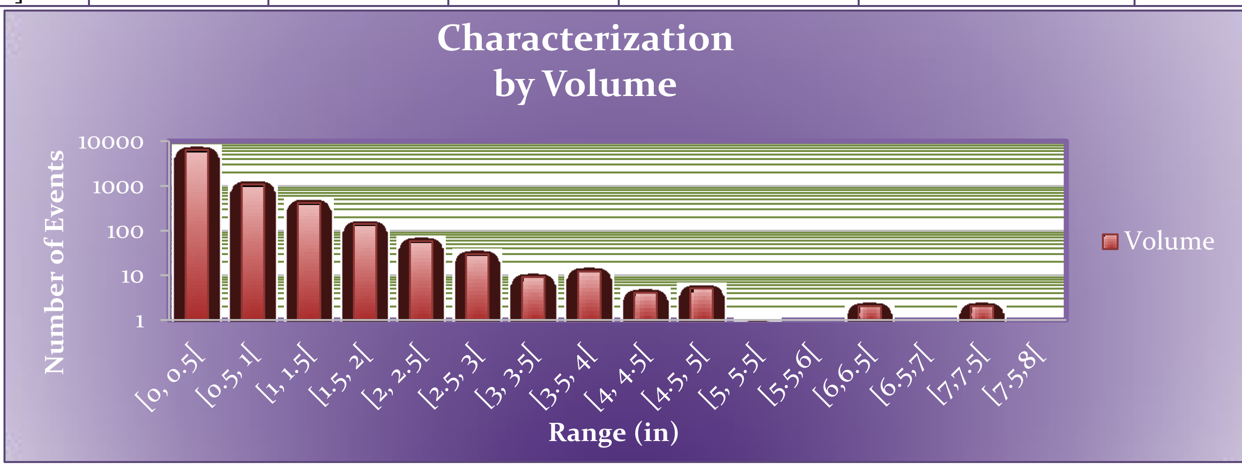
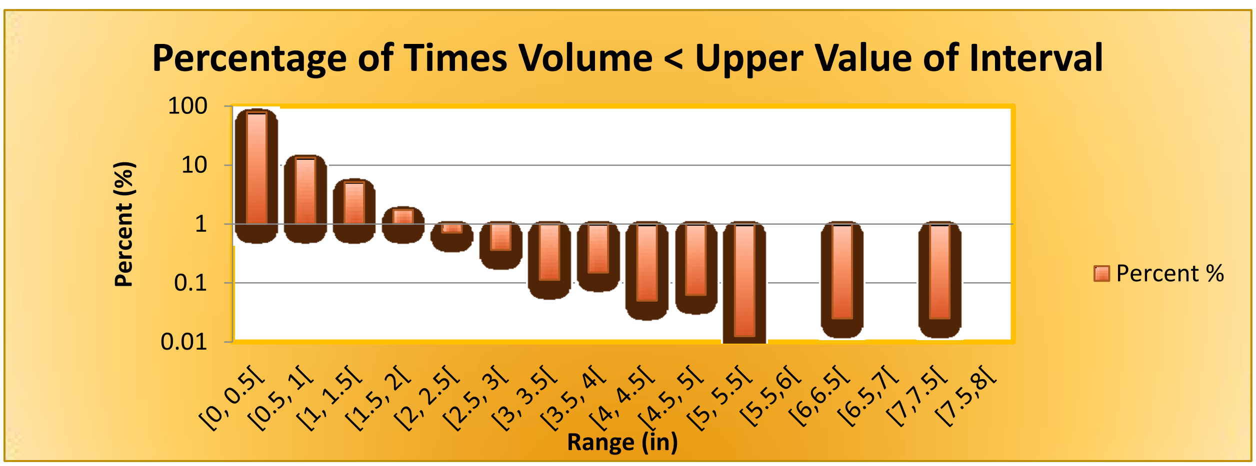
- **Characterization by volume:**

range	L.Value	U.Value	Volume	Cumulation	HPCP Volume (in)	%
[0, 0.5]	0	0.5	6267	6267	1861	78.3963
[0.5, 1]	0.5	1	1060	7327	4443	13.25994
[1, 1.5]	1	1.5	408	7735	6270	5.103828
[1.5, 2]	1.5	2	138	7873	7055	1.726295
[2, 2.5]	2	2.5	57	7930	6805	0.713035

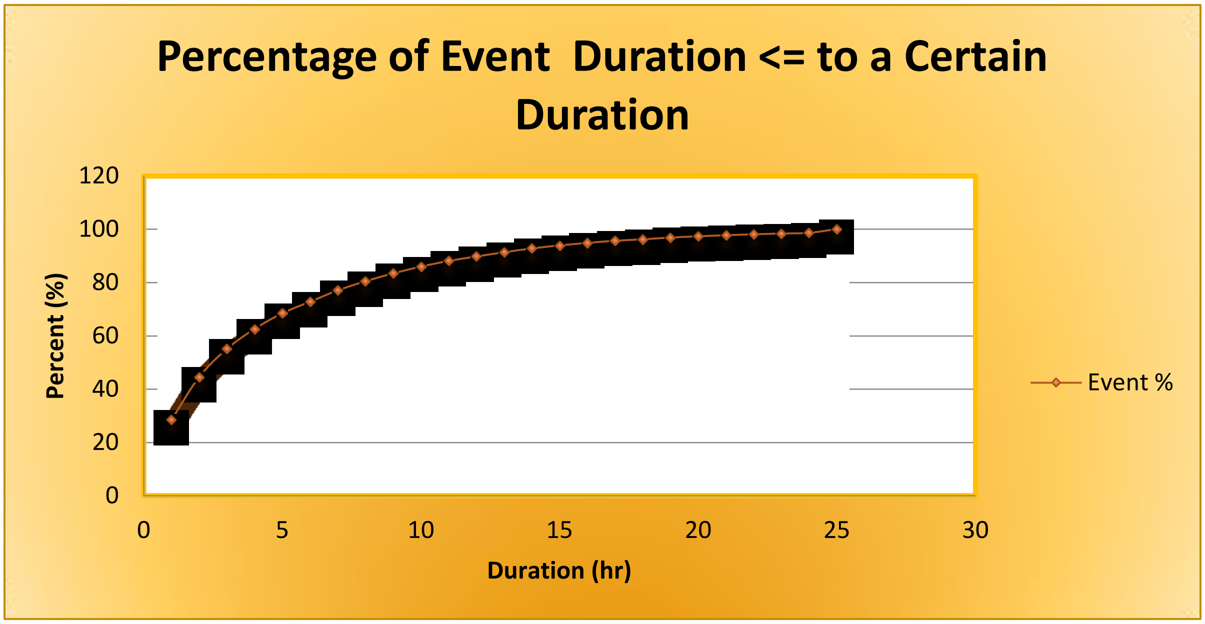




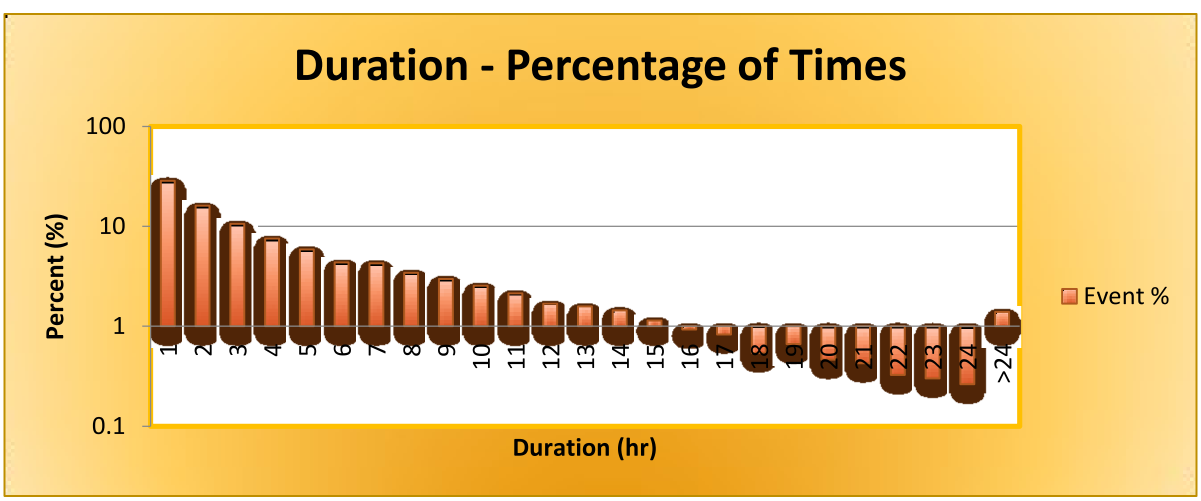
As we can see from the graphs when we increase the volume ranges, the number of events in the given rang decreases, while the percentage of event less than that range increases. Characterizing event based on the volume ranges, within which the minor components of the bigger event fall, is a key in our final volume analysis of the entire event.

- **Characterization by Duration:**

Accuracy Range		Duration (hr)	#of Events	Cumulated # Event	% Event	% Cum. Event
0.5	1.5	1	2274	2274	28.4463348	28.44633
1.9	2.1	2	1282	3556	16.0370278	44.48336
2.9	3.1	3	844	4400	10.5579184	55.04128
3.9	4.1	4	601	5001	7.5181386	62.55942
4.9	5.1	5	468	5469	5.85439079	68.41381
5.9	6.1	6	347	5816		72.75457
6.9	7.1	7	340	6156	4.25318989	77.00776

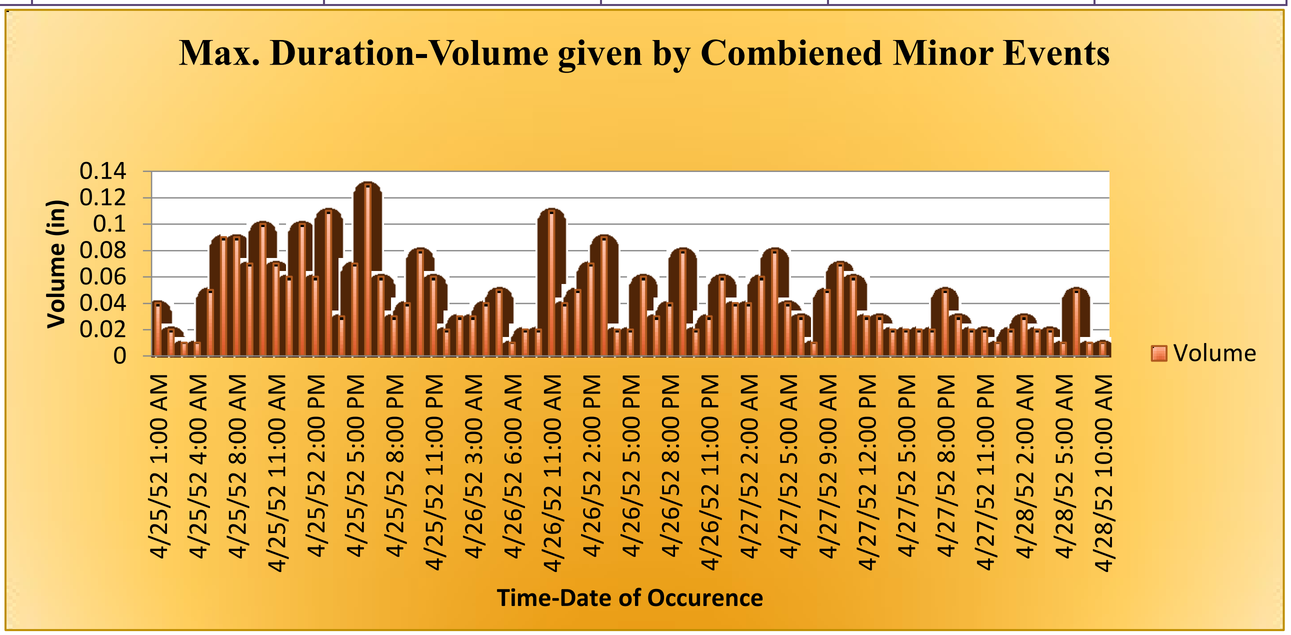


As we can see from the graphs, as the duration increases, the percentage of event decreases, while the percentage of events less or equal to that duration increases. This type of characterization can be used in different types of storm water system design application. For instance, if I wanted to design a system and I am looking for duration of 5 hours, I know that about 70% of the events have a smaller duration. If we increase the duration for our design to let's say 10hr, the number of event below that duration becomes about 90%, which is much safer and conservative.



- **Characterization by Large Event Duration:**

Event #	Start Time	End Time	Duration (hr)	Volume (in)	Intensity (in/hr)
1	4/25/52 12:00 AM	4/28/52 10:04 AM	82	3.24	0.040
2	10/15/09 5:02 AM	10/18/09 5:02 AM	72	2.54	0.035
3	10/28/12 5:02 PM	10/30/12 6:00 PM	49	4.84	0.099
4	3/1/94 10:04 AM	3/3/94 10:04 AM	48	2.07	0.043
5	11/11/09 3:07 AM	11/12/09 11:02 PM	44	1.54	0.035



5. Project outcomes, presentations, publications (book chapter journals or conference proceedings)

Pradeep K. Behera, and Brahim Sidi Mhamed, “Analysis of External and Internal Storm Event Characteristics for Mid-Atlantic Region”, *World Environmental & Water Resources Congress, 2016, West Palm Beach, FL, May 22-26, 2016.*

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6. Student supports

Student Support

Category	Number of Students Supported
Undergraduate	1 Civil Engieering
Master	
Ph.D.	

Post Doc.	
Total	1

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7. Conclusion

The planning, analysis, design, operation and maintenance of urban storm water management (SWM) systems is primarily governed by local meteorology which is random in nature. The local input meteorology is represented by measurable parameter, precipitation and its associated frequency. The design of different elements of SWM systems requires utilization of different precipitation characteristics such as conveyance of stormwater (transportation elements) is a function of rainfall intensity whereas storage of stormwater volumes is a function of rainfall volume. In order to better understand the local precipitation, this research presents an analysis of external and internal storm event characteristics for Mid-Atlantic Region. The long-term hourly data from a number of stations within the region were collected and a storm event analysis was conducted at each of the stations. The storm event analysis was conducted based on the inter-event time definition (IETD). The time series of storm events for different IETDs were analyzed to obtain (i) characteristics of storm events with high and low rainfall volumes, (ii) characteristics of storm events with large durations, (iii) characteristics of consecutive storm events, (iv) internal characteristics of large storm events, (v) relationships between event volume magnitudes and theirs frequencies. The results of such analysis are very useful for planners and engineers in understanding the local meteorology and provide insights to design the new SWM systems and to manage the existing SWM systems efficiently. The understanding of external and internal storm events characteristics is specifically critical for highly urbanized areas such as Washington DC where small storm events becomes runoff events because of high imperviousness

8. Acknowledgement

We really appreciate the DC WRRI and Director, Dr. Tolessa Deksissa for providing the support for this research and success of the project. .

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31P NMR Studies on the oxidative degradation of Glyphosate and its primary metabolite aminomethylphosphonic acid (AMPA) by transition metal oxide nanomaterilas in soil, water and sediment samples

Basic Information

Title:	31P NMR Studies on the oxidative degradation of Glyphosate and its primary metabolite aminomethylphosphonic acid (AMPA) by transition metal oxide nanomaterilas in soil, water and sediment samples
Project Number:	2016DC183B
Start Date:	3/1/2016
End Date:	2/28/2017
Funding Source:	104B
Congressional District:	DC-001
Research Category:	Water Quality
Focus Categories:	Education, Toxic Substances, Non Point Pollution
Descriptors:	None
Principal Investigators:	Xueqing Song

Publications

There are no publications.

WRRI Progress Report for 2016-2017 Academic year

^{31}P NMR Studies on the oxidative degradation of Glyphosate and its primary metabolite aminomethylphosphonic acid (AMPA) by transition metal oxide nanomaterials in soil, water and sediment samples

Xueqing Song

Division of Sciences and Mathematics
College of Arts and Sciences
University of the District of Columbia
4200 Connecticut Avenue NW, Washington DC

ABSTRACT

The widespread application generates problems regarding environment contamination and therefore, determination of glyphosate in crops, vegetables, and fruits has gained increasing importance. However, in comparison to all herbicides used in agriculture, glyphosate is probably the most difficult to analyze. One objective of this project is to develop analytical method able to provide rapid, sensitive, easy and reliable detection of degradation residues of glyphosate and AMPA residue using ^{31}P NMR spectroscopy. Abiotic oxidative degradations of both glyphosate and AMPA to sarcosine induced by manganese oxide have been demonstrated by Barrett and McBride. The degradation of PMG into AMPA is of particular interest. In this project, the catalytic degradation of glyphosate and AMPA in aqueous samples with ZnS, Fe_2O_3 and TiO_2 nano particles as the catalyst will be studied. The effects of various parameters, such as the amount of the catalyst, degradation time, initial pH value, metal ions, and anions on the catalytic degradation of glyphosate and AMPA will be investigated. One undergraduate chemistry student was involved in the project. He was responsible for the use of chemical literature, preparation of samples for NMR analysis and aid in preparing NMR samples. The students involved in this project hade chance to experience chemical research in organic chemistry, analytical chemistry and environmental chemistry. The following is the typical schedule for the student's research activities in this project. Preliminary NMR data show that glyphosate didn't undergo decomposition at room temperature. Stirring for 24 hrs at room temperature shows no changes in both proton and phosphorous NMR spectra. While decomposition was observed when glyphosate was stirred for 24 hrs. with commercial available soil purchased from Home Depot, there was no evidence for the decomposition when glyphosate was stirred under the same conditions for 24 hrs with pre-frozen sediment soils. The reason for that could be because the there were no micro-organisms in pre-frozen sediment soil. This strongly supports that the decomposition of glyphosate in soil depends heavily on the concentration of the micro-organisms in the soil.

Introduction

Pesticide pollution of the aquatic environment is a major concern for our society because of the potential adverse effects of these compounds to ecosystems and humans (1). Organophosphorous (OP) pesticides are usually preferred rather than organochlorine ones because they show a lower persistence and bioaccumulation and a higher biodegradability (2). Glyphosate, a phosphonate and amino acid group-containing pesticide is a broad spectrum, nonselective, and postemergence herbicide for the control of long grasses and broad-leaved weeds, constitute an important category among those OP.

Glyphosate currently has the highest global production volume of all herbicides. The largest use worldwide is in agriculture. The agricultural use of glyphosate has increased sharply since the development of crops that have been genetically modified to make them resistant to glyphosate. Glyphosate is also used in forestry, urban, and home applications. Glyphosate has been detected in the air during spraying, in water, and in food. The general population is exposed primarily through residence

In **March 2015,** the International Agency for Research on Cancer (IARC), the specialized cancer agency of the World Health Organization, has assessed the carcinogenicity of **five organophosphate pesticides**. The herbicide **glyphosate** and the insecticides **malathion** and **diazinon** were classified as *probably carcinogenic to humans* (Group 2A). IARC report says that, for the herbicide **glyphosate**, there was *limited evidence of carcinogenicity* in humans for non-Hodgkin lymphoma. However, there is convincing evidence that glyphosate can cause cancer in laboratory animals. On the basis of tumours in mice, the United States Environmental Protection Agency (US EPA) originally classified glyphosate as *possibly carcinogenic to humans* (Group C) in 1985. After a re-evaluation of that mouse study, the US EPA changed its classification to *evidence of non-carcinogenicity in humans* (Group E) in 1991. The US EPA Scientific Advisory Panel noted that the re-evaluated glyphosate results were still significant using two statistical tests recommended in the IARC Preamble. The IARC Working Group that conducted the evaluation considered the significant findings from the US EPA report and several more recent positive results in concluding that there is *sufficient evidence of carcinogenicity* in experimental animals. Glyphosate also caused DNA and chromosomal damage in human cells, although it gave negative results in tests using bacteria. One study in community residents reported increases in blood markers of chromosomal damage (micronuclei) after glyphosate formulations were sprayed nearby.

Glyphosate is transformed in the environment into a number of substances, among which the metabolite aminomethylphosphonic acid (AMPA) is the most common. Degradation of AMPA is generally slower than that of glyphosate possibly because AMPA may adsorb onto soil particles more strongly than glyphosate and/or because it may be less likely to permeate the cell walls or membranes of soil microorganisms. In streams sediment glyphosate and AMPA were also detected in 66% and 88.5% of the samples respectively.

Natural degradation by microorganisms in soil sample can be limited especially for Glyphosate in water samples as very limited number of microbes can be found, therefore there is a need to investigate the chemical degradation of glyphosate and AMAP. We propose to test several of non-toxic transition metal oxide as the catalysts to investigate the abiotic degradation possibility pf plyphosate and AMPA.

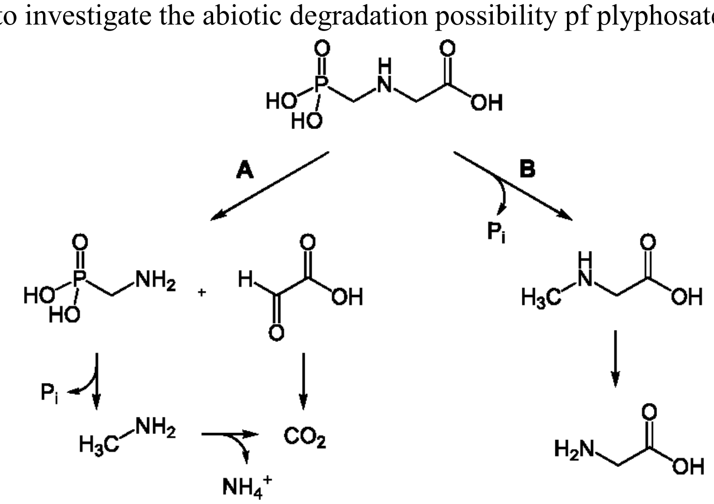

Fig. 1 Biodegradation process of Glyphosate

Studies have shown when glyphosate comes into contact with the soil it rapidly binds to soil particles and is inactivated. Unbound glyphosate is degraded by bacteria. Low activity because of binding to soil particles suggests that glyphosate's effects on soil flora will be limited. However, some recent work shows that glyphosate can be readily released from certain types of soil particles, and therefore may leach into water or be taken up by plants. Due to its strong retention on soil components, high solubility in water and long half-life in the environment (about 47 days), glyphosate may still be detected long after application or even far from the site of application. However, because its effects on non-target organisms and overall environmental impact have not been fully investigated, questions regarding the environmental safety with its increasing use have to be addressed. The widespread application generates problems regarding environment contamination and therefore, determination of glyphosate in crops, vegetables, and fruits has gained increasing importance. However, in comparison to all herbicides used in agriculture, glyphosate is probably the most difficult to analyze. One objective of this project is to develop analytical method able to provide rapid, sensitive, easy and reliable detection of degradation residues of glyphosate and AMPA residue using ^{31}P NMR spectroscopy.

Abiotic oxidative degradations of both glyphosate and AMPA to sarcosine induced by manganese oxide have been demonstrated by Barrett and McBride. The degradation of PMG into AMPA is of particular interest. This is because (i) AMPA is the main degradation product of glyphosate, (ii) AMPA is toxic to some plant species, including GR crops, and (iii) recent results indicate that injury to GR crops after application of glyphosate may be caused by AMPA formed from glyphosate degradation, with the extent of this damage strongly depending upon AMPA levels.

In this project, the catalytic degradation of glyphosate and AMPA in aqueous samples with ZnS, Fe_2O_3 and TiO_2 nano particles as the catalyst will be studied. The effects of various parameters, such as the amount of the catalyst, degradation time, initial pH value, metal ions, and anions on the catalytic degradation of glyphosate and AMPA will be investigated. From the collected data, the best condition for the effect of the parameters on the photocatalytic degradation of glyphosate will be obtained. Possible degradation mechanism will be discussed

Materials and methods

Water, Soil and Sediment Sample preparation:

The soil samples were purchased commercially from Home Depot, and some soil samples were also be collected from different locations in DC metropolitan area, and sediment samples were chosen from various locations in the Potomac and Anacostia rivers. Sediment samples were collected from surface of the sediments in clean glass bottles as recommended by the Environmental Protection Agency (EPA) method 3050 "Acid Digestion of Sediments, Sludges, and Soils". The samples were stored frozen in plastic bags until analyses. Soil or sediment sample (20 g) is placed in bottles and known concentrations of glyphosate and AMAP solutions are added to provide concentration level of 5, 10 and 15 $\mu g\ g^{-1}$. The bottles are shaken manually or stirred by using magnetic stirrer for uniform mixing and kept for 1 day, 2 days, 4 days and 1 week at various temperatures (10^oC, 20 ^oC, 20 ^oC, 50 ^oC). Catalytical amount of Fe_2O_3 or ZnO will be used in all of the degradation experiment with one experiment free of any catalyst as the control.

Soil and sediment sample extraction

Preparation of soil and sediment samples for ^{31}P NMR analysis was done according to the procedure in the literature. According to this method, a 20-g soil sample is extracted with 200mL of demineralized water by shaking in an end-over-end shaker for 18 h at 25 ^{o}C. The extracts are centrifuged for 40 min at 10,000 g and the supernatant is discarded. Soil and/or sediment residue will be extracted twice with 40mL of 0.4M NaOH for 4 h, and the extracts are combined. After each extraction, the samples are centrifuged for 40 min at 10,000 g. The supernatants from each sample are pooled and subjected to gel filtration to remove NaOH. A G-25 Sephadex column (with a fractionation range of 100–5,000 mol wt, dry bead diameter of 20–80 mm, volume of 4–6 mL g^{-1}, column volume of 75.0 mL) will be used. Twenty mL of the extract are then pipetted onto the top of the column and eluted with demineralized water by pumping at a rate of 0.6 mL min^{-1}. Leachate is then collected until litmus paper indicated an alkaline pH, suggesting that NaOH is passing through the column. A total of 110mL of the leachate, free from NaOH, is then freeze-dried for subsequent use for ^{31}P NMR analysis. Each sample will be performed in triplicates.

NMR experiments and Instrumentation

All measurements were conducted on a Bruker Avance III Ultrashield 400-MHz NMR spectrometer equipped with a 5-mm inverse z-gradient broad-band probe head at 298 K. Topspin (Bruker) is used for data processing and analysis with further data analysis carried out in Microsoft Excel and Graph Pad Prism. All spectra were collected without X nucleus decoupling to prevent sample heating during the measurement influencing the enzymatic reaction and causing drifts in the chemical shifts. The proton pulse length is calibrated by the 360° pulse method whereas the phosphorus pulse is calibrated by optimization in the 1D ^{1}H–^{31}P HSQC experiment. The pulse sequence used for the 1D ^{1}H–^{31}P HSQC is that published in the literature. By using the microemulsion as the solvent, the proton signals of the organophosphorus compounds may not be observed individually because of the strong background signal of the microemulsion itself, making the 360° pulse method unfeasible. For this reason the proton pulse will be optimized starting from the optimized value obtained for the aqueous buffered solution directly in the HSQC experiment analogous to the phosphorus pulse. All samples were shimmed by automated gradient shimming and automatically tuned. The spectra will be weighted with an exponential function and a line broadening of 0.3 Hz will be applied. The transmitter frequencies are 4 ppm for the proton pulses and 32 ppm for the phosphorus pulses. Values for chemical shifts of protons in the HSQC and in the presaturation experiments will be assigned by using a normal ^{1}H NMR experiment measured with TSP as the reference.

1D ^{1}H–^{31}P HSQC NMR Experiment

^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy are routinely applied in verification laboratories for screening samples for the presence of organophosphorus. Problems arise when the compounds of interest are in complex media where other components can mask resonances in standard ^{1}H NMR spectra. Furthermore the low sensitivity of ^{31}P can be problematic when the organophosphorus compounds are present in trace amounts. A logical step is to combine the sensitivity of ^{1}H NMR with the selectivity of ^{31}P NMR to identify phosphorus containing compounds. This can be achieved by introduction of inverse $^{1}H–^{31}P$ experiments, for example the $^{1}H–^{31}P$ HSQMBC (heteronuclear single quantum multiple bond coherence), HSQC (heteronuclear single quantum coherence), and ^{31}P decoupled HSQC experiments. These experiments exclusively detect signals from protons coupled to phosphorus nuclei with the sensitivity of ^{1}H NMR while removing the sample background effectively. It was recently shown that a 1D $^{1}H–^{31}P$ HSQC experiment could be successfully used to detect trace amounts of organophosphorus compounds in complex decontamination media at the low parts per million level.

Undergraduate Research Training

One undergraduate chemistry student was involved in the project. He was responsible for the use of chemical literature, preparation of samples for NMR analysis and aid in preparing NMR samples. The students involved in this project hade chance to experience chemical research in organic chemistry, analytical chemistry and environmental chemistry. The following is the typical schedule for the student's research activities in this project.

Week One and Two

- Basic Chemistry Research training for undergraduate student
- NMR training for undergraduate student
- Literature Reading

Week Three and Four

- Initiate the preparation of soil samples with glyphosate and AMPA
- Initiate the NMR analysis of standard glyphosate and AMPA

Week Five and Six

- Run decomposition reaction of glyphosate and AMPA with nanomaterial as the catalyst
- Prepare NMR samples to analyze the decomposition rate of glyphosate and AMPA

Week Seven and Eight

- Analyze NMR data to detect and identify the decomposition species
- Repeat decomposition reactions with various nano catalysts

Preliminary Results

Preliminary NMR data show that glyphosate didn't undergo decomposition at room temperature. Stirring for 24 hrs at room temperature shows no changes in both proton and phosphorous NMR spectra. While decomposition was observed when glyphosate was stirred fro 24 hrs with commercial available soil purchased from Home Depot, there was no evidence for the decomposition when glyphosate was stirred under the same conditions for 24 hrs with pre-frozen sediment soils. The reason for that could be because the there were no micro-organisms in pre-frozen sediment soil. This strongly supports that the decomposition of glyphosate in soil depends heavily on the concentration of the micro-organisms in the soil.

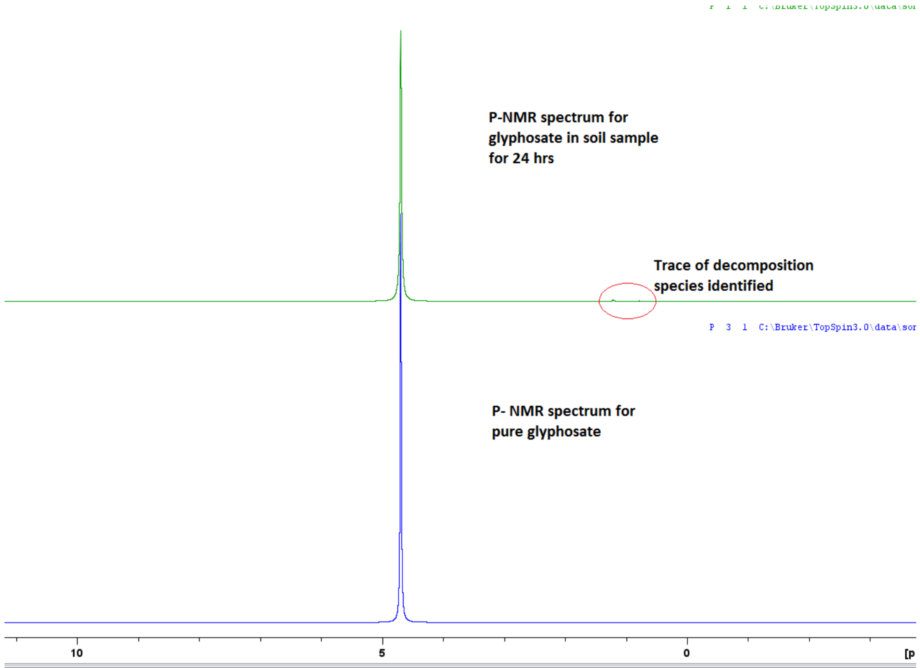

Fig 1. Decomposition of glyphosate in soil sample.

The preliminary data also showed that soil samples have very strong affinity to glyphosate, after 24 hrs, no glyphosate can be extracted from the soil. Increase the concentration of glyphosate in the soil sample can increase the concentration of glyphosate in the extract.

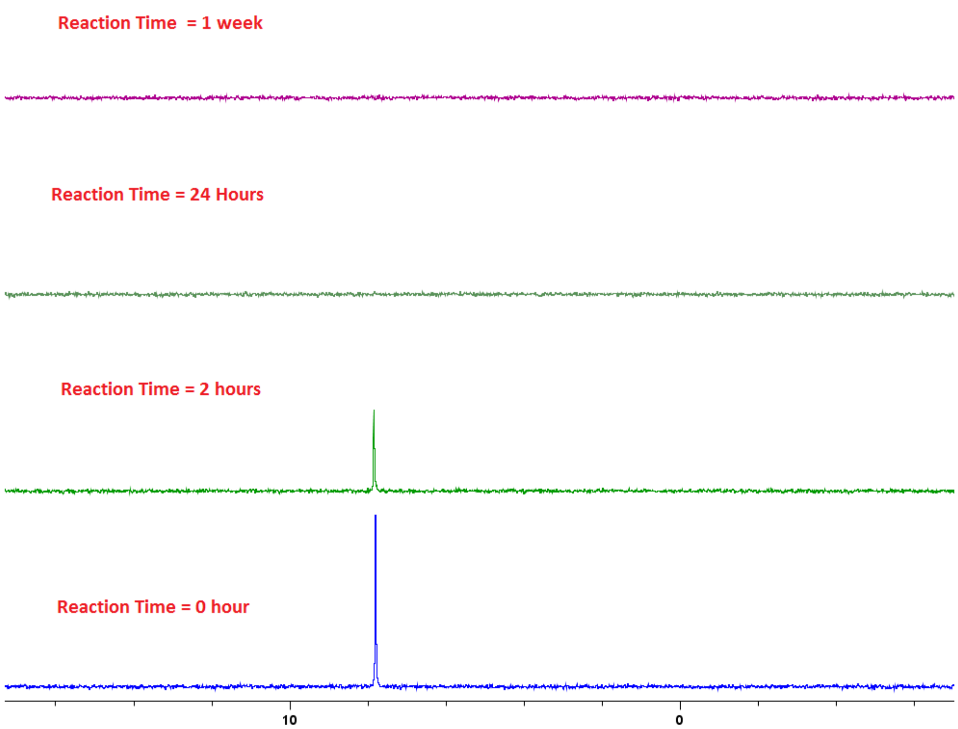

Fig. 2. Strong affinity of soil sample to glyphosate. (no glyphosate can be detected after 24 hrs.

Related research:

1. Coutinho, C. F. B.; Coutinho, L. F. M.; Mazo, L. H.; Nixdorf, S.L.; Camara, C. A. P.; Lancas, F. M. "Direct determination of glyphosate using hydrophilic interaction chromatography with coulometric detection at copper microelectrode." *Anal. Chim. Acta* **2007**, *592*, 30–35.

2. Khrolenko, M. V.; Wieczorek, P. P. "Determination of glyphosate and its metabolite aminomethylphosphonic acid in fruit juices using supported-liquid membrane preconcentration method with high-performance liquid chromatography and UV detection after derivatization with p-toluenesulphonyl chloride." *J. Chromatogr. A* **2005**, *1093*, 111–117.
3. Kudzin, Z.H.; Gralak, D.K.; Andrijewski, G.; Drabowicz, J.; Luczak, J. "Simultaneous analysis of biologically active aminoalkanephosphonic acids." *J. Chromatogr. A* **2003**, *919*, 183–199.

4. Borjesson, E.; Torstensson, L. "New methods for determination of glyphosate and (aminomethyl) phosphonic acid in water and soil." *J. Chromatogr. A* **2000**, *886*, 207–216.

5. Kudzin, Z.H.; Gralak, D.K.; Drabowicz, J.; Luczak, J. "Novel approach for the simultaneous analysis of glyphosate and itsmetabolites." *J. Chromatogr. A* **2002**, *947*, 129–141.

6. Tadeo, J. L.; Sanchez-Brunete, C.; Perez, R. A.; Fernadez, M. D. "Analysis of herbicide residues in cereals, fruits and vegetables." *J. Chromatogr. A* **2000**, *882*, 175–191.

7. Hu, J. Y.; Chen, C. L.; Li, J. Z. "A simple method for the determination of glyphosate residue in soil by capillary gas chromatography with nitrogen phosphorus." *J. Anal. Chem.* **2008**, *63*, 371–375.

8. H. Koskela, M.-L. Rapinoja, M.-L. Kuitunen, P. Vanninen, "Determination of Trace Amounts of Chemical Warfare Agent Degradation Products in Decontamination Solutions with NMR Spectroscopy" Anal. Chem. **2007,** *79*, 9098-9106.

9. Jürgen Gäb, Marco Melzer, Kai Kehe, Stefan Wellert, Thomas Hellweg and Marc-Michael Blum "Monitoring the hydrolysis of toxic organophosphonate nerve agents in aqueous buffer and in bicontinuous microemulsions by use of diisopropyl fluorophosphatase (DFPase) with 1H–31P HSQC NMR spectroscopy" *Anal Bioanal Chem*. **2010,** *396*, 1213–1221

Information Transfer Program Introduction

There is no formally funded outreach and training programs, but the Institute continued its outreach and training activities in various ways, including annual water symposium starting April 2013. The links to the conferences are as follows: o 2017 NCR-AWRA Water Symposium: http://www.awrancrs.org/events/70-2017-symposium.html o 2016 NCR-AWRA Water Symposium: http://www.awrancrs.org/events/62-2016-symposium.html • 2016 Mid-Atlantic Sustainable Water Resources Roundtable: https://acwi.gov/swrr/proceedings/SWRR- Proceedings_MidAtlantic_12-6-16.pdf We also lounched laboratory testing services by establishing nationally accredited water quality lab: https://www.udc.edu/eqtl/ We continued training future water professionals through our Professional Science Master's degree program in Water Resources Management: https://www.udc.edu/causes/professional- science-masters-program/ We continued training students in advanced water quality testing technologies through our nationally accredited lab (NELAP).

USGS Summer Intern Program

None.

Student Support					
Category	**Section 104 Base Grant**	**Section 104 NCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	8	0	0	0	8
Masters	6	0	0	0	6
Ph.D.	1	0	0	0	1
Post-Doc.	0	0	0	0	0
Total	15	0	0	0	15

Notable Awards and Achievements

The WRRI seed grants have helped many young faculties to receive large extramural funding. For example:

1. Dr. Jiajun Xu received $299,934.00 from NSF as a principal investigator. He also received about $60,000.00 grant from NIFA.

2. Dr. Nian Zhang received $99,998.00 and $18,321.00 as a Co-PI from NSF for two different projects.