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NSF/REU Site

Interdisciplinary Water Sciences and Engineering

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1- Engineering Education, 2 - Civil and Environmental Engineering, 3 – Biological Sciences
4 - Crop and Soil Environmental Sciences, 5 – Geosciences, 6 – Biological Systems Engineering

Host Lab: www.lewas.centers.vt.edu

LEWAS LAB
LEARNING ENHANCED WATERSHED ASSESSMENT SYSTEM

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Acknowledgements

We would like to express our sincere thanks to REU/NSF Site Research Mentors for their kind cooperation and excellent mentoring during summer 2015. Our thanks are also to our graduate student mentors, REU Fellows for their dedication and excellent performance, laboratory staff, seminar speakers, professionals who assisted in field trips and all other individuals who directly/indirectly contributed to the success of our 10-week research program at VT. The program is supported by the National Science Foundation (NSF-REU Grant No. 1359051*).*

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Summary

This Research Proceedings includes papers of undergraduate research that was conducted at Virginia Tech during summer 2015 as part of an NSF/REU Site on Interdisciplinary Water Sciences and Engineering. This was the second year of the 3rd cycle of the NSF/REU Site that will be implemented during 2014, 2015, and 2016. This 3rd cycle of this REU Site follows two very successful REU Site cycles that were implemented 2007-09 and 2011-13. Research Proceedings of all these years are available at: www.lewas.centers.vt.edu. At the end of summer 2015, 76 REU Fellows (47 women and 29 men) have graduated from REU Sites.

Our Site continues to expose qualified undergraduates to interdisciplinary research issues in water sciences and engineering. Faculty members from five departments (Engineering Education, Civil and Environmental Engineering, Biological Sciences, Geo-sciences, biological Systems Engineering, and Crop and Soil Environmental Sciences) at Virginia Tech mentored 10 excellent undergraduates who were recruited out of a nation-wide competition. Ten graduate students from these departments assisted the faculty mentors and got a valuable experience in mentoring undergraduate research students. Figure 1 shows a word cloud of the keywords that describe the research activities undertaken during the 10-week research at VT.

Figure 1: Word Cloud of Keywords – 2015 Research Work

Ms. Erwin, an REU scholar from West Carolina University and her co-authors, used the high frequency water data from the Learning Enhanced Watershed Assessment System (LEWAS) lab and grab sample data to investigate the empirical relationship between turbidity and specific conductance. Also, nutrients phosphorus and nitrogen were considered for establishing the empirical relationships. Since most of the observation were taken during base flow conditions, minimal variation in the parameters was observed and need for taking such observations during storm flow events is emphasized. An REU scholar from the University of

Texas at Austin, Ms. Deo, and her co-authors investigated drought conditions in Northern Shenandoah River Valley. They analyzed various drought indicator data such as precipitation, stream discharge, and ground water levels. In addition, drought indices such as standardized precipitation index (SPI) and standardized streamflow index (SSI) were analyzed to characterized drought conditions in the region which was shown useful for the purpose of water supply planning. An REU scholar from SUNY College of Environment Science and Forestry, Ms. Canham, and her co-authors investigated sediment transport due to hurricane overwash events in barrier islands. Xbeach model was used for the purpose of simulation and seven different idealized hurricane events were analyzed. Mr. Fry, and REU scholar from Colorado State University, and his co-investigators did a preliminary study in the LEWAS lab to identify locations that are of interest in identifying potential sources of pollution within the watershed that drains at the LEWAS monitoring site. A preliminary web-based data collection tool was developed that allows photographs around the Webb Branch Watershed to be uploaded into the LEWAS database, as well as display geographic and timestamp information about the photograph. Ms. Johnson, and REU scholar from Boston College, and her co-investigators studied distribution of neonicotinoids (such as Thiamethoxam (TMX) and its metabolite Clothianidin (CLO)) in Stroubles Creek watershed. These are widely used insecticides commonly coated on planting seeds and do travel from fields to waterways. Based on 7 sediment samples along the Creek, it was found that TMX does not stay contained within the application area. An REU scholar from Virginia Tech, Ms. Carolan, and her co-investigators analyzed the effects of flow rate on turbidity and microbial growth in premise plumbing systems. The motivation was to investigate the water and energy-conserving plumbing systems for their potential to promote microbial growth and it was found that lower flow rates create favorable conditions for microorganism regrowth. Ms. Ryan, an REU scholar from Virginia Tech, and her co-authors analyzed the drivers of vertical cynobacteria, one phytoplankton group, distribution in Beaverdam Reservoir (BVR), an unmanaged drinking water source in Vinton, Virginia. They also analyzed percentage of living and nonliving phytoplankton in a managed reservoir (Falling Creek Reservoir) and compared data with the BVR. Ms. Molitor, an REU scholar from University of Wisconsin, Platteville, and her co-investigators examined simultaneous resource recovery and treatment of landfill leachate, a high strength wasterwater, by combining microbial electrolysis cell (MEC) to forward osmosis (FO). The results provided support to the potential of coupled MFC-FO systems to recover valuable resources from landfill leachate. Mr. Shilling, an REU scholar from Milwaukee School of Engineering, and his co-authors investigated amount of dissolution of copper and iron nanoparticles in different digestive fluids (saliva, gastric, and intestinal) and also looked at the reactivity of common nano-particles (nano-iron, silver, copper) in the human digestive system. Results indicated that nanoparticles' reactivity significantly differed among each other and among each digestive fluid. Finally, Ms. Marsh, and REU scholar from Clarkson University, and her co-authors examined the impact of livestock exclusion from streams on greenhouse gas flux. Two streams, one fenced off and another unfenced, were investigated for greenhouse gas concentrations and preliminary data suggested that the tributary where cows have access to the stream produced higher emission for all greenhouse gases (CO_2, CH_4, etc.).

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Research Papers

For Resource Recovery from Landfill Leachate through Microbial Electrolysis Cells Coupled to Forward Osmosis

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Abstract

Global concerns over diminishing resources, specifically water scarcity, have prompted investigation of technologies that salvage valuable resources from waste. This study examined simultaneous resource recovery and treatment of landfill leachate, a high strength wastewater, by coupling a microbial electrolysis cell (MEC) to forward osmosis (FO). The synergistic relationship of this coupled system makes it an attractive option for energy-efficient recovery of ammonia, electricity, and water from leachate. The coupled system utilizes anaerobic microbes in the MEC anode to oxidize organic contaminants in leachate for electricity generation, which drives ammonium from the wastewater to be collected in the MEC cathode. The recovered ammonium is then used as a draw solute in the FO for water recovery from the MEC effluent (treated leachate). The performance of the coupled system was evaluated in batch mode through analysis of the chemical oxygen demand (COD) removal, ammonia removal, and water recovery from the leachate. The MEC removed up to 27% of COD, and 40% to 68% of ammonium. Obtained batch-profile current generation was affected by substrate supply and consumption. The FO achieved 50.5% water recovery from the treated leachate with a 2 M ammonium bicarbonate draw solution. The results indicate that coupled MEC-FO systems may be applied to recover valuable resources from landfill leachate, which would significantly offset the economic and energy requirements of leachate treatment. The coupled system may offer an appealing and sustainable approach to leachate management.

Keywords: microbial electrolysis cells, forward osmosis, leachate treatment, water scarcity, waste water.

1. Introduction

1.1 Water Scarcity

One of our most pressing global issues is water scarcity, which presents itself in two forms: physical and economic. Physical scarcity occurs when the land cannot provide enough water to meet the water resource demands of its population. Economic scarcity occurs when water is available but a population does not have the monetary means to access what should be an adequate source of water. Economic scarcity is often about unequal resource distribution due to political or ethnic conflict. Though economic scarcity can be remedied through improved policy or local engineering solutions, physical water scarcity is a greater challenge. It is increasingly "common that physical water scarcity is a man-made condition" (The Water Project, 2015). A significant portion of our world population faces the challenge of finding clean water, a basic need for survival (Figure 1).

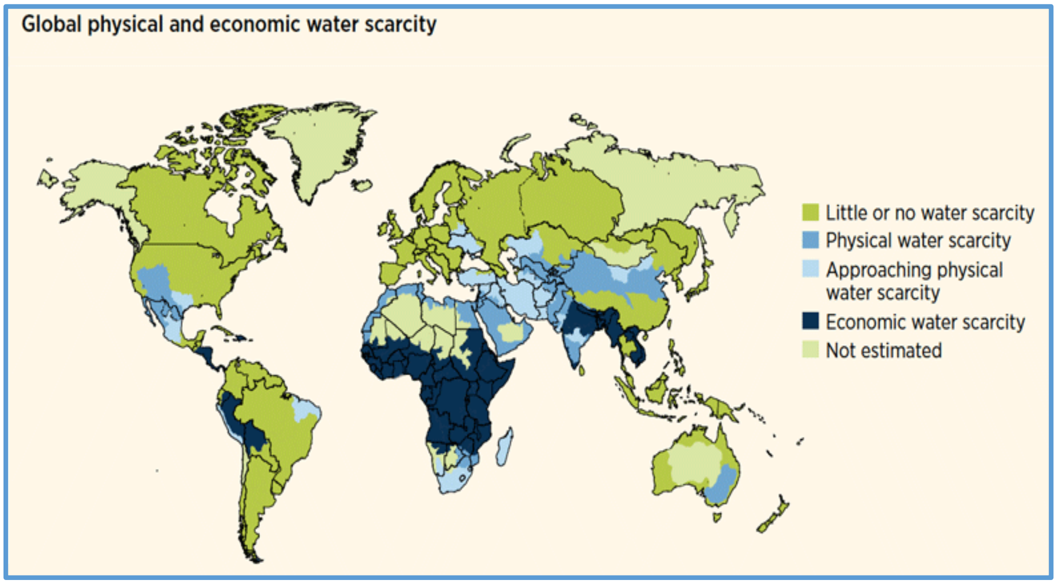

Figure 1. Global physical and economic water scarcity (UN World Water Development Report 4, 2014)

As of 2014, 1.2 billion people lived in areas of physical water scarcity and 1.6 billion were confronted with economic water scarcity (Unwater.org, 2014). It is predicted that 1.8 billion will face absolute water scarcity by 2025. Water scarcity is defined by the United Nations (UN) as less than 1000 m^3 of water per person and absolute water scarcity is below 500 m^3 of water per person, annually.

Water shortages are predicted to cause future conflicts over access to this resource, especially freshwater. In his keynote address to the 2000 Stockholm Water Conference, United States environmental analyst Lester Brown acknowledged “It is now commonly said that future wars in the Middle East are more likely to be fought over water than over oil.” Demand for such a critical resource in short supply would cause political and economic unrest, as water scarcity would quickly deteriorate overall quality of life and economic stability. Water scarcity in the most seriously affected regions (arid to semi-arid) is predicted to displace between 24 million and 700 million people (Unwater.org, 2014). Water scarcity often drives individuals to use water of poorer quality, which carries inherent dangers.

1.2 Sanitation Concerns

Wastewater treatment is exceedingly important to human health. Insufficiently treated wastewater, or water that entirely lacks treatment, exposes communities to bacteria, viruses, and protozoa that threaten physical wellbeing. Our food sources may also be contaminated through contact with untreated wastewater, creating another route for serious health impacts. Many are exposed to these risks, especially those in developing countries where 80% of produced wastewater is untreated (UN-Water Decade Programme on Advocacy and Communication, 2011). Rapid urbanization that exceeds the progress of sanitation facilities leaves substantial quantities of wastewater untreated and direct discharge to water bodies threatens those downstream. Due to a severe lack of wastewater treatment in developing countries (Figure 2), 20 million gallons of sewage and other effluents drain to global waters on a daily basis.

Note: Ratio of wastewater treatment (March 2010).
Source: UNEP/GRID-Arendal (http://maps.grida.no/go/graphic/ratio-of-wastewater-treatment1, adapted from a map by H. Alhenius with sources UNEP-GPA [2004]).

Figure 2. Ratio of treated to untreated wastewater discharged into water bodies

The magnitude of the global sanitation problem requires implementation of sustainable and economical treatment technologies since untreated wastewater is a serious health threat to our health and environment.

1.2 Environmental Impact

The negative effects of wastewater discharge into the natural environment are not limited to humans. Environmental pollution can damage aquatic ecosystem health and contaminants can be subsequently transferred through the food web or contaminant migration. High pollutant levels, eutrophication, high coliform bacteria counts, hypoxia, and fish-kills are caused by wastewater pollution. One of the most evident forms of aquatic environmental harm is eutrophication of water bodies. Eutrophication in a water body is caused by accumulation of high nutrient concentrations, typically nitrogen and phosphorous in effluents, which promotes disproportionate algal growth. As the algae die off, the decomposition process consumes dissolved oxygen in the water and may create hypoxic conditions. Hypoxic conditions, or oxygen depleted conditions, cause fish-kills in extreme cases (Environmental Performance Index, 2015). Environmental damage may be mitigated through nutrient removal from wastewater. The necessity of nutrient removal is more attractive when it is taken into consideration that these nutrients are valuable resources that may be recovered from wastewater (Li, Yu & He, 2013). Nitrogen is crucial to plant growth and applied as ammonia fertilizer to many crops on a large scale. However, ammonia fertilizer is produced via the energy-intensive and costly Haber-Bosch process.

1.4 Energy Demand

Water and energy production and consumption are inextricably linked. Water resources are used for production and delivery of energy as in hydroelectric, nuclear, and thermal energy sources. According to UN-Water, approximately 8% of our world energy is used for pumping, treating, and transporting water. Advantages, therefore, may lie in co-production of water and energy. Other basic needs, such as our global food supply, depend on water and energy availability. As of 2014, agriculture accounted for

70% of global water use and 30% of global energy consumption. In consideration of the current and growing demand for basic resources, it is necessary to work toward sustainable solutions for water, food, and energy security (Unwater.org, 2014).

1.5 Resource Recovery & Simultaneous Treatment of Waste

As a global community we face the diminishment of our natural resources, such as fresh water, while our population, and therefore demand, increases. Our energy use continues to climb, yet we are still fossil fuel dependent. Significant portions of our global population lack access to safe water because they are without wastewater treatment. These factors take a toll on the quality of our environment and lives. The world is becoming increasingly aware of the advantages of resource recovery from wastes, and the possibilities with respect to wastewater. The wastewater treatment discussion is no longer exclusively about management; it's about extraction of the remaining value. Wastewater contaminants, such as nitrogen and phosphorous, may now be considered resources if processed by the appropriate technology. Solutions are certainly needed to face the problem of our dwindling resources as demands on them grow; however, the processes must also be economical and energy-efficient. Therefore the design of an economically realistic system that effectively treats wastewater, recovers water and nutrients, and offsets some of its own energy usage is highly desirable (Li, Yu & He, 2013). One such energy-efficient, emerging technology for wastewater treatment and resource recovery is the coupled MEC-FO system. MECs can remove organic carbon species, recover ammonia from wastewater, and generate electricity. Coupling MEC to FO lends the system the additional benefits of water recovery and waste stream reduction.

1.6 MEC

An MEC consists of two electrodes, an anode and a cathode, which are connected by a conductive wire but are separated by an ion selective membrane (Kuntke, Sleutels, Saakes & Buisman, 2014) (Figure 3).

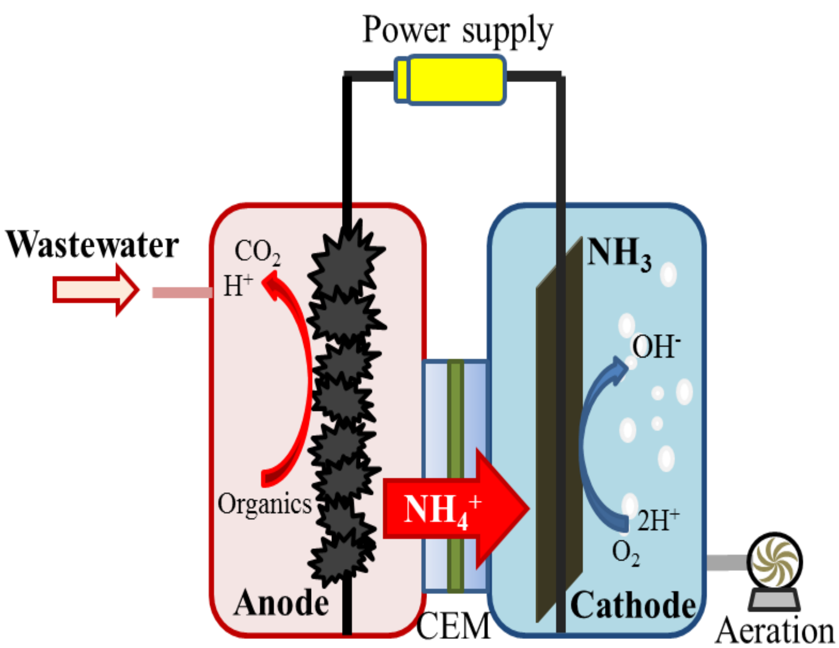

Figure 3. Microbial Electrolysis Cell Schematic (Yaobin Lu, 2014)

The anode and catholyte solutions are termed anolyte and catholyte, respectively. Within the anode chamber of the MEC, anaerobic microbes form a biofilm on the high surface area, conductive carbon brush anode. The microbes are able to oxidize the organic carbon species, and thereby treat the wastewater. COD (chemical oxygen demand) is an index for the concentration of organic species. The dominant microbial species responsible for external transfer in most bioelectrochemical systems are *Geobacter sulfurreducens* and *Shewanella oneidensis* (Pant, Van Bogaert, Diels & Vanbroekhoven, 2010). These anaerobic microbes are classified as exoelectrogens, microbes that release electrons when they degrade COD to carbon dioxide (CO_2), protons (H^+), and electrons.

$$COD \rightarrow CO_2 + H^+ + e^- \qquad \text{(Eq. 1)}$$

Production of CO_2 decreases the pH of the anolyte due to its slightly acidic character. Electrons released from oxidation of COD are transferred to the anode electrode, which is the only available electron acceptor in the anode, and then flow to the cathode electrode through a conductive wire. Within the cathode, electrons reduce protons to hydrogen (H_2) gas.

$$H^+ + e^- \rightarrow H_2 \qquad \text{(Eq. 2)}$$

The electron flow generates current that is supplemented by an additional external 0.8 V power supply in order to provide sufficient energy for the proton reduction reaction.
Ammonium (NH_4^+) from the leachate migrates across a cation exchange membrane (CEM) to the catholyte to balance the flow of negatively charged electrons with positive charge. The high pH in the cathode causes NH_4^+ to be converted to volatile ammonia (NH_3). Gas that evolves from the catholyte is rich in ammonia, which can be collected at the liquid-gas boundary into an absorption solution. The absorption solution may be either an acidic solution or a CO_2 saturated solution. Reaction of NH_3 with CO_2 generates ammonium bicarbonate (NH_4HCO_3), a thermolytic salt, which may be used as an FO draw solute.

1.7 FO

An FO system has two chambers, a draw chamber and a feed chamber, separated by an FO membrane (Figure 4).

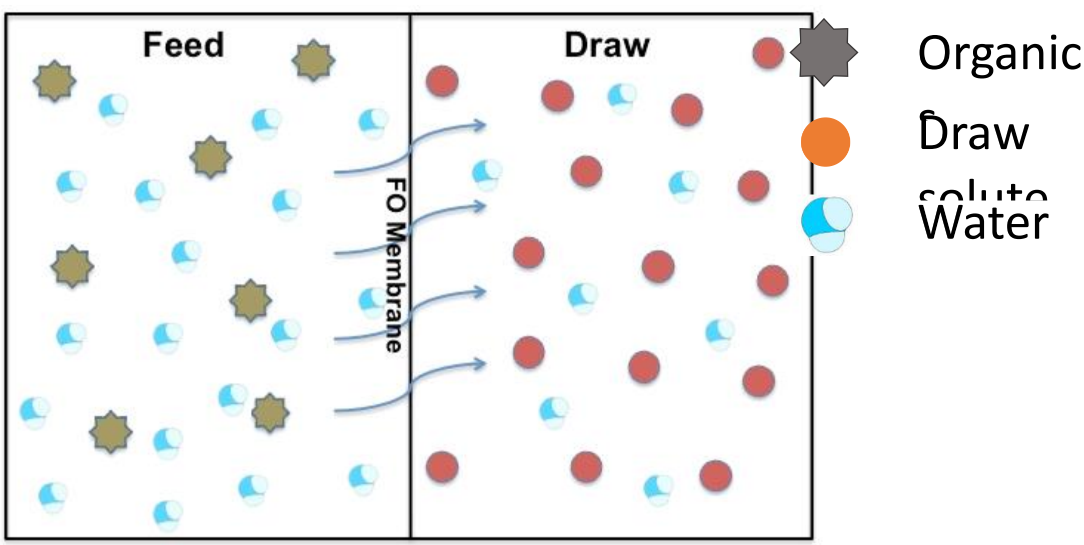

Figure 4. Forward osmosis cell schematic. (Hannah Molitor, 6/15/15)

The FO feed and draw solutions are circulated through their separate chambers. Water may be extracted from the feed side across the FO membrane using NH_4HCO_3 draw solution. An osmotic pressure gradient is created between the draw and feed solutions and water is drawn from the low to high salt concentrations (feed to draw side). When applied to wastewater streams, FO can recover water from wastewater and reduce the volume of the wastewater stream.

Thermolytic salts, which can be liberated from solution with low heat, are a practical option for FO draw solutes because they are recyclable (Qin & He, 2014). NH_4HCO_3 is one such thermolytic salt and requires approximately 60°C to be recovered as gaseous NH_3 and CO_2 from FO draw solution. The recovery process temperature is sufficiently low as to not require an actual heat source, but could utilize available waste heat (i.e. from a power plant). The cost-effectiveness of FO technologies may be compromised if the draw solute is not efficiently recycled and frequent chemical purchase is required. Loss of draw solute could occur through incomplete recovery from FO draw effluent or reverse salt flux, loss of solute from the draw solution to the feed solution. Reverse salt flux is problematic because it further contaminates the waste stream and it reduces the osmotic pressure gradient that draws water from the feed.

1.8 Coupled MEC-FO

A coupled MEC-FO closed-loop system would be a cost-effective treatment option through simultaneous resource extraction and wastewater treatment (Figure 5).

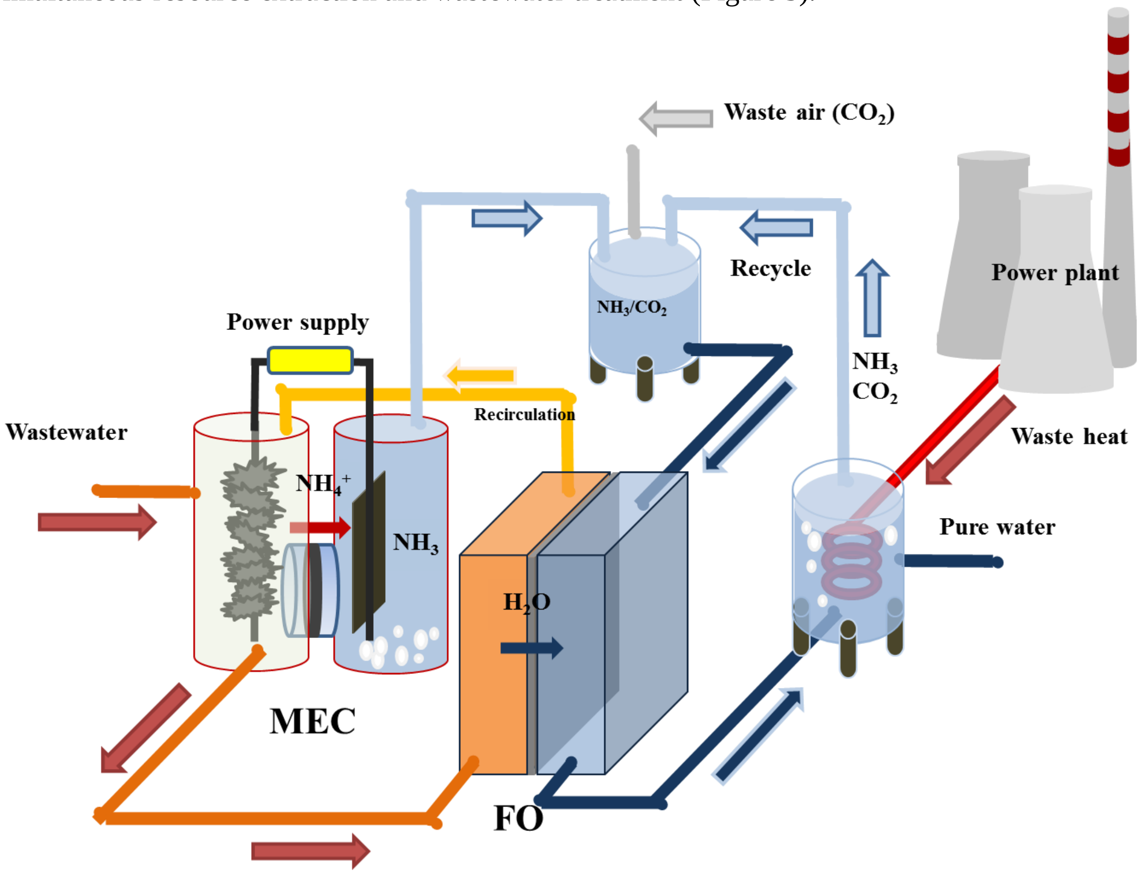

Figure 5. Coupled MEC-FO system. (Dr. Yaobin Lu, 2014)

In the coupled MEC-FO system, anolyte enters the MEC anode where COD and NH_3 are removed. Anolyte then continues from the anode to the FO cell as feed influent. Water is recovered across the FO membrane and the concentrated feed effluent is circulated back to the anode, which could prevent deterioration of the wastewater quality from reverse salt flux.

Recovered NH_3 is stripped through aeration of the catholyte, and reacted with waste CO_2 to produce NH_4HCO_3 draw solute (Qin & He, 2014). Once the draw solute is diluted by water permeation (and the water flux across the FO membrane is significantly decreased), the draw solution is sent to a heat recovery unit to be concentrated using waste heat, separated from the recovered water, and recycled.

1.9 Landfill Leachate

Landfill leachate, the liquid that drains from a landfill, may be produced through decomposition of landfill materials or drainage of precipitation that permeates and percolates through the landfill. Any landfill in temperate to tropical climates will produce landfill leachate, which must be safely treated to prevent environmental contamination. Though there is a great societal push to reduce waste streams, recycle, and reuse, it is predicted that landfills will continue to be created and filled in the coming years due to their economic advantage over other waste management strategies. Without additional input, existing landfills would still produce leachate for decades. Landfill leachate contains both dissolved and suspended solids but the composition varies as the landfill ages. The discharge standards for landfill leachate are becoming increasingly strict in most countries, which require better purification through treatment processes. Membrane technologies are frequently employed to effectively treat leachate; reverse osmosis (RO) in particular is often an integral treatment or post-treatment step for landfill leachate purification (Renou, Givaudan, Poulain, Dirassouyan & Moulin, 2008). However, RO requires energy to apply pressure to the wastewater feed, which increases cost. Furthermore, leachate composition varies across sites and over time. Therefore, treatment technologies must be adaptable and universal.
Landfill leachate is a complex liquid that contains salts, ammonia, and wide range of organics (including volatile fatty acids). Leachate is classified as high strength wastewater, which has elevated concentrations of organic matter (approximately 10,000 mg/L COD or greater). Leachate also has relatively high conductivity, which indicates high salt concentrations, and high ammonia concentrations (Table 1). The chloride content of landfill leachate is especially high with respect to other ions present. Heavy metals were detected (Cu, Fe, Ni, and Zn) albeit at low concentrations and the pH of the leachate was slightly alkaline. Iron (23.8 ppm) and humic substances likely caused the leachate's dark brown color.

Table 1. Chemical Characteristics of Landfill Leachate

Parameter	Value	Unit
pH	7.94	
Conductivity	28.1	mS cm^{-1}
COD	9,175	mg L^{-1}
NH_4^+-N	4,540	mg L^{-1}
Na	3,342	mg L^{-1}
Cl	25,184	mg L^{-1}
Mg	130.8	mg L^{-1}
Si	60.9	mg L^{-1}
P	16.4	mg L^{-1}
Ca	72.5	mg L^{-1}
Fe	23.8	mg L^{-1}
Cu	0.8	mg L^{-1}
Ni	0.2	mg L^{-1}
Zn	0.7	mg L^{-1}

High concentrations of COD represent significant potential for energy production from wastewater using MEC technology. Under ideal conditions, or 100% efficiency, one liter of the collected landfill leachate (9,175 mg/L COD) could generate 110,700 C of charge when oxidized in the MEC anode; enough to power a home's 60 W light bulb for 60 hours. The significant levels of ammonia in leachate indicate that it could be efficiently recovered to produce draw solute for the FO process. These characteristics, in addition to its continued production, make landfill leachate an attractive MEC anolyte. However, the high salt concentrations can inhibit oxidation of COD by damaging the anaerobic microbes.

1.10 Justification

Previous studies of landfill leachate treatment via MEC have either failed to demonstrate treatment efficiency, energy recovery, or economic feasibility. One such study performed three-fold to nine-fold dilutions of the landfill leachate with distilled water then used phosphoric acid to adjust the solution to pH 7 (Greenman, Gálvez, Giusti & Ieropoulos, 2009). Neither increasing the volume of the wastewater to be treated nor chemical pH adjustment are efficient or economical. Prior works have neglected the importance of ion accumulation and migration within the MEC and accounted for the ion flux across FO in a coupled MEC-FO system. In addition to NH_3 and COD concentrations, ion concentrations are key to the quality of wastewater. Microbial fuel cell (MFC) studies have demonstrated wastewater treatment and energy generation with landfill leachate. MFC power production performance may benefit from the high salinity of leachate because it lowers the internal resistance (Puig et al., 2011). However, the implications of increased salinity for COD removal were not examined.

2. Methods

2.1 Experimental Setup

2.1.1 Microbial Electrolysis Cell

Landfill leachate treatment experiments used a tubular bench-scale MEC assembled with and inner cathode chamber separated by a cation exchange membrane (CMI-700, Membranes International, Ringwood, NJ, U.S.A.) from the surrounding anode chamber. The liquid volumes of the anolyte and catholyte were 500 mL each. The anode and cathode electrodes were 1 m folded carbon brush and 160 cm^2 carbon cloth with platinum catalyst (0.3 mg Pt cm^{-2}), respectively. The anode was filled with landfill leachate anolyte to maintain an anaerobic environment for the microbes introduced via inoculation with anaerobic digester sludge. Deionized water was added as catholyte and the MEC circuit was supplemented with a 0.8 V power supply. Gas collection containers were attached separately to the anode and cathode chambers for capture and analysis.

2.1.2 Forward Osmosis

A bench-scale SEPA CF FO Cell (Sterlitech Corporation, Kent, WA, U.S.A.) with cellulose triacetate FO membrane (Hydration Technologies, Inc., Albany, OR, U.S.A.), with its active layer toward the feed side, was used for all FO experiments. Feed and draw influents and effluents were analyzed before and after operation to determine water flux and reverse salt flux.

2.2 Operation

2.2.1 Microbial Electrolysis Cell

Five non-aerated, batch-mode MEC cycles were begun with a 50:50 mixture of fresh to treated leachate (effluent from a previous cycle). During the non-aerated phase, a gas collection bag was attached to the cathode for NH_3 collection. Each cycle was continued until current generation was significantly low (3 mA), at which time the 50% of the anolyte effluent was removed and replaced with fresh leachate. Current was monitored and recorded at two-minute intervals. The pH of the catholyte was adjusted from pH 10.11 to pH 12.60 with sodium hydroxide (95 mL, 1 M) at the start of the fifth cycle to encourage ammonia gas evolution.

2.2.2 Forward Osmosis

The masses of the feed and draw solution bottles were monitored and recorded every 30 seconds during operation to observe the change in water flux over the course of the experiment. The feed and draw solutions were circulated through their respective chambers at 0.18 L/min during operation. FO experiments were complete when either the feed solution was depleted or the water flux had reached zero. The change in feed volume was used to calculate the water recovery during operation.

2.3 Measurement and Analysis

Solution pH was measured with a pH meter (Oakton pH 700, Oakton Instruments, Vernon Hills, IL, U.S.A.) and conductivity was measured with a conductivity meter (Mettler-Toledo, Columbus, OH, U.S.A.). MEC treatment performance was judged through removal of ammonia and COD. Total ammonia concentrations in 10 mL samples were quantified using an ammonia meter (Fisher Scientific Accumet AB250, Pittsburgh, PA, U.S.A.) after sodium hydroxide (0.2 mL, 10 M NaOH) was introduced to convert all ammonium to ammonia. COD concentrations were measured using a colorimeter (Hach DR/890, Hach Company, Loveland, CO, U.S.A.). Ion concentrations were quantified through either ion chromatography (Dionex LC20 ion chromatograph, Sunnyvale, CA, U.S.A.) equipped with an ED40 eletrochemical detector or inductively coupled plasma- mass spectrometry (Thermo Electron X-Series ICPMS, Waltham, MA, U.S.A.). Concentrations of NH_3 and CO_2 gases in MEC samples were quantified via a Shimadzu GC-14A gas chromatograph equipped with a thermal conductivity meter (TCD) as in a previous study (Qin & He, 2014).

2.4. Calculations

2.4.1 Coulombic Efficiency

Current generation is affected by substrate supply and consumption. The Coulombic efficiency in batch-fed mode, $\in_{Cb}$, depends on the Coulombs transferred from the substrate to the MEC anode electrode compared to the possible Coulombs transferred if all consumed substrate produced current. It is calculated by the ratio of measured (produced) current to the maximum current possible from the oxidation of COD in the anode,

$$\in_{Cb} = \frac{M\int_{0}^{t_b} I dt}{F b v_{An} \Delta COD} \qquad \text{(Eq. 3)}$$

where M = 32 (molecular weight of oxygen, g mol^{-1}), F (96485.3 C mol^{-1}) is Faraday's constant, b = 4 (moles of electrons exchanged per mole of oxygen), v_{An} is the anolyte volume (L), and ΔCOD (g L^{-1}) is the change in COD concentration over the period of a batch t_b (h) (Logan et al., 2006). The Coulombic efficiency of an MEC typically exceeds 100% due to the extra charge transfer caused by the application of an external power supply. The Coulombic efficiency may be decreased by other anaerobic microbes that compete with the exoelectrogens for substrate, bacterial growth, or use of electron acceptors other than the anode (species that migrate through the CEM or those present in the leachate) (Logan et al., 2006).

2.4.2 Flux

During FO it is desirable to quickly recover significant volumes of water from the FO feed to the draw solution. Performance of the FO was quantified by the rate of water flux J_w, or the volume of water that crosses the FO membrane per membrane area per time, which is calculated through

$$J_w = \frac{V_{initial} - V_{final}}{A_{membrane} * t} \quad \text{(Eq. 4)}$$

where V is the volume (L) of the feed solution before and after the FO experiment, $A_{membrane}$ is the membrane area (m^2) , and t is the duration (h) of the experiment. The calculated water flux would have units of L m^{-2} h^{-1}, denoted as LMH. Movement of solutes is calculated similarly through

$$J_s = \frac{\left| m_{initial} - m_{final} \right|}{A_{membrane} * t} \quad \text{(Eq. 5)}$$

where m is the mass of a particular species. The flux units then become g m^{-2} h^{-1}, denoted gMH. The salt flux is the mass of a species that crosses the FO membrane per membrane area per time from the feed to the draw solution. Reverse salt flux is the loss of draw solute to the feed side of the FO membrane.

3. Results and Discussion

3.1 MEC

3.1.1 COD Removal

COD removal is a primary parameter by which the effectiveness of wastewater treatment is judged. Our studies demonstrate that COD can be removed from landfill leachate but that the percent removal generally decreased and the effluent concentrations increased for subsequent cycles (Tables 2 and 3).

Table 2. Influent and Effluent COD Concentrations

Sample	COD (mg L^{-1})
Raw Leachate	9175
Batch 1 Influent	3090
Batch 1 Effluent	4440
Batch 2 Effluent	6450
Batch 3 Effluent	6270
Batch 4 Effluent	7110
Batch 5 Effluent	8610

Table 3. COD Removal Efficiency

Batch	COD Removed
1	27.6%
2	5.3%
3	19.7%
4	7.9%
5	0%

As COD removal efficiency decreased, and MEC anode effluent had higher concentrations of COD, the influent COD concentration of the next batch was consequently greater because 50% of the effluent was retained in the anode. The maximum COD removal during a single batch was 27%, and occurred during the first cycle.

3.1.2 Current Generation

MEC generates current in cycles when batch fed. The produced current reached a maximum after it was fed with new anolyte (50% fresh leachate and 50% returned effluent) and decreased as substrate was consumed and depleted

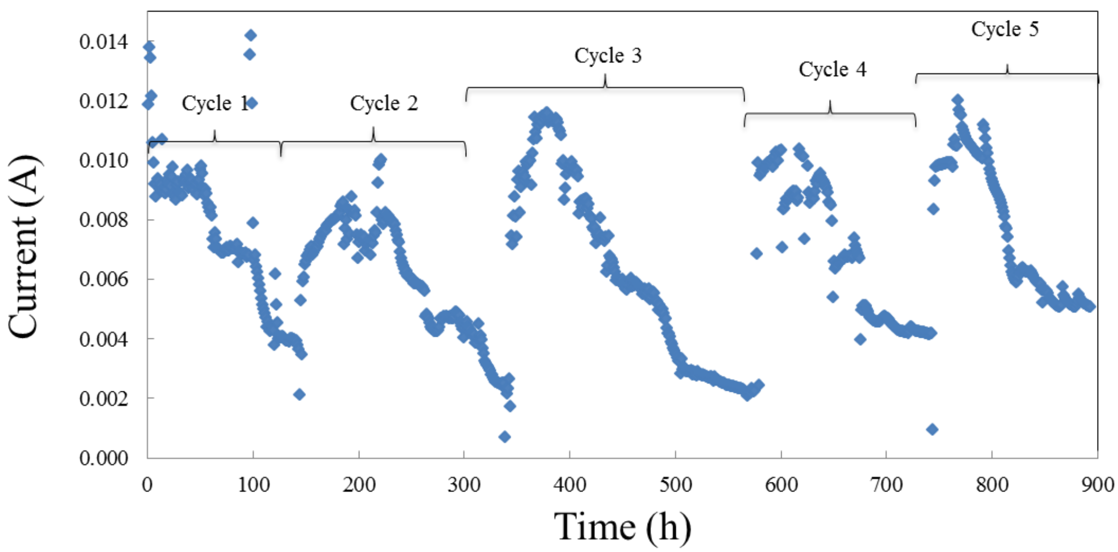

Figure 9. Current generation from MEC operated in batch-mode.

Coulombic efficiency is the ratio of produced current to the maximum current possible from the oxidation of COD in the anode (Eq. 3).

Though current generation was steady, variable and decreasing COD removal caused significant variation in the Coulombic efficiency of the MEC over five batches (Table 4).

Table 4. Coulombic Efficiency of MEC across 5 Batches

Batch	Coulombic Efficiency
1	37.6%
2	195%
3	55.2%
4	110%
5	-

Variable Coulombic efficiency in the MEC may be partially attributed to the complexity and instability of its landfill leachate feed. The Coulombic efficiency of Batch 5 was not calculated because there was no COD removal.

3.1.3 Ammonia Removal & Recovery

A second important gauge of wastewater treatment efficiency is the quantity ammonia removed. The ammonium as nitrogen (NH_4^+-N) concentrations within anolyte slightly increased across subsequent cycles, though the concentration of ammonia in the cathode has significantly increased (Figure 6).

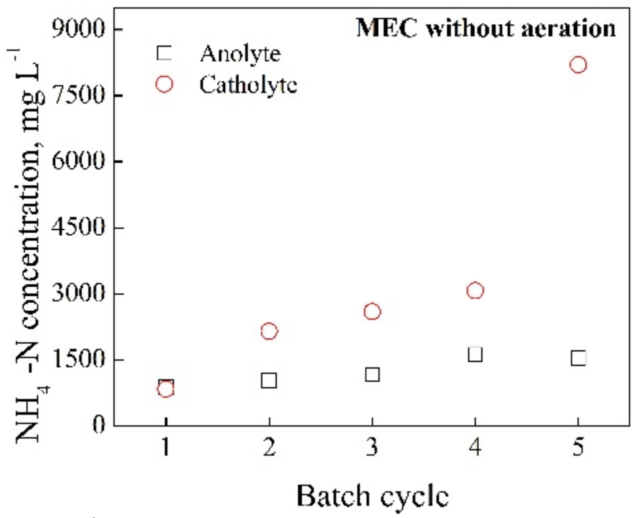

Figure 6. NH_4^+-N concentrations in MEC anolyte and catholyte.

At the end of each cycle, 50% of the treated anolyte remains and the remaining 50% of anolyte volume is replenished with raw landfill leachate. The catholyte was not replaced over the duration of the 5 cycles, which allowed ammonia to accumulate more dramatically than in the anolyte. Removal of ammonia from the landfill leachate anolyte decreased across 5 batches but remained between 40% and 68% (Figure 7).

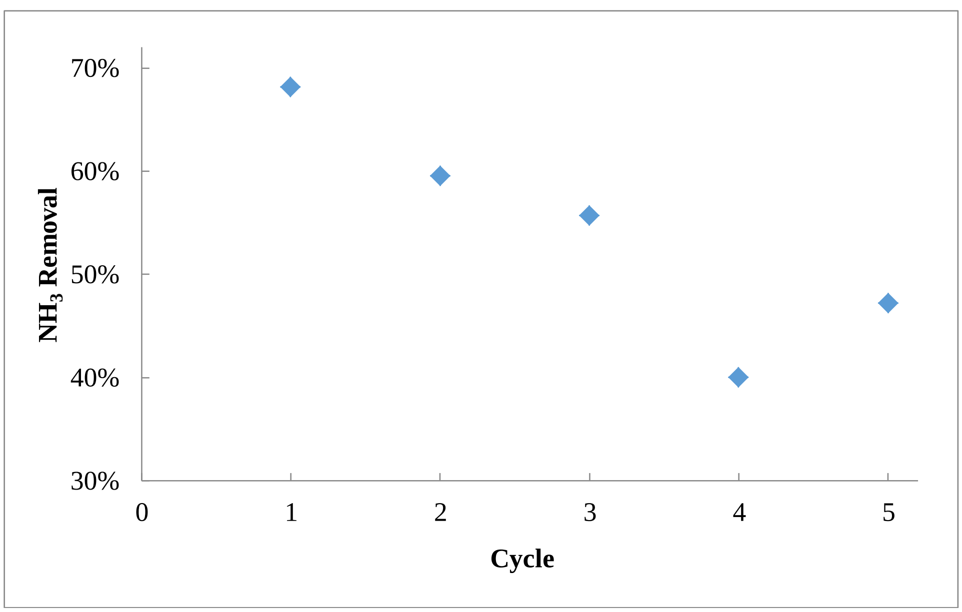

Figure 7. Ammonia removal in MEC fed with landfill leachate.

Ammonium removal from the landfill leachate was likely hindered by its accumulation in the catholyte. The increased catholyte concentration hindered the migration of NH_4^+ across the cation exchange membrane because the catholyte NH_4^+ concentrations exceeded that of the anolyte concentrations. Additional migrating NH_4^+ was required to oppose the concentration gradient, which also decreased the removal efficiency. Hindered NH_4^+ migration may also have reduced the current generation of the MEC since NH_4^+ migration is required to balance electron flow from COD removal.

Despite increasing NH_3 concentrations in the cathode, NH_3 gas was not collected. Gas production typically depends on the catholyte pH. However, the pH has been adjusted to significantly basic ranges (up to 12.6) to encourage gas release from the catholyte without any success. To determine whether or not there is a possibility of ammonia gas recovery and to improve the current generation, the catholyte will next be aerated to strip and collect the gas.

3.1.4 Ion Concentrations

Ion concentrations in the anolyte and catholyte were measured over five batches through inductively coupled plasma- mass spectrometry (ICP-MS) (Figure 8).

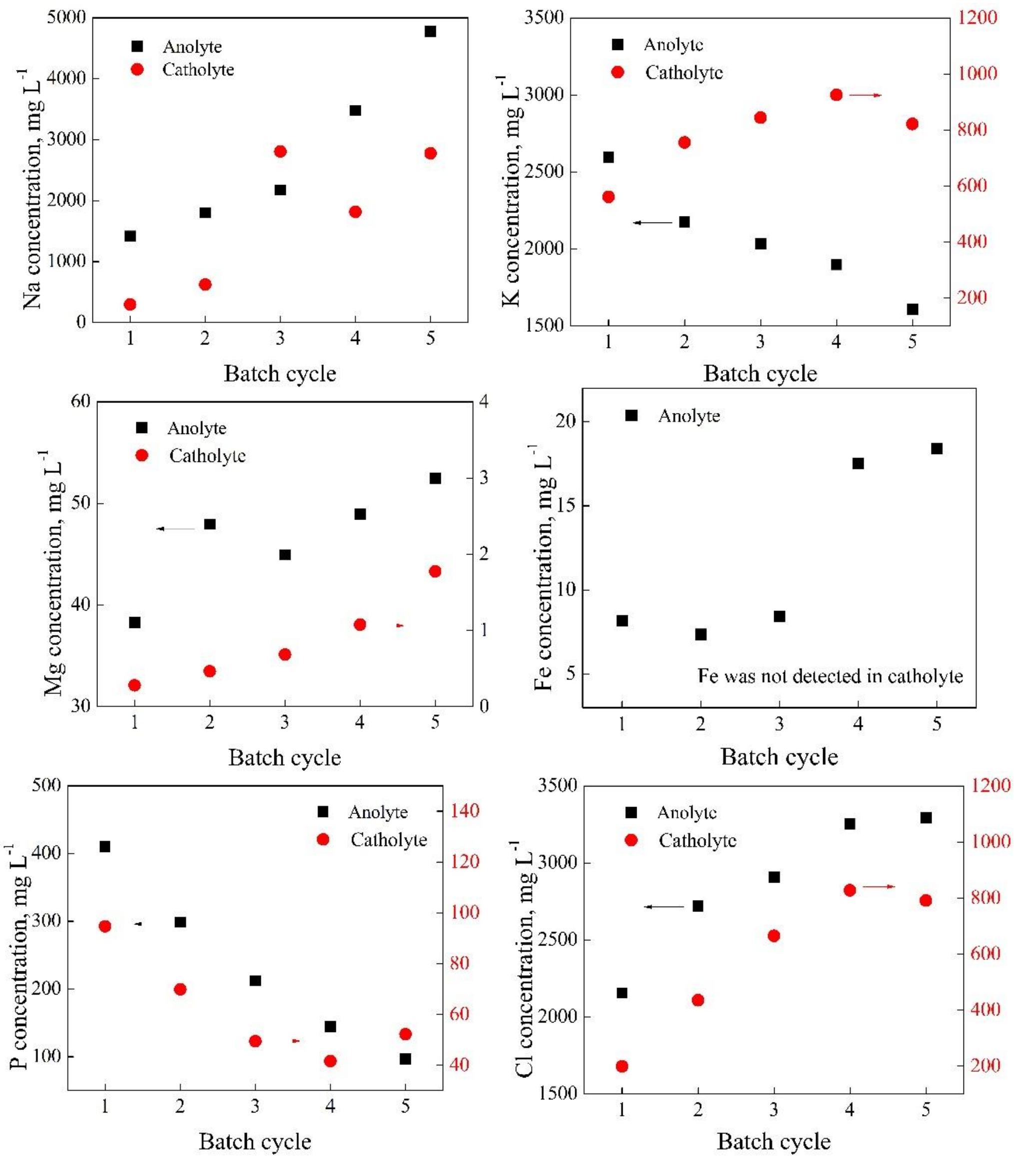

Figure 8. Ion concentrations (Na, K, Mg, Fe, P, Cl) in MEC fed with landfill leachate (ICP)

It was supposed that increasing salt concentrations were damaging the anode's microbial community and therefore also negatively affecting the COD removal. Sodium (Na), magnesium (Mg), iron (Fe), and chloride (Cl) concentrations each increased within the anolyte over five batches. The increase in overall salt concentration may have been sufficient to hinder COD removal. After the fifth cycle, the anolyte was entirely replaced with raw leachate to flush out any accumulated salts or metal species.

Over five batches, the catholyte acquired a yellow color but continued to be clear. The ion concentrations of the catholyte were quantified in an attempted to identify the cause of the yellow color. However, the ions present were unlikely to cause the color. Though iron was present in the landfill leachate, it was not detected in the catholyte through ICP-MS.

iron concentration of the Batch 5 catholyte was determined to be 0.34 ppm, which would be insufficient to cause the observed strong yellow color. Further efforts examined the possibility of humic acid as the cause. Only 22% of the total organic carbon (TOC) in the catholyte sample was humic acid but precipitation of the humic acid from solution decreased the yellow hue. Tests with XAD-8 resin will be used to determine whether or not the yellow color may be attributed to fulvic acid.

3.2 Forward Osmosis

3.2.1 Water Recovery through FO

The FO process recovered water from the landfill leachate and concentrated it while the volume requiring further treatment was reduced. Water recovery was examined for DI water, treated leachate, and raw leachate (Figure 10).

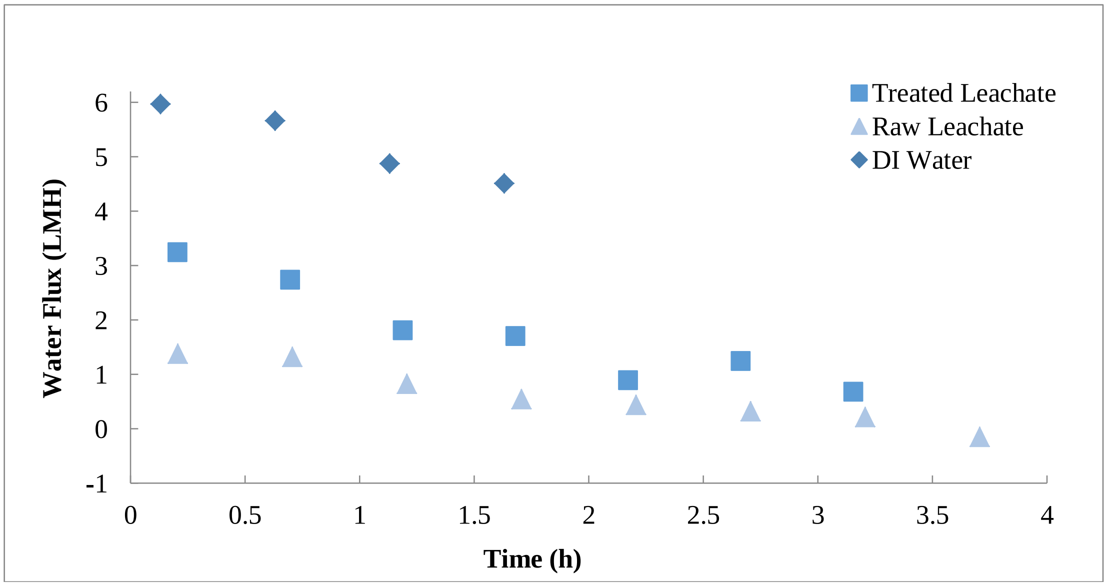

Figure 10. Water flux comparison of deionized water, MEC treated leachate, and raw leachate feeds using 1 M NH4HCO3 draw solution.

Deionized water had the greatest water flux (6.0 LMH), followed by treated leachate (3.2 LMH) and raw leachate (1.4 LMH). The FO process recovered 50.4%, 29.6%, and 12.8% of the feed water using 1 M NH_4HCO_3 from deionized water, treated leachate, and raw leachate, respectively. Water flux decreased regardless of the feed type because there was less osmotic pressure gradient to draw water as water permeate diluted the draw solution. MEC effluent (treated leachate) has less salt content than raw and therefore had a greater osmotic gradient compared to the ammonium bicarbonate draw solution that caused greater water flux across the FO membrane.

Further experiments achieved 50.5% water recovery from MEC effluent using 2 M NH_4HCO_3 draw solution and 54.4% recovery with 4 M NH_4HCO_3. The 4 M solution achieved similar recovery as the 2 M solution but in approximately half the time.

3.2.2 Reverse Salt Flux

Reverse salt flux occurred in FO trials with all three feed solutions (deionized water, treated leachate, and raw leachate) (Table 5).

Table 5. Reverse Salt Flux of NH_4HCO_3 in Forward Osmosis

Feed Solution	Operation Time (h)	Reverse Salt Flux (gMH)
Deionized Water	2.5	59.1
Treated Leachate	4	64.2
Raw Leachate	4.5	27.5

The reverse salt flux values were high as is common for FO processes that use NH4HCO3 as a draw solute. Exploration of other thermolytic salts may be required in order to better optimize the system and to prevent chemical loss and damage to the quality of the wastewater.

4. Conclusion

Coupled MEC and FO have a synergistic relationship beneficial to wastewater treatment and resource recovery. The MEC treats landfill leachate via removal of COD and NH_3. Up to 27% of COD removal was achieved and ammonia removal was between 40% and 68% each batch. The MEC anolyte should be replaced with 100% raw leachate to avoid damage from accumulated salts or metals and to improve COD removal. Water from the treated landfill leachate was recovered through FO, using thermolytic NH_4HCO_3 draw solution. Forward osmosis was able to recover 51% of water from MEC effluent. Treated leachate had higher rates of flux than raw leachate, which demonstrates that MEC treatment is beneficial to FO processes. Overall, the waste stream is reduced, treated, and its value is extracted.

It is expected that aeration of the cathode will strip NH_3 from the catholyte to be collected. The decreased catholyte concentration should then ease the migration of NH_4^+ from the anode to the cathode.

5. Acknowledgements

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Appendix A

Figure A 1. Benchtop tubular MEC.

Figure A 2. Benchtop FO cell.

Barrier Island Sediment Transport due to Hurricane Overwash Events

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Abstract

Barrier island sediment transport and deposition can be simulated through the use of numerical models. The occurrence of a hurricane storm event has the potential for catastrophic effects on an island. In the event of overwash, large quantities of sediment may be transported and deposited into the inner bay, and could result in total loss of the island. Differences in barrier island bathymetry may have an influence on sediment transport and deposition. Modeled results may be compared with sediment core samples from the inner bay to provide insight into strength, and frequency of historic events. Three barrier island profiles: Santa Rosa Island, Florida; Mantoloking, New Jersey; and Bay Head, New Jersey with varying dune heights and berm widths were used in simulations conducted with the numerical model XBeach. Seven different idealized hurricanes were created with varied wave height, wave period, and storm surge, and intensities. Through a comparison of post event bathymetry, hurricane sediment transport is heavily influenced by barrier island bathymetry. Storm surge and dune height have a distinctly large effect on the likelihood and severity of an overwash event. Significantly more work must be done in order to appropriately compare hurricane sediment transport results with other events.

Keywords: Barrier Island, Hurricane, Overwash, Sediment Transport, Storm, XBeach

1. Introduction

United States coastal regions are highly vulnerable to impacts from several different types of events, including storms, such as hurricanes and Nor'Easters, and tsunamis. Coastlines also have a relatively high population density, with many cities located in these regions. Barrier islands are popular places to live or to travel to for vacation. As of the 2000 census, 1.4 million people live on barrier islands along the United States coasts. This number has been steadily increasing over the past 30 years (Zhang & Leatherman, 2011). As a result, the protection and fortification of barrier islands and coastal regions against hurricanes are priority investments for many coastal communities.

1.1 Barrier islands and overwash events

Barrier islands serve as the first line of defense for the coastline, and, as a result, they are especially vulnerable to the destruction of a hurricane event. Storms may result in inundation of the island by water, causing the creation of overwash fans. An overwash event usually results in damage of infrastructure, such as roads and buildings, and loss of property. It is possible for an overwash event to result in the complete erosion and loss of the island. Barrier islands are especially prevalent along the Atlantic Coast of the United States and the Gulf of Mexico. These islands are surprisingly old formations that have steadily migrated across the continental shelf chasing the migration of the coastline. Overwash events are import for the redistribution of the barrier island sediment and crucial to their migration (Stone et al., 2004). A basic but typical barrier island profile, seen in Figure 1, consists of the ocean, beach, raised berm, dunes, and a gently sloping marshy backbeach which extends to the inner bay. All barrier islands are different, and none are uniform along their length. Every aspect of the barrier island will vary along its length and between islands.

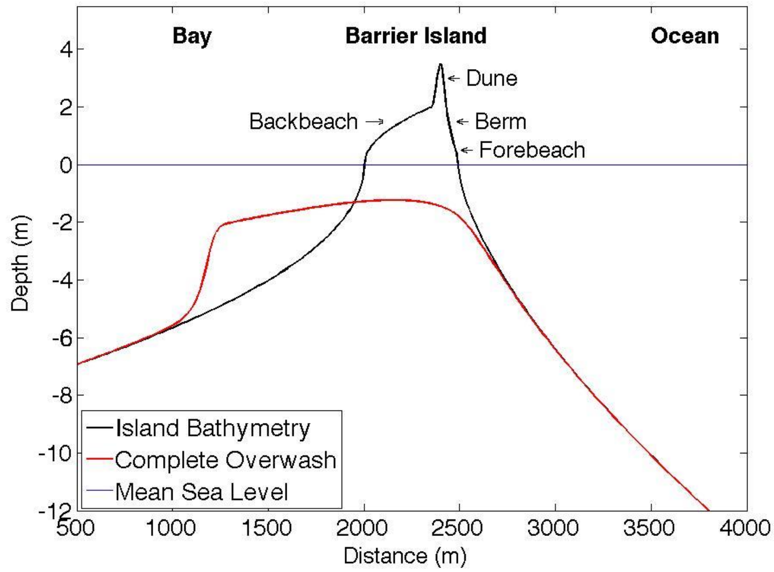

Figure 1. Generalized barrier island and complete overwash bathymetry, from ocean to bay (Canham, 7/25/2015).

1.2 Previous studies and literature review

The effects of different types of events on barrier islands have been extensively studied. Studies on hurricane events are especially prevalent because of the abundance of data relative to other types of events. Stone et al. (2004) investigated the impact of hurricanes on barrier island bathymetry. It was found that barrier islands, over time, will recover from an overwash event, and they will conserve sediment mass in the event of a catastrophic event (Stone et al., 2004). Studies have been done comparing storm sediment deposits with other types of event deposits, such as tsunamis. Morton et al. (2007) conducted a study comparing sediment deposits from two hurricanes: Hurricane Carla, 1961 and Hurricane Isabel, 2003; and two tsunamis: Papua New Guinea, 1998 and Peru, 2001. Through this study, storm sediment deposits were found to be characterized by several layers of normally graded sediment. Conversely, the tsunami sediment deposits were characterized by a single, normally graded sediment layer. The storm deposits were also found to be thinner than the tsunami deposits and tended to level the landscape by filling in low areas (Morton et al., 2007).

Studies have also been done on modeling storm sediment transport and deposits. Roelvink et al. (2009) and McCall et al. (2010) both performed studies on barrier island sediment transport with the numerical model XBeach, the model also used in our study. Both papers describe the validation of the model for hurricane events on barrier islands. The model validation is further discussed in Section 1.3.

This paper is an extension of the work done by Keith et al. (2014), who performed a numerical study on the comparison of storm and tsunami sediment deposition. In the report, several recommendations for future work were listed, including the inclusion of storm surge energy in storm energy calculations (Keith et al., 2014).

1.3 XBeach Model

XBeach is a numerical model developed by Deltares Inc. used to model “wave propagation, long waves and mean flow, sediment transport and morphological changes of the near shore area, beaches, dunes, and back barrier during storms” (Deltares Inc.). XBeach has been used for numerous similar studies of sediment transport of barrier islands.

An in depth description of the XBeach model is given in Roelvink et al. (2009) detailing many of the different aspects of the model. These include the coordinate system and grid, wave action and shallow water equations, roller energy balance, transport formulations, wave boundary conditions, and flow boundary conditions. Several cases are also detailed supporting the validity of the model (Roelvink et al., 2009). McCall et al. (2010) performed a study on the effects of Hurricane Ivan on Santa Rosa Island, Florida. This study resulted in validation of the XBeach model for simulating “complex runup and inundation overwash over longshore varying terrain” of barrier islands (McCall et al., 2010). This study compared pre and post storm lidar data with modeled results. To supplement the Xbeach model, available bathymetric, altimetric, wave, and surge data were included in the simulation. The storm was run for 36 hours, with significant wave height centered on the storm surge peak. In Appendix I, Figure 5 shows the comparison of the lidar and modeled results. Although, post storm comparisons were limited to a narrow swath of post storm lidar data, sediment transport patterns created by XBeach are similar to the lidar data. A sensitivity analysis was also conducted on wave forcing, surge forcing, storm duration, and model parameter sensitivity, and it was determined small variations did exist between the lidar and modeled results; however, it did not lead to significant differences (McCall et al., 2010). Based on the validation of overwash of a barrier island due to a storm event, XBeach is chosen as an appropriate model to use for this study.

1.4 Model Familiarization

In order to effectively run simulations using the Xbeach model, it is necessary to be familiar with both the model and many other supporting tools. The model must be downloaded and complied on a Mac, requiring familiarization with Mac OS. In order to run a simulation with XBeach, use of terminal is necessary, requiring familiarity with this command line interface tool, which is used to control the operating system. Simulations with large grid sizes require large computational time making a super computer necessary to run simulations. The BlueRidge cluster system is available to researchers at Virginia Tech to reduce runtime by utilizing multiple nodes and cores. Also, familiarity with a programming language, such as MatLab or Python, is a requirement to create all XBeach input files. Terminal is then used to upload all necessary files to the BlueRidge cluster. Once XBeach has been run, results must be viewed through a programming language. See Figure 6 in Appendix I for a visual representation of all the necessary steps to run an XBeach simulation. Familiarization with every step of the XBeach process takes a significant amount of time. Due to time constraints of this project, significant time was spent becoming familiar with the entire process before any data could be collected.

1.5 Problem Statement

The ability to predict sediment transport due to storms and tsunamis is an important factor for protecting barrier islands. By modeling sediment transport of an erosive event, a comparison of sediment deposition patterns can be conducted based on varying forcing and barrier island bathymetry. Differences in barrier island bathymetry will have an effect on the sediment transport and deposition patterns of hurricanes. Originally, a comparison between hurricane and tsunami sediment transport and deposition was a significant part of this project. However, due to time constraints, the tsunami wave was unable to be validated within the given time.

Beyond the scope of this paper, it is expected that modeled predictions of sediment transport and deposition from different types of events may be compared with sediment cores taken from the barrier island inner bay. By analyzing sediment core samples, the frequency and intensity of historic events may be determined and used to make predictions for the future. By having the ability to predict the likelihood and intensity of future events, we are better able to prepare these highly vulnerable barrier islands for future events.

2. Methods

2.1 Island Parameter Identification

Based on the typical profile of a barrier island (Figure 1), the berm width and the dune height were identified as parameters that are varied in this study. This is based on the ability to 'build' or modify the barrier island profile in real life. Three barrier islands were identified as base profile sites to be used to study the effects of changes in dune height and berm width on the sediment transport. Identified barrier islands include: Santa Rosa Island, Florida; Bay Head, New Jersey; and Mantoloking, New Jersey. These locations were identified based on lidar and profile data availability from a variety of sources, including McCall et al. (2010) and the National Oceanic and Atmospheric Administration (NOAA). A one-dimensional cross-section profile was created for each of the three sites, assuming each island is longshore uniform. In Appendix I, Figures 7 through 9 show the base profiles for each of the three sites, and Figure 10 shows the location of each site on the United States coast.

2.2 Hurricane Identification

Hurricane parameters were identified to include wave height, wave period, wave direction, and storm surge. For all simulations, an idealized event was assumed with waves input at 20m depth approaching at a direction of 90 degrees (shore normal). For every idealized hurricane, all parameters were held constant for the entire six-hour duration of the event.

Idealized hurricane parameters were assumed based on data from historic events, including Hurricane Sandy, Isaac, Irene, Ike, Gustav, Rita, Katrina, and Ivan. Data was collected from the National Oceanic and Atmospheric Administration (NOAA) Water Level and Meteorological Data Report for each respective storm (NOAA, n.d.). Seven different idealized events were created. Hurricane energy, a measure of intensity, was calculated for each event, and more detail is given in section 2.3. The parameters for each event are detailed in Table 1. For simplicity, storm surge only on the ocean side was considered. Bay side storm surge was not considered because this would require substantial site-specific data on the site location. Due to time constraints, bay side surge is outside the scope of this project.

Table 1. Created idealized hurricanes (Canham, 7/22/2015)

Storm_number	**Storm Energy (m^2/s^2 per hour *1,000,000)**	**Wave Height (m)**	**Wave Period (s)**	**Storm Surge (m)**
Storm_1	0.58	6	8	1
Storm_2	2.01	10	10	1.25
Storm_3	2.02	10	10	2
Storm_4	3.03	12	10	2.5
Storm_5	3.33	12	12	3.5
Storm_6	4.67	14	12	1.5
Storm_7	6.82	16	14	3

2.3 Storm Intensity

The total energy of each idealized hurricane was calculated, providing a method to compare the storms. The level of energy of each event directly corresponds with the intensity of the event, where higher energy indicates a more intense event. Linear wave theory (Equation 1) accounts for the energy of incident waves, where ρ is water density, g is gravitational acceleration, H is the total height of the wave, and L is the length of one wave (Dean and Dalrymple, 1991). To account for energy from storm surge, hydrostatic pressure can be used, as seen in Equation 2, where h is the surge height. Linear wave theory and storm surge energy are added together to determine the energy per wave in Equation 3, where A is one square unit of area.

$$E_L = \frac{1}{8}\rho g H^2 L \qquad \text{Equation 1}$$

$$P_H = \rho g h \qquad \text{Equation 2}$$

$$E_T = \frac{1}{8} g H^2 L + ghA \qquad \text{Equation 3}$$

The total energy of the event can then be calculated using equation 4, where D is the duration of the event in hours and $\underline{v}$ is wave velocity.

$$Hurricane\ Energy = \frac{E_T D v}{L} \qquad \text{Equation 4}$$

2.4 Data collection and analysis

The programming language MatLab was used to create the island profile, model grid, hurricane input, and all other necessary XBeach input files. One of the files created, the 'params.txt' file was the primary file used to adjust the input and output of the model and ensure consistency of model runs. The XBeach model was used to run simulations of three island profiles with seven storms using a variety of berm widths and dune heights. Since shore normal waves are specified for every hurricane, one-dimensional grids were created from island profiles and are shown in this report as cross-shore profiles. Again, with a 2-dimensional grid, significant computational time is needed to run a full simulation, requiring multiple nodes and processors available via BlueRidge. Because the one-dimensional grid was fairly small, a significantly lower computational time was needed, allowing simulations to be all run on the local computer. The benefit of this simplification is the ability to run more simulations faster allowing for more data collection. Numerous simulations were run for the three barrier island profiles. Each of the seven hurricanes was simulated with seven variations of modified barrier island bathymetry, as seen in Table 2.

Table 2. Barrier Island profile variations (Canham, 7/27/2015)

Variation_number	**Dune Height**	**Berm Width**
Variation_1	Original	Original
Variation_2	No Dune	Original
Variation-3	Original	No Berm
Variation_4	½ Dune	½ Berm
Variation_5	4/3 Dune	4/3 Berm
Variation_6	4/3 Dune	½ Berm
Variation_7	½ Dune	4/3 Berm

After simulations were completed, they were viewed and analyzed in a variety of ways. A simple check on a simulation could be done using the xb_view command, located in the XBeach add-on toolbox for MatLab. However, this method does not allow for direct comparison or analysis of storm sediment transport and deposition. MatLab files were created to more easily view, compare, and analyze the results of hurricane simulations.

3. Results

Sediment transport and deposition during hurricanes were analyzed with respect to changing barrier island profiles. Figure 2 is an example of the sediment transport as a result of Storm 6 on Santa Rosa Island for four different profile variations. Similar results were achieved for the Bay Head and Mantoloking sites, and for the other 6 storms. Here, complete overwash can be seen in the original, no dune, and no berm profile variations while the profile with a built up berm and dune has not been completely eroded.

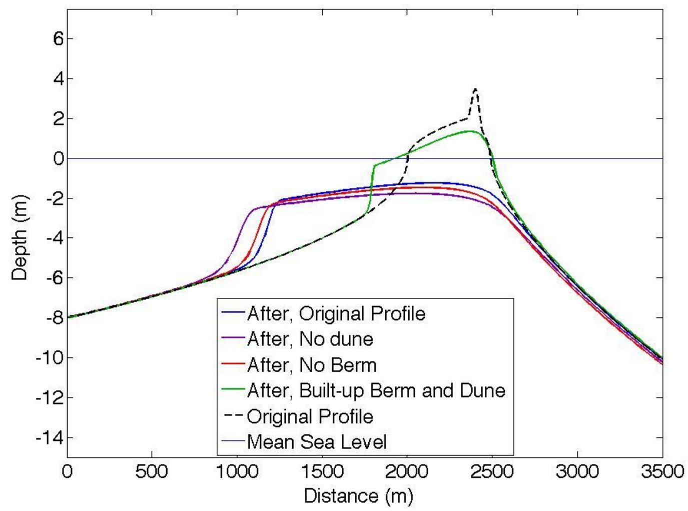

Figure 2. Santa Rosa Island, FL bathymetry and sediment transport from Storm 6, (Canham,7/20/2015).

Storms 2 and 3 had a very similar level of intensity, as shown in Table 2. Storm 3 had a significantly greater storm surge however, leading to differences in the sediment deposition and likelihood of overwash for all three profiles. Santa Rosa Island had a particularly distinct difference between the two storms for the original profile, as seen in Figure 3.

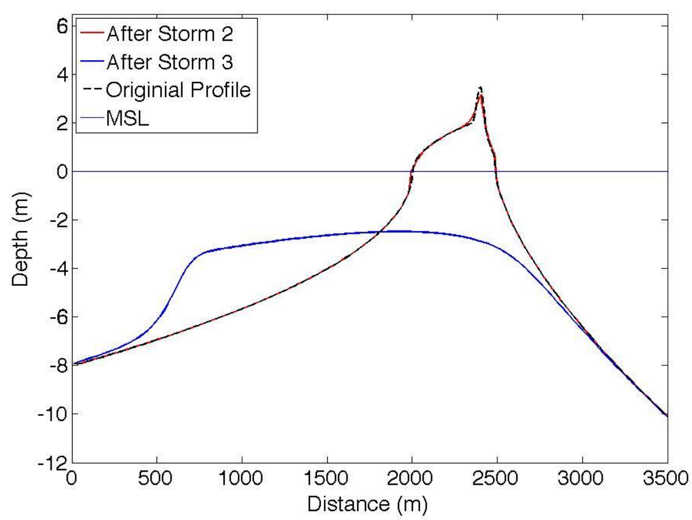

Figure 3. Santa Rosa Island, FL comparison of Storms 2 and 3, with approximately the same level of intensity but a large difference in storm surge and sediment transport (Canham, 7/22/2015)

Data collected from all simulations was combined into a single plot, and Figure 4 shows the data collected for Santa Rosa Island, FL.

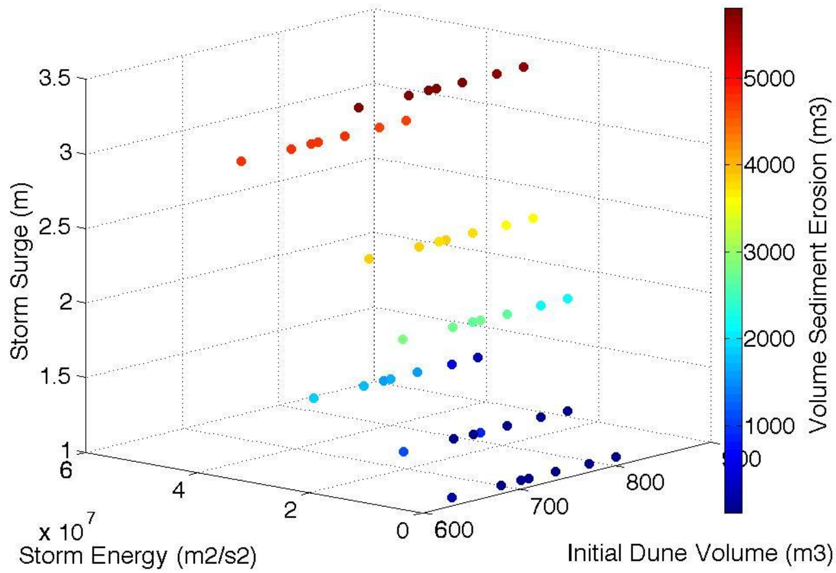

Figure 4. Hurricane sediment transport for Santa Rosa Island, FL. Each data point represents a different simulations run with the different island parameters. The seven storms can also be easily differentiated. (Canham, 7/29/2015).

4. Discussion

4.1 Hurricane Sediment Transport

The pattern seen in the hurricane overwash deposits is consistent with barrier island storm overwash fans from previous studies. When overwash occurs, the sediment deposit is a fairly thick deposit, with sediment pushed into the bay, and suddenly ending and dropping down to the original bathymetry. Figure 2 shows a difference in the extent of sediment deposited into the bay based on the bathymetry of the island. The original profile and the profile variation with no berm were very similar in extent, while the profile variation with no dune extends further than the two previously mentioned. Although the built-up dune and berm variation was overwashed, it was not completely eroded, showing that these parameters do have a significant impact on overwash severity.

Figures 3 and 4 show a greater influence of storm surge than wave energy on volume of sediment erosion. Storms with similar levels of energy but different storm surge levels are seen to have very different volumes of sediment erosion. Figure 4 shows that the storm with the greatest energy does not have the highest volume of sediment erosion. This storm, however, does have a greater storm surge. Since greater volumes of sediment erosion correlate to higher storm surges, these results indicate the likelihood of overwash increases as storm surge increases, and the likelihood of overwash is less dependent on wave energy.

In some simulations, sediment deposits reached the end of the bay in an asymptote-like manner. It is concluded the deposit would likely extend further, given a longer bay. These simulations were still included in the analysis of the results. When calculating the sediment volume at the beginning and the end of the simulation, it was found they were not always equal, and sediment was being either added or lost during the simulation. Less than a 3% sediment volume discrepancy was found for all profiles, but the simulations that reached the end of then bay with an asymptote-like deposit had a distinctly higher value than those that did not.

4.2 Future Work

Based on the time constraint and limitations of this paper, several items have been identified for future investigation.

Bay side storm surge, not included in this work, is an important factor in the likelihood and severity of overwash. Again, this would require significant site-specific data on the location of the bay inlet relative to the location of the barrier island profile site.

In some of the more intense hurricane results, the sediment reaches the end of the bay. To avoid this, the bay should be extended. This will eliminate the asymptote-like effect at the end of the bay in some of the events. By doing this, it is also expected the gain or loss of sediment within the simulations would decrease. If this is not the case, this should be further investigated.

Figures 2 and 4 show storm surge has a greater influence on volume of sediment erosion than storm energy. The likelihood of barrier island overwash seems to be greatly affected by these parameters. When designing fortification methods of a barrier island from a hurricane event, designing for storm surge rather than storm energy may have a significant difference. The relationship between storm surge level and likelihood of overwash should therefore be further investigated for a similar trend.

Finally, other events, such as the cnoidal tsunami wave, should be validated for the XBeach model. This would allow for direct comparison and differentiation of sediment transport and deposition patterns between different events. At this time, there is work being done to validate a tsunami wave with the non-hydrostatic version of XBeach. If the tsunami wave validated for this other version of XBeach, the storm would need to be validated for this version as well. The validation of the tsunami event would allow for differentiation between it and the hurricane, and comparisons can be made of sediment core samples and aid in analysis of historic events.

5. Conclusions

The XBeach model effectively simulates hurricane events and the resulting sediment transport of barrier islands. Our results have shown the dune height has a significantly greater impact on the likelihood or severity of an overwash event than the berm width. Storm surge is also shown to have a greater effect on the likelihood of barrier island overwash than storm energy. When designing for the fortification of a barrier island against a hurricane event, dune height and expected storm surge level must be considered. These two parameters are seen to have a greater effect on the likelihood of an overwash event and the volume of sediment eroded.

Due to time constraints, there were several limitations to this project and many assumptions made. These include a uniform 1D profile, stationary waves and water levels, idealized hurricane events, and lack of storm surge in the bay.

An assessment of the effects of hurricanes on sediment transport along barrier islands has been conducted. Hurricane overwash events and sediment deposits must be further analyzed to better prepare for future events.

6. Acknowledgments

Thank you Dr. Jennifer Irish and Dr. Robert Weiss for advising me, and Stephanie Smallegan and Wei Cheng for mentoring me through this project. We acknowledge the support of the National Science Foundation through NSF/REU Site Grant EEC-1359051. Any opinions, findings, and conclusions or recommendations expressed in this paper are those of the authors and do not necessarily reflect the views of the National Science Foundation.

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Appendix A

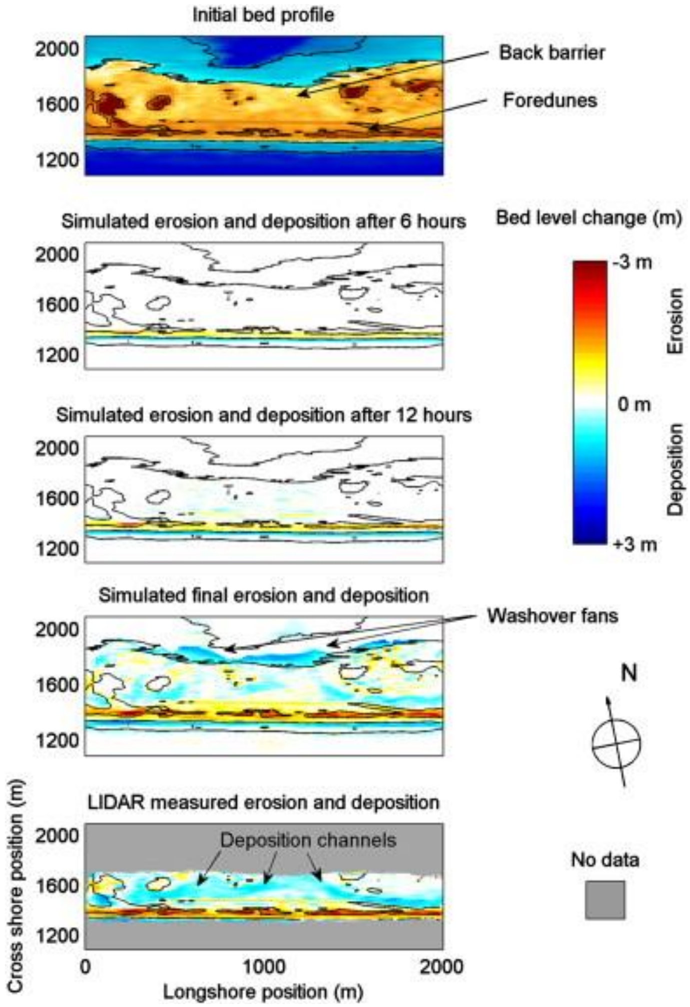

Figure 4 . Santa Rosa Island, Florida pre and post storm LIDAR data compared with XBeach modeled results from Hurricane Ivan. This comparison was done by McCall et al. (2010) and is an example of XBeach model performance for storm overwash events of barrier islands (McCall et al., 2010).

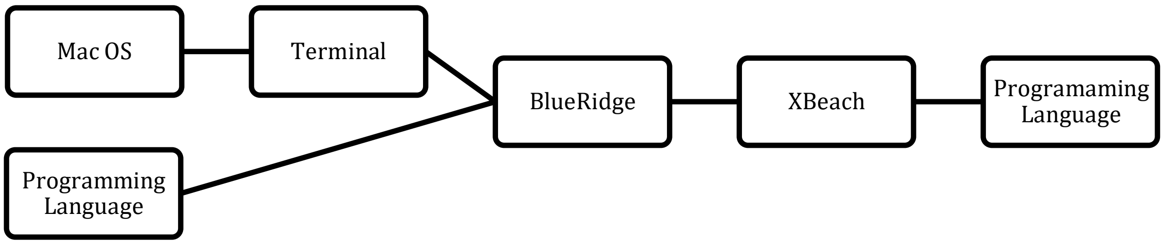

Figure 5. Steps needed to become familiar with running XBeach model simulations (Canham, 7/26/2015)

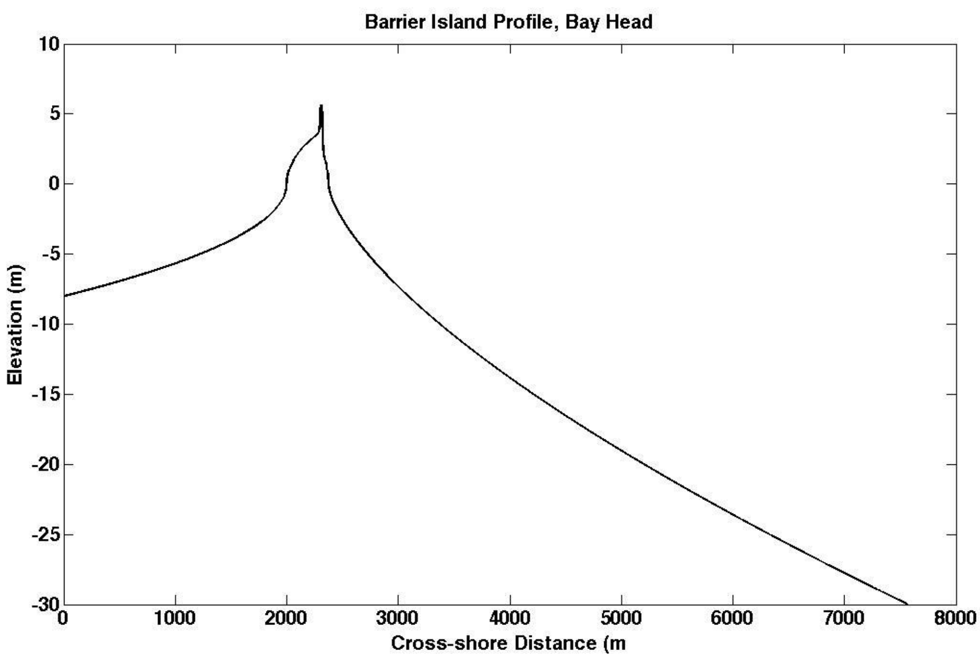

Figure 7. Bay Head, New Jersey base profile, ocean is on right (Canham, 7/20/2015).

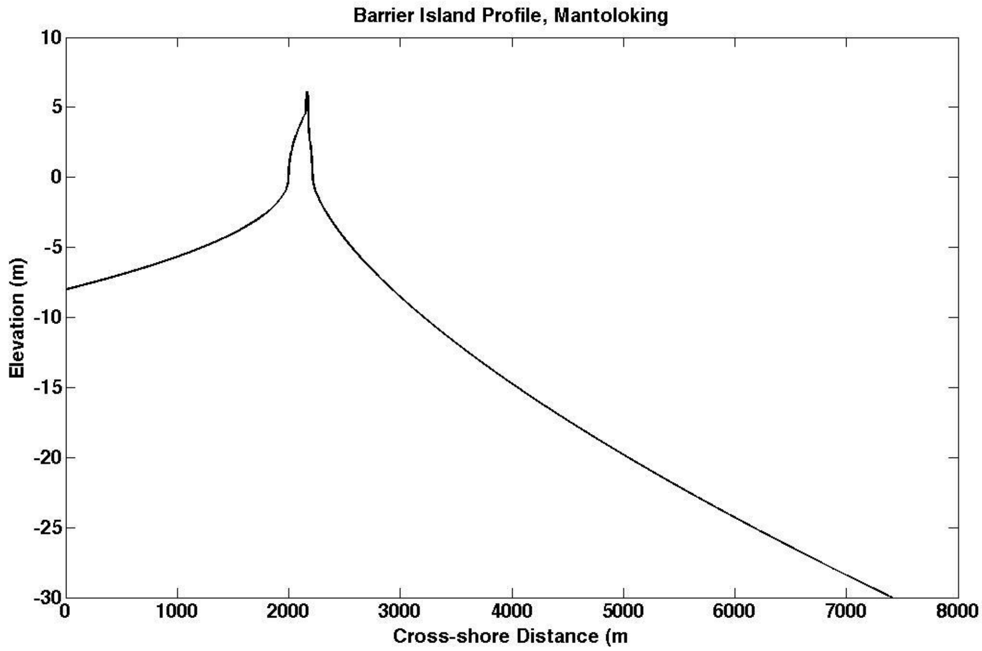

Figure 8. Mantoloking, New Jersey base profile, ocean is on right (Canham, 7/20/2015).

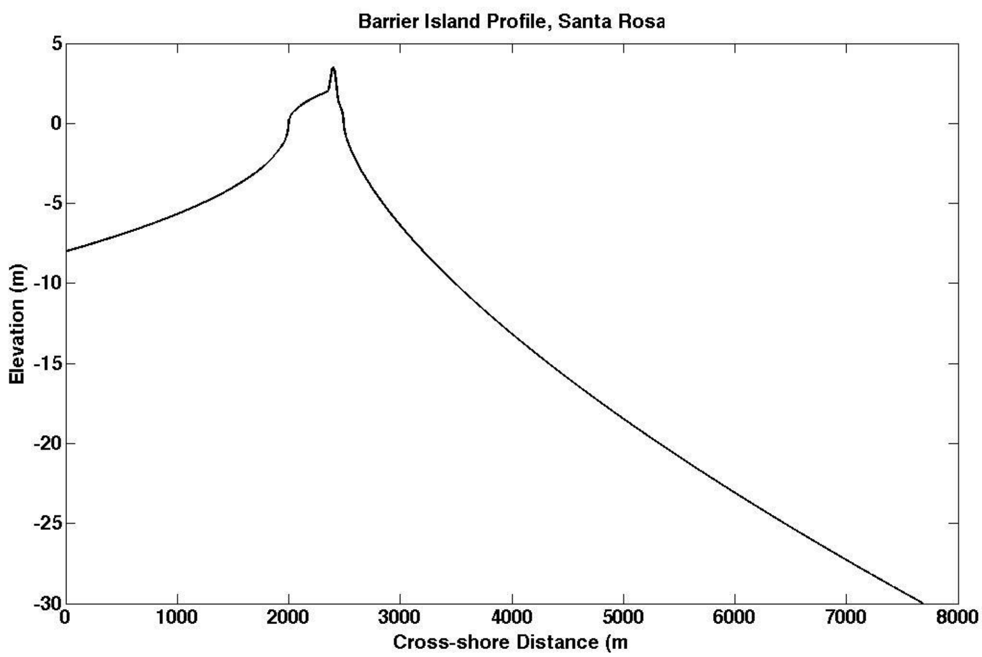

Figure 9. Santa Rosa Island, Florida base profile, ocean is on right (Canham, 7/20/2015).

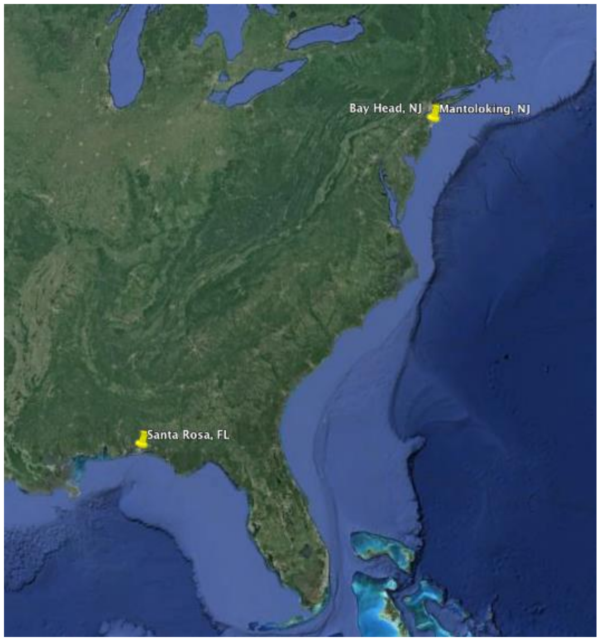

Figure 10. Barrier island site locations (Canham, 7/20/2015)

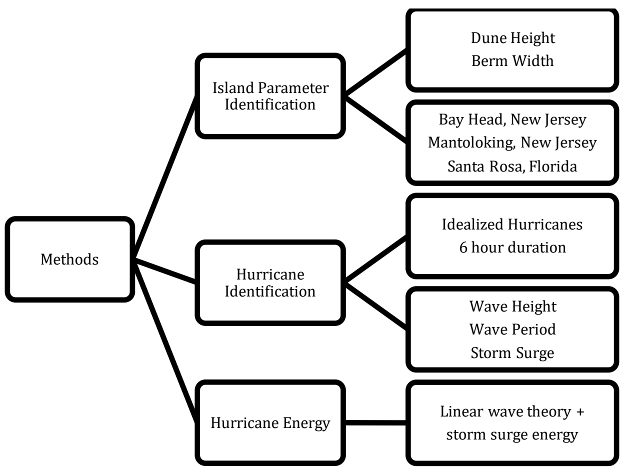

Figure 6. Methods for running XBeach Hurricane simulations (Canham, 7/23/2015)

The vertical distribution of phytoplankton in Beaverdam Reservoir, and the percentage of living and nonliving phytoplankton in managed versus unmanaged reservoirs

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Abstract

Phytoplankton have high biodiversity, and have long been used to study populations and community structures. They are an important indicator of water quality, and can potentially have negative effects on human health and carbon sequestration. One phytoplankton group, the cyanobacteria, are of particular concern to water quality managers due to their ability to form toxic and nuisance blooms. The objective of this research was to investigate the drivers of vertical cyanobacteria distribution in Beaverdam Reservoir (BVR), an unmanaged drinking water source in Vinton, Virginia, USA, and to determine the percentage of living versus nonliving phytoplankton in BVR and its heavily managed counterpart, Falling Creek Reservoir (FCR). We used in-situ fluorometry to measure the abundance of four main phytoplankton groups: diatoms, green algae, cyanobacteria and cryptophytes. We took weekly light, dissolved oxygen, temperature, and pH profiles, and analyzed water samples for metals and nutrients, in order to determine the variables most closely correlated with high cyanobacterial abundance. We combined these techniques with manually filtered chlorophyll measurements to determine the concentrations of living versus nonliving phytoplankton in FCR and BVR. On average, the proportions of living versus nonliving phytoplankton were very similar in both reservoirs. Phosphorus, iron and manganese had an effect on the distribution of the cyanobacteria. These results support previous findings that suggest some cyanobacterial communities are subject to iron-phosphorus co-limitation (North et al. 2007), and may help drinking water managers prioritize water management actions in the future.

Keywords: phytoplankton, water quality, cyanobacteria

1. Introduction

Phytoplankton form the base of the food web in open waters of lakes and reservoirs. Phytoplankton provide food for a wide range of organisms, but, under certain conditions, can form potentially toxic algal blooms, (Sellner et al. 2003; Tuner and Tester 1997). Phytoplankton have a high level of biodiversity, and depend on carbon dioxide, sunlight and nutrients to survive. The presence of certain types of phytoplankton can indicate the water quality of a reservoir or lake. For example, the presence of some cyanobacteria groups may indicate high nutrient concentrations (Medupin 2011). High phytoplankton diversity indicates good water quality, and can be a major controller of population and ecosystem dynamics in a reservoir (Striebel et al. 2012). Phytoplankton play a key role in the global carbon cycle, and have been shown to export about 11 to 16 Gt of carbon from the atmosphere to the ocean per year (Falkowski et al. 2000). Phytoplankton take up dissolved carbon dioxide, sequestering some carbon as some cells die and sink, as well as transferring carbon to higher trophic levels (Falkowski et al. 2000). Though all phytoplankton use chlorophyll-a, different classes have evolved a host of accessory pigments that allow each group to capitalize on different light wavelengths, reducing competition for light and promoting biodiversity. Furthermore, nonliving cells and living cells fluoresce at slightly different wavelengths. Here, we will use in-situ fluorometry to differentiate between these pigments and measure concentrations of four main phytoplankton groups: diatoms, green algae, cyanobacteria, and cryptophytes. We combine this technique with manually filtered chlorophyll measurements to elucidate the proportion of total living versus nonliving phytoplankton.

Some drivers of phytoplankton communities include nutrient ratios and underwater light climate (Stomp et al. 2011). Nutrients used by phytoplankton include nitrogen, phosphorus, carbon and micronutrients such iron and silica (Hecky and Kilham 1988). Some cyanobacteria have evolved nitrogen-fixing capabilities to overcome nitrogen limitation and outcompete other phytoplankton (Moisander et al. 2008). Nitrogen fixing cyanobacteria are known to form persistent blooms that can be toxic to humans and wildlife (Sellner et al. 2003; Berg and Sutula, 2015). Phosphorus is commonly the limiting nutrient to algal growth in lakes and reservoirs (D.W. Schindler 1974); phosphorus limitation can be especially important to groups that are able to fix nitrogen, and there is recent evidence for iron-phosphorus co-limitation of phytoplankton populations (North, et al. 2007). Nutrients enter freshwater ecosystems through natural processes, including debris, sediments, lake processes, and the atmosphere, as well as from human activity. Phytoplankton populations can quickly grow and utilize nutrient resources, but they are also susceptible to high death rates due to grazing, competition, and aquatic viruses (Hecky and Kilham 1988). Live phytoplankton take up nutrients and carbon from the water column, making them available for higher trophic levels. Nonliving phytoplankton are a source for nutrients, and may contribute to oxygen depletion via bacterial respiration during algal decomposition (Scholten, M.C.T. et al. 2005). Anoxia resulting from algal decomposition changes the redox conditions at the sediments and can trigger sediments to release metals and nutrients. Iron and manganese are released from sediments during anoxic periods, posing a threat to drinking water quality (Miao, et al. 2006) Furthermore, in the absence of oxygen, bacteria turn to respiration processes such as methanogenesis, potentially releasing greenhouse gases into the atmosphere (Kasting, et al. 2002). Nonliving phytoplankton can cause depletion of oxygen in the water, and can create off-flavor compounds that cause large financial losses in municipal drinking water (Chislock et al. 2013). In this study, we examine not only the water quality variables and nutrient concentrations in a reservoir experiencing seasonal cyanobacterial blooms, but also the relative proportions of living versus nonliving phytoplankton, as this may have implications for water quality and reservoir biochemistry.

Changing land use and increased anthropogenic nutrient inputs have resulted in a worldwide increase in algal blooms and eutrophication. Eutrophication is characterized by increased algal growth, increased algal and cyanobacterial blooms, a decrease in the abundance of species and degraded water quality. Eutrophication causes anoxic conditions and unpleasant odor, and is enhanced by increased nutrient concentrations in the water and decreased dissolved oxygen (Chislock et al. 2013, Scholten, M.C.T. et al. 2005). Phytoplankton blooms caused by eutrophication can release toxins into water and have potentially negative effects on human health, carbon sequestration, and water quality (Berg and Sutula, 2015). Eutrophication can alter competitive interactions between phytoplankton, and can cause decreased carbon dioxide in the water. Dominance of one phytoplankton species can switch as eutrophication increases (Scheffer and van Nes. 2007) Algal blooms can also cause a reduction in the irradiance in the water column. This can reduce the growth of other producers because the bloom can shade phytoplankton that could be eaten by higher trophic levels, or can shade out macrophytes that feed and shelter young fish. The effects of eutrophication are far-reaching and this process of degrading water quality threatens lakes and reservoirs worldwide (Chislock et al. 2013). The algal blooms can cause oxygen depletion and can decrease pH to potentially lethal levels to aquatic organisms. Though the factors leading to phytoplankton blooms are different in each case, many phytoplankton groups can produce and release algal toxins. Not every bloom results in toxic release, and the function of phytotoxins is still somewhat unclear, but blooms do pose a concern to drinking water managers, especially when they cause high biomass accumulation (Stumpf and Tomlinson 2005).

This study focuses on a cyanobacterial bloom in the seasonally anoxic Beaverdam Reservoir (BVR) in Vinton, Virginia, USA. Though cyanobacteria dominate the hypolimnion, plankton diversity is high in the epilimnion; we used *in situ* fluorometry through the water column to measure concentrations of four major phytoplankton groups: diatoms, green algae, cryptophytes, and cyanobacteria. Each group plays a different role in the aquatic ecosystem, utilizing group-specific "accessory pigments" to maximize production while reducing competition for light (Tester et al. 1995). Some phytoplankton taxa are commonly found near the water's surface, while others are often found in deeper waters (Tester et al.

1995). A goal of this study is to determine the proportion of nonliving phytoplankton in our two reservoirs. The ratio of nonliving versus living phytoplankton can be determined by fluorescence from manually filtered chlorophyll samples and a spectrophotometer. (Fitch and Kemker 2014).

Cyanobacterial blooms have been a concern for water quality managers, as blooms have become more pervasive and harder to manage in recent years. Blooms tend to occur when water temperatures are above 20°C and when dissolved nitrogen is depleted (Karl E. Havens 2008). Most cyanobacteria are capable of producing cyanotoxins (Paerl et al. 2011). Cyanotoxin exposure occurs most frequently through recreation and drinking water (Gilroy et al. 2000); therefore, preventing and controlling cyanobacterial blooms is a priority for many lake and reservoir managers.

To answer our research questions, we performed weekly water quality monitoring during early summer 2015 in the unmanaged Beaverdam Reservoir (BVR) and the heavily managed Falling Creek Reservoir (FCR). Both reservoirs contain sediments rich in metals and nutrients, but Falling Creek Reservoir contains a hypolimnetic oxygenation system that effectively prevents seasonal anoxia and mitigates the effects of eutrophication (Gerling et al. 2014). Both reservoirs are owned and managed by the Western Virginia Water Authority (WVWA), are located in private, forested catchments, and provide drinking water to the residents of Roanoke, Virginia. Beaverdam Reservoir (BVR) is virtually unmanaged, and is the larger of the two reservoirs. Beaverdam experiences seasonal anoxia during summer stratification, which results in high concentrations of dissolved nitrogen, phosphorus, iron and manganese. Beaverdam Reservoir has had a hypolimnetic cyanobacterial bloom in the summers of 2014 and 2015. This cyanobacterial bloom is dominated by the species *Planktothrix rubescens*, which is typically found in clean, deep lakes that are seasonally stratified, and can produce harmful toxins during blooms (Ostermaier and Kurmayer 2009). We are interested in investigating the drivers of vertical phytoplankton distribution in Beaverdam Reservoir; specifically, why do the cyanobacteria remain at depth when light is stronger in shallower waters? Members of the genus *Planktothrix* are able to survive at depths where there is little light (Bossard et al. 2001); are these cyanobacteria taking advantage of a limiting resource not available at shallower depths? We will combine our investigation into the drivers of vertical phytoplankton distribution in BVR with weekly water quality monitoring of FCR and laboratory pheophytin analyses to compare the proportions of living versus nonliving phytoplankton in the epilimnion and hypolimnion of managed versus unmanaged reservoirs. We predict the drivers of vertical phytoplankton distribution in BVR to be iron and phosphorus, which together may drive the cyanobacterial community to depth. Assuming the rate of natural death is the same in FCR and BVR hypolimnia, the managed reservoir, FCR, should have a lower nonliving percentage because anything that dies will be decomposed more quickly due to the availability of dissolved oxygen for bacterial respiration. In BVR, nonliving phytoplankton will likely be decomposed relatively slowly due to anoxic conditions.

2. Research Methods and Experiment Setup

2.1 Study sites

Falling Creek Reservoir (FCR) and Beaverdam Reservoir (BVR) are located in Bedford County, Virginia, and supply water to citizens of Roanoke, Virginia. Both are owned and managed by the Western Virginia Water Authority (WVWA). Beaverdam Reservoir (z_{max} = 13m at full pond, 11.5m summer 2015) is not directly used for drinking water, but flows directly into Falling Creek Reservoir through a tributary stream. Both reservoirs are located in catchments that were previously farmed but are now almost completely forested; therefore, though there is no human activity in the catchments, the sediments of each reservoir remain rich in metals and nutrients. Beaverdam experiences seasonal anoxia during summer stratification, which results in high concentrations of dissolved nitrogen, phosphorus, iron and manganese. Beaverdam Reservoir has had a hypolimnetic cyanobacterial bloom in the summers of 2014 and 2015. This cyanobacterial bloom is dominated by the species *Planktothrix rubescens*, which is typically found in clean, deep lakes that are seasonally stratified, and can produce harmful toxins during blooms (Ostermaier V, Kurmayer R, 2009).

Falling Creek Reservoir (z_{max} = 9.3m) is heavily managed; the WVWA has installed a hypolimnetic oxygenation system that prevents anoxia, suppressing sediment nutrient and metal release (Gerling et al. 2014). This system was installed due to past water quality problems in the reservoir.

Photo1. Beaverdam Reservoir (Madeline Ryan, 05/28/2015)

Photo2. Falling Creek Reservoir (Madeline Ryan, 05/22/2015)

2.2 *Vertical distribution of phytoplankton in Beaverdam Reservoir*

We sampled Beaverdam Reservoir weekly and Falling Creek Reservoir biweekly from May 14, 2015 to July 9, 2015. We used a CTD (Conductivity, Temperature, Depth: Seabird Electronics) to measure temperature, dissolved oxygen, turbidity, conductivity and total chlorophyll at 10-cm depth resolution in each reservoir. We used a Fluoroprobe (Moldaenke) to measure totally chlorophyll and concentrations of cyanobacteria, cryptophytes, diatoms and green algae in BVR and FCR at ~20-cm intervals. We measured light (PAR meter), and pH (YSI Multiparameter Instrument) at 1-meter intervals in each reservoir.

Photo3. CTD instrument

(Madeline Ryan, 07/07/2015)

2.3 *Percent of nonliving and living phytoplankton in managed versus unmanaged reservoirs*

We collected water in a Van Dorn depth sampler from 0m, 3m, 6m, 9m, 11m in Beaverdam Reservoir, and 1.6m, 3.8m, 5.0m, 6.2m, 9.0m from Falling Creek Reservoir. Water samples were bottled directly for chlorophyll-*a* analysis, and bottled and frozen for water chemistry analysis; dissolved analyte samples were filtered immediately in the field using 0.7-µm GF/C filters. Chlorophyll-*a* samples were then filtered in the laboratory using a vacuum pump and 42.5mm glass microfibre filters, then put in the freezer until they could be analyzed. We followed the American Public Health Association's SOP for the "Spectrophotometric Analysis of Chlorophyll a after Ethanol Extraction" to analyze chlorophyll-*a* and pheophytin concentrations. Filters were placed in 10mL of 96% ethanol buffered with $MgCO_3$ solution in centrifuge tubes overnight, allowing chlorophyll-*a* trapped on the filters to dissolve into solution. Filters were removed the next day in order to centrifuge the samples. The remaining liquid in the centrifuge tubes was centrifuged for 10 minutes, and then run in the spectrophotometer. For each sample, we took an initial reading, then acidified the sample with 0.1mL 0.1N HCl. We recorded absorbance at 750, 664, and 665nm initially and 2-3 minutes after acidification, and used these values to calculate chlorophyll-*a*, pheophytin and percentage of living versus nonliving according to standard methods.

Photo 4. Manual chlorophyll filtering (Madeline Ryan, 06/11/2015)

3. Results

3.1 Vertical distribution of phytoplankton in Beaverdam Reservoir

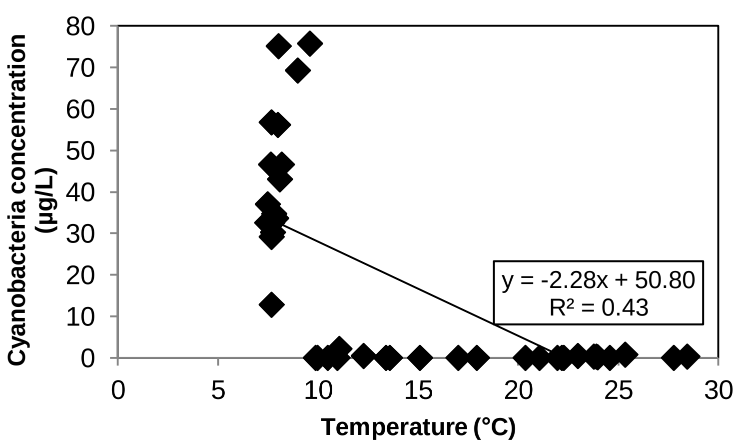

Figure 1. Cyanobacterial concentrations and temperature in Beaverdam Reservoir, early summer 2015.

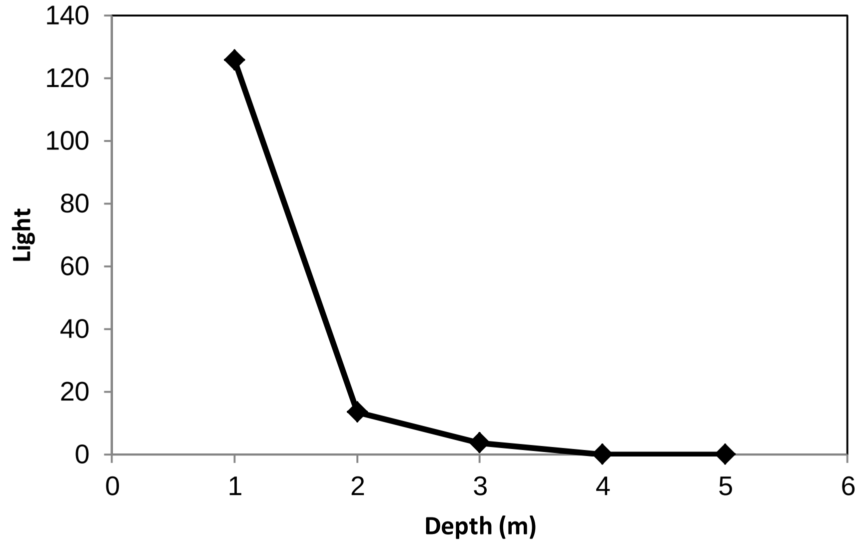

Figure 2. Light profile on June 4, 2015 in Beaverdam Reservoir

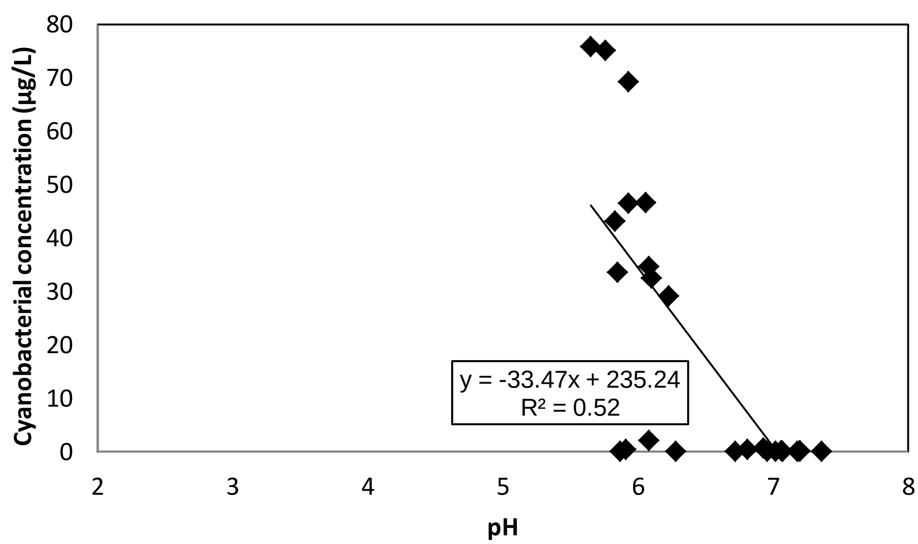

Figure 3. Cyanobacterial concentrations and pH in Beaverdam Reservoir, early summer 2015.

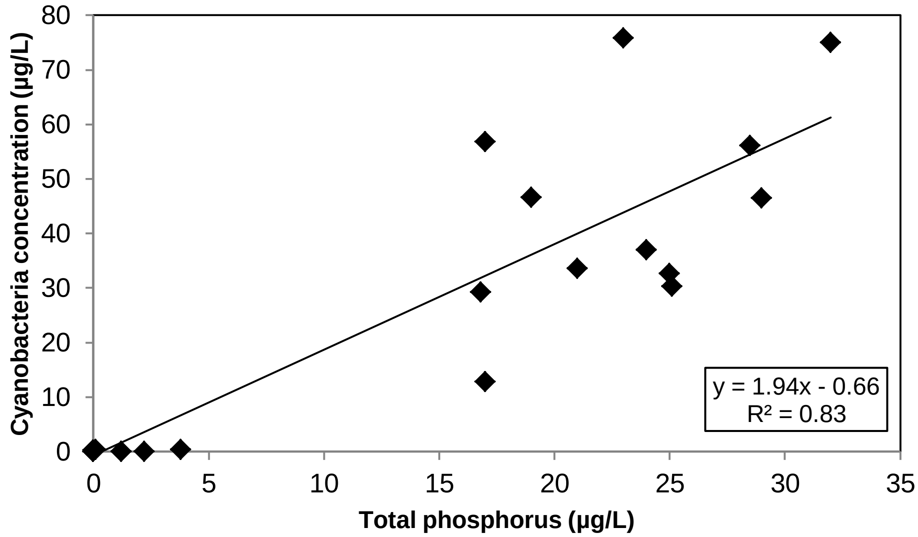

Figure 4. Cyanobacterial and total phosphorus concentrations in Beaverdam Reservoir, early summer 2015.

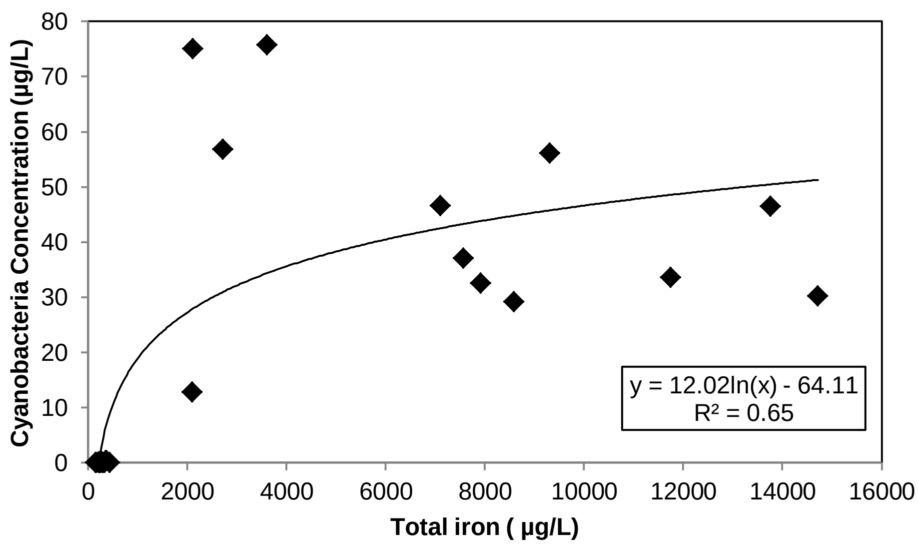

Figure 5. Cyanobacterial and total iron concentrations in Beaverdam Reservoir, early summer 2015.

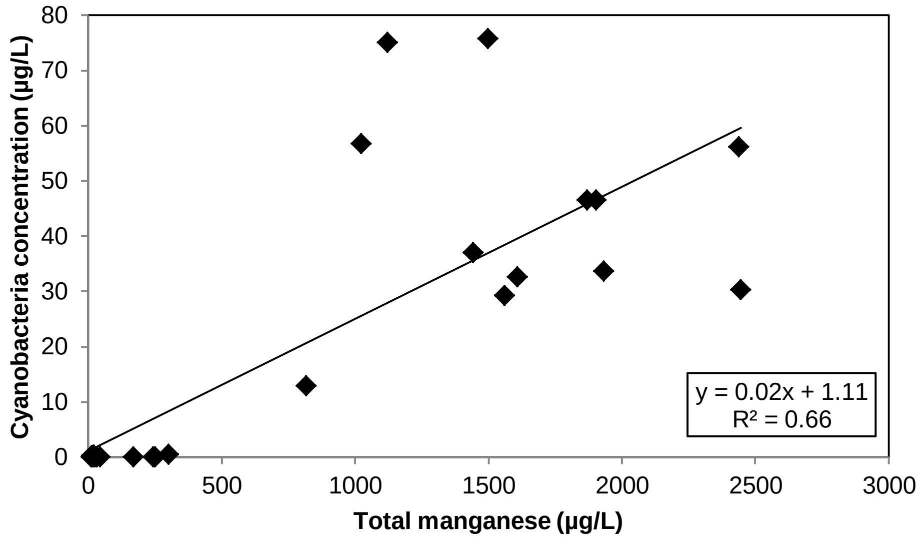

Figure 6. Cyanobacterial and total manganese concentrations in Beaverdam Reservoir, early summer 2015.

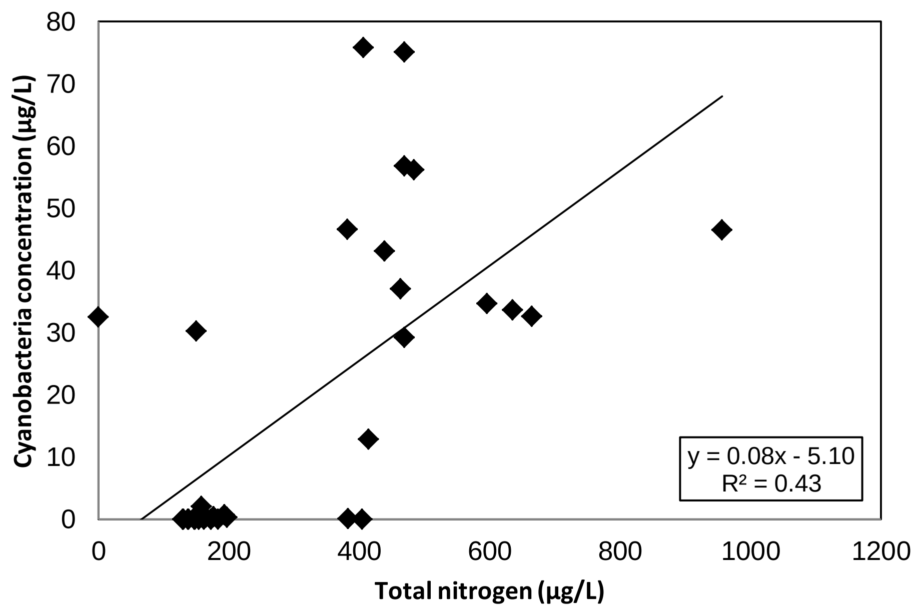

Figure 7. Cyanobacterial and total nitrogen concentrations in Beaverdam Reservoir, early summer 2015.

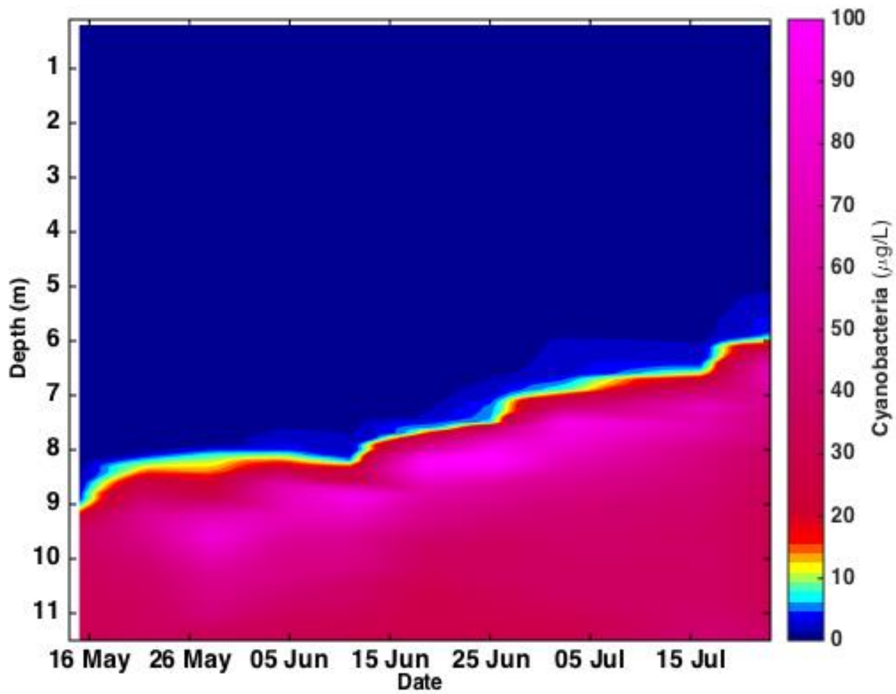

Figure 8. Cyanobacteria concentration and distribution in Beaverdam Reservoir, early summer 2015.

3.2 Percent of nonliving and living phytoplankton in managed versus unmanaged reservoirs

The percentages of nonliving phytoplankton in Beaverdam Reservoir and Falling Creek Reservoir were similar. There was no difference in the percent of nonliving phytoplankton in FCR and BVR (ANOVA, F = 1.37, P= 0.14, n=41).

4. Discussion

4.1 Vertical distribution of phytoplankton in Beaverdam Reservoir

Temperature showed little correlation to cyanobacteria concentration (R^2 = 0.43) (Figure 1). It has been demonstrated that cyanobacteria exhibit highest growth in warmer water (Paerl and Huisman 2008); therefore, though cyanobacteria are most abundant in the cooler hypolimnion of BVR, their vertical distribution was likely driven by variables other than water temperature. Light (example in Figure 2) did not show a strong correlation with the cyanobacteria. Some cyanobacteria prefer longer light wavelengths, and though there was little light in the reservoir hypolimnion, there was a small amount suggesting that these phytoplankton were still able to photosynthesize at depth (Jacquet et al. 2005). There was a relationship between pH and cyanobacteria concentration (Figure 3), but this relationship was less strong than following correlations with phosphorus and iron.

Cyanobacterial concentrations were strongly correlated with phosphorus (R^2 = 0.83), iron (R^2 = 0.65), and manganese (R^2 = 0.66). There was also a positive relationship between nitrogen concentrations and cyanobacteria, though this relationship was less strong than with other variables (R^2 = 0.43). The cyanobacterial concentrations were positively correlated with increasing total phosphorus (Figure 4). We used single linear regressions for all correlations except iron, because a logarithmic regression was more appropriate for the range of iron concentrations. Iron may stimulate cyanobacteria at moderate (2000-4000 µg/L) concentrations, while high concentrations may be too high for maximum cyanobacterial growth (Figure 5). Iron and phosphorus additions combined have yielded a higher biomass than adding phosphorus alone, which indicates iron and phosphorus co-limitation on cyanobacterial growth (North et al. 2007). Manganese (Figure 6) and nitrogen (Figure 7) showed positive correlations with cyanobacteria concentrations. Manganese is required in small concentrations for photosynthesis (Shcolnick and Keren 2006). This relationship, however, may have been a coincidence; iron and manganese are released from sediments under similar conditions, so both metals are found in the hypolimnion of BVR. Cyanobacteria were essentially absent in the epilimnion, but a cyanobacterial bloom dominated the hypolimnion (Figure 8). The band of cyanobacteria seems to move to shallower depths over the experimental period (Figure 8), and further monitoring will allow us to explore the drivers of vertical phytoplankton distribution.

4.2 Percent of nonliving and living phytoplankton in managed versus unmanaged reservoirs

There was no difference in average nonliving percentages in FCR and BVR. There was a trend toward reservoir hypolimnia containing a greater percent of nonliving phytoplankton than the epilimnia ($p=0.50$, $n=41$), but this result may be largely due to one outlier.

5. Conclusion

Phytoplankton play an important role in reservoir ecosystems, and can drive changes in water quality and ecosystem function. Their distribution in the water column can be important in determining their effects on a reservoir, and is often affected by what nutrients or resources are present. The results of this study support our hypothesis; cyanobacteria were most concentrated at depths where iron and phosphorus were abundant. The cyanobacteria likely remain at depth in order to obtain these nutrients in higher concentrations. There was not a difference in percentages of nonliving phytoplankton in FCR and BVR, which contrasted our hypothesis that the managed reservoir would have fewer nonliving phytoplankton due to the hypolimnetic oxygenation system in place there, and that the unmanaged reservoir would have a greater percentage of nonliving phytoplankton due to anoxic conditions. Though they are not actively photosynthesizing, respiring, or reproducing, nonliving phytoplankton may still have a profound effect on water quality. Dead cells can contribute to oxygen depletion via bacterial respiration during decomposition, and can cause unpleasant odors or flavors in drinking water. Additionally, nonliving cyanobacteria may include heterocysts and akinetes that may re-enter the life cycle if induced (Baker 1999; Hori et al. 2001), especially during fall mixing. Lysis of dead cells can release cyanotoxins into the water. Therefore, determining the relative proportions of living versus nonliving phytoplankton can be informative for water quality managers. Finally, this research supports findings that iron and phosphorus may together limit cyanobacterial communities; reducing hypolimnetic concentrations of iron and phosphorus, possibly via hypolimnetic oxygenation, may prevent cyanobacterial blooms and maintain higher water quality in drinking water reservoirs.

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Distribution of Neonicotinoids in a Surface Stream and their Transformation in Sediment and Soil

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Abstract

Neonicotinoids, such as Thiamethoxam (TMX) and its metabolite Clothianidin (CLO), are widely used insecticides commonly coated on planting seeds, causing an unknown amount to travel through the environment from fields to waterways. However, their accumulation in anthropods and aquatic organisms is sub-lethal, possibly attributing to the decline of the honey bee. In order to understand the distribution of TMX and CLO in an agricultural-urban-mixed impacted stream, their levels in sediments from seven locations along Stroubles Creek, Blacksburg were investigated. The sediment samples were extracted using the liquid/solid extraction, cleaned up using PSA, and analyzed on an ultra performance liquid chromatography-tandem mass spectrometer (UPLC/MS/MS). The levels of TMX at all but one location along the creek ranged from below the detection limit to 0.16 ppb, with the highest level detected at the location directly below a cornfield at 0.79 ± 0.12 ppb. The levels of TMX at three locations upstream of the corn field were below the detection limit. This indicated that the cornfield plays an active role in the accumulation of TMX in Stroubles Creek, suggesting that the insecticide coating the corn seeds has the ability to travel from the field to contaminate the creek. The levels of CLO, transformation product of TMX, in the sediment samples collected along Stroubles Creek were below the detection limit of 0.1 ppb. This study suggested that TMX does not stay contained within its application area and has the ability to travel into the adjacent aquatic system. The half-life of TMX in the Stroubles Creek sediment was found to be about 8 days while the half-life of CLO was found to be about 9 days. The concentration of TMX in soil decreased about 25% in the first 7 days of incubation, yet there was a very low concentration of CLO at the end of the 28 day study period. The transformation times were expected, yet the low concentration of CLO was unexpected and requires further research in order to definitively contradict previous studies.

Keywords: neonicotinoids, insecticides, Thiamethoxam, metabolite Clothianidin, sediment, urban watershed, contamination

1. Introduction

Neonicotinoids are highly soluble insecticides applied to soil and seeds to be taken up by the plant in order to target anthropods. These pesticides are thought to be a cause in the sharp decline of honey bees in recent years. Though it is doubtful that the accumulation of neonicotinoids in surface water is harmful to honeybees, concentrations of 0.14 to 18 ppb are sublethal to non-target aquatic anthropods and have been found in 80% of surface waters across nine countries (Sánchez-Bayo, 2014).
First marketed in 1998, TMX, a second generation neonicotinoid, is an ingredient in the pesticides Platinum, Actara, Centric, Cruiser, Flagship, and Helix produced by Syngenta (Syngenta, 2005). Though neonicotinoids are mainly used for agricultural purposes, other uses include structural pest control, landscaping, and pet treatment for fleas and ticks (Murray, 2015). Their use is widespread to the point where in the US all corn seeds and a third of soybean seeds are treated with neonicotinoids (Samson-Robert et al., 2014).

To understand the occurrence of neonicotinoids in wetlands adjacent to fields harvesting various types of crops, a study in the Prairie region of Canada analyzed both water samples and sediment samples for neonicotinoids. The water samples, which were as central as possible and distant from vegetation and surrounding plants, proved that neonicotinoids were present in 62% of wetlands' water after seeding occurred in the fields. Where detected, there was 2.3 ng/L to 121 ng/L of TMX and 0.8 ng/L to 142 ng/L of CLO. At the same time, and in these same wetlands, sediment samples were taken. Only 6% of the wetlands had sediment that contained neonicotinoids, with 20 µg/kg TMX and 2.8 µg/kg CLO to 4.4 µg/kg CLO where detected (Main et al., 2014). Because neonicotinoids are detected more often in water instead of sediment, it is assumed that they are more likely to be in a body of water rather than in the sediment at the bottom. However, in those locations where neonicotinoids are found in the sediment, the concentration of the compounds is significantly higher than the concentrations in the water samples, suggesting that neonicotinoids accumulate more readily in sediment than they do in water.

Due to the high use of these pesticides, the length of time they survive in the soil before degradation is important in understanding the possibility of accumulation in both soil and water sources. In a lab setting of normal field conditions the half-life of TMX in lab soil is 34-75 days (Maienfisch et al., 2001). However, half-life could triple if conditions were unfavorable, such as dry soil with less microbial activity (Maienfisch et al., 2001). TMX tends to adsorb more into the soil with time, meaning that it binds and becomes immobile (Syngenta, 2005). TMX has shown to degrade in water with a half-life of 24-44 days in anaerobic conditions and 8-16 days in aerobic conditions (Hladik et al., 2014), while CLO has shown a degradation of 148 to 1155 days in soil and 27 days in anaerobic aquatic conditions (EPA, 2003) Although TMX is shown to become less mobile in soil with time, some of the compound is still able to move away from the intended area and into surrounding water sources before the applied TMX becomes completely adsorbed; TMX has a high water solubility of 4.1 g/L, making it highly mobile in water (Schaafsma et al., 2015). According to a study in Ontario, the main reasons for this transfer are carry over soil residues from previous applications, spilled seed, planted seed, and contamination of fugitive planter dust on the soil surface (Schaafsma et al., 2015). Water samples, from puddles of standing water, were analyzed within and outside of maize fields during the planting season. The concentration of neonicotinoid residue was found to be consistent outside of the fields, yet within the fields, the concentration increased during the first five weeks after planting and after a rain event (Schaafsma et al., 2015). Another study on potato fields showed how accumulation of leachate occurs due to irrigation of water runoff from the fields and rainfall. The killing of vines during potato production causes more leachate to mobilize in the soil (Huseth & Groves, 2014).

A study in the Midwestern US found TMX in 47% of 79 stream flow water samples collected at nine sites while CLO was found in 75% of samples (Hladik et al., 2014). The TMX and CLO concentration ranged from 5.6 ng/L to 185 ng/L and 6.3 ng/L and 257 ng/L, respectively. Because TMX degrades rapidly under aerobic, aquatic conditions, it is thought to not be a high threat to non-target species, such as vertebrates. However, TMX has shown to metabolize readily to CLO on leaves and insect larvae. It was even shown after a soil drench in TMX that the concentration of CLO on the leaves was twice that of the TMX concentration (Nauen et al., 2003). CLO has shown to be more antagonistic to non-target species than TMX and its degradation is not as rapid.

1.1 Objectives

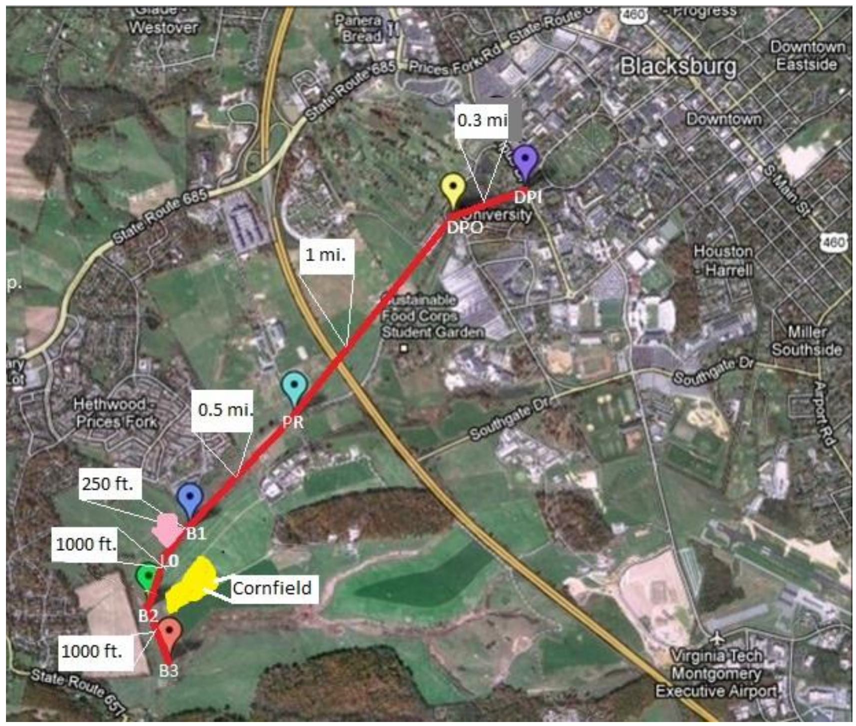
This experiment investigated the occurrence of TMX and CLO residues present across seven locations of Stroubles Creek in Blacksburg, VA. As suggested through previous studies, due to the solubility and mobilization of these compounds, there is the possibility that they are detectable in the sediment of Stroubles Creek at locations where it receives runoff and leachate from an adjacent cornfield. In addition, the aerobic transformation rates of TMX and CLO in both sediment and soil were investigated. Because TMX can transform to CLO, the levels of both TMX and CLO were analyzed when investigating TMX transformation rate.

2. Materials and Research Methods

2.1 Sediment Collection

Sediment was collected from seven locations along Stroubles Creek (Figure 1). The sediment was then separated from water in a centrifuge in vials containing 40 mL of sediment each, at the following parameters: temperature 8°C, 4000 rpm, and 10 minutes. The water was taken out of the vials, and the sediment was then freeze dried overnight. The freeze dried sediment was combined with all the sediment from its corresponding location, which was about 100 g total sediment. Two grams of sediment sieved through 2 mm was used for each sample during the extraction, cleanup, and analysis process, in order to detect a more accurate representation of the concentration of neonicotinoids in the sediment.

Figure 1. Sample Location Map Address of VT. Ag. Exp. Station: 3192-3262 Prices Fork Rd, Blacksburg, VA 24060 Location coordinates:
1) VT. Ag. Exp. Station (orange arrow): coordinates 37.217621, -80.463028
2) DPI (purple pinpoint): 37.225836, -80.425506
3) DPO (yellow pinpoint): 37.224711, -80.429688
4) PR (teal pinpoint): 37.215254, -80.439468
5) B1 (blue pinpoint): 37.210102, -80.445094
6) L0 (pink arrow): 37.209568, -80.446049
7) B2 (green pinpoint): 37.206446, -80.447449
8) B3 (red pinpoint): 37.203884, -80.446334



2.2 Sediment Incubation Study

Sediment was collected from L0 location of Stroubles Creek (Figure 1), separated from its water content, and then frozen for future use for the sediment incubation study to investigate TMX and CLO transformation.

Across nine wide mouth mason jars with 1 inch deep of sediment each, three treatments were set up in triplicate to determine the degradation of TMX and CLO in sediment in natural conditions. The three sediment treatments consisted of blank sediment, a concentration of 57.6 ng TMX per gram of sediment and water, and a concentration of 52.5 ng Clothianidin per gram of sediment and water. The jars were kept at room temperature and covered tightly with lids to keep conditions consistent. The sediments were spiked with TMX or Clothianidin then stirred thoroughly to incorporate the compound all the way through each jar. The sediment was covered in 2 inches of water from the same location as where the sediment was collected from.

Sampling occurred on days 0, 3, and 10. A micro spoon was used to collect about 12 g of soaked sediment from each jar. The samples from each jar went into a test tube to be freeze-dried overnight and 1 g each was to be extracted for the target analytes at a later date.

2.3 Soil Incubation Study

The soil used for the degradation study was obtained from the Virginia Agricultural Experiment Station (Figure 1). No pesticides were used on this soil before, making this soil free of neonicotinoid concentrations. The soil was air dried, sieved through a 2 mm sieve, and then ground before ready for the incubation study for TMX transformation.

A water holding capacity test was performed on the soil in order to determine the soil moisture content at its 70% water holding capacity, the water content that would be kept at throughout the study. To determine the soil water holding capacity, in duplicate, 100 g of air-dried soil was put into a disposable cup, which had 12 small holes cut out of the bottom. Enough water was then added to fully submerge the soil, and was allowed to drain out for 2 days in order to reach 100% water holding capacity. Based on weight differences of the cup, it was possible to calculate the amount of water needed to keep the jars at 70% water holding capacity.

Across six wide mouth mason jars with 100 g soil each, two treatments were set up in triplicate to determine the degradation of TMX in soil at field conditions. The two soil treatments consisted of blank soil and TMX concentration of 2.3 μg per gram air dried soil. The soils were spiked with TMX at the target levels, and then stirred thoroughly to incorporate the TMX with the rest of the soil in each jar. The appropriate amount of deionized water was added to each jar in order to reach a water content at its 70% water holding capacity in each jar. This water content was maintained during the entire incubation time by periodically weighing each jar and adding water accordingly. The jars were kept at room temperature and covered with Parafilm to keep aerobic conditions (Kwon et al., 2010).

Sampling occurred on days 0, 3, 7, and 28. A micro spoon was used to collect about 1 g of moist soil from 3 different places in each jar and composited. The composite samples from each jar went into a test tube to be freeze-dried overnight and 1 g each was to be extracted for the target analytes at a later date.

2.4 Neonicotinoids

Thiamethoxam (abbr. as TMX), purchased through Sigma Aldrich and manufactured by FLUKAR, has a purity of 99.6%. A white powder with a molecular mass of 291.71 g/mol, a TMX in acetonitrile stock solution of 11.52 mg/mL was used. Clothianidin (abbr. as CLO), purchased through Sigma Aldrich and manufactured by Chem Service, has a purity of 99.5%. A white powder with a molecular mass of 249.68 g/mol, a CLO stock solution of 10.49 mg/mL was prepared. The stock solutions were serially diluted 10X to prepare usable concentrations of the compounds. Both the TMX and CLO stock solutions were used to prepare standards for use on the LC-MS/MS.

2.5 TMX and CLO extraction, cleanup, and analysis for sediment and soil samples

Freeze dried and sieved sediment/soil was measured out using an analytical balance to 2g (for sediment detection) or 1g (for incubation studies) and put into 35 mL round-bottom vials. A vial containing no sediment/soil was also put through the clean-up procedure for comparison purpose. Samples containing a specific amount of added TMX or CLO were spiked at this time (usually 100 μL of 100 ppb compound). Ten milliliters of acetonitrile was added to each of the vials, which were covered with foil and lids. The samples were vortexed for 10 seconds each on speed 6.5. To each vial, 2 g $MgSO_4$ (anhydrous) and 0.5 g NaCl per gram of sediment/soil were added. The samples were vortex mixed for 2 minutes on speed 6-7 then centrifuged in swinging-bucket adapters at these parameters (used for the entire duration of the extraction): 3500 rpm, 23°C, 6/max accel/decel, and 10 minutes. The supernatant from these vials was transferred to another set of 35 mL round-bottom vials containing 0.5 g $MgSO_4$ (anhydrous) and 0.1 PSA sorbent per gram of sediment/soil that had been in the other sample vial. Five milliliters of acetonitrile was added to the sediment/soil vials, which were then vortexed for 1.5 minutes on speed 7-8 and centrifuged. The supernatant from these vials was transferred to the supernatant vials. These vials were then vortexed for 2 minutes on speed 6 and centrifuged. Ten milliliters of the supernatant was transferred using a 10 mL pipet to 25 mL test tubes to be dried down in the RapidVap at these general parameters: Round 1) 60 minutes, 130 mbar, 60% spin, 35°C; Round 2) 20 minutes, 140 mbar, 60% spin, 40°C. The dried down samples were then redissolved in 1 mL of 9:1 H_2O/MeOH with 5 mM NH_4Ac. Each final extract was diluted appropriately to fit the upper and lower standard range. Then, using a 1 mL syringe, filtered through a 0.2 µm PTFE filter into a 2 mL HPLC vial for the UPLC/MS/MS analysis.

The instrument used in this study was the Agilent 6490 Triple Quad LC/MS with the ZORBAX Extend C-18 analytical guard column 4.6x12.5mm, 5 micron. The temperature of the column was 40°C. The mobile phase used was (A) 5mM NH_4Ac in water and (B) 5mM NH_4Ac in methanol. The following gradient of mobile phase was used: increase 10% to 95% (B) from 0 to 5 mins., held at 95% (B) for 2 mins., and then decrease to 10% (B) for 1 min. The flow rate used was 0.5 mL/min, with post time of 3 mins., and injection volume of 5.00 µL.

3. Results and Discussion

3.1 Instrument Use

All samples were analyzed on a triple quadruple ultra performance liquid chromatography-tandem mass spectrometer (UPLC/MS/MS). As shown in Figures 2 and 3, the retention times of TMX and CLO in samples were 3.15 min. and 3.65 min., respectively, and the ratios between the quantifier and qualifier daughter ions of TMX and CLO in samples were around 40 and 100, respectively.

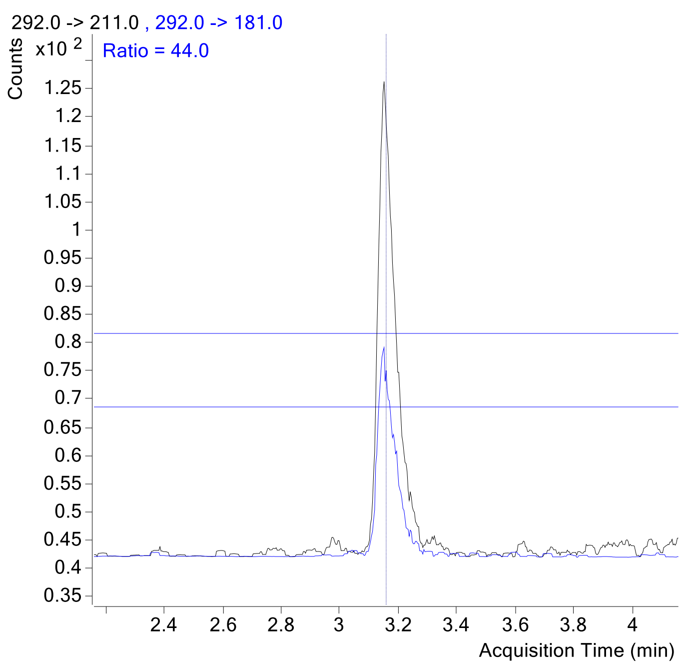


Figure 2. Chromatogram of TMX standard (0.58 ppb) showing peak retention time and ratio of quantifier and qualifier daughter ions

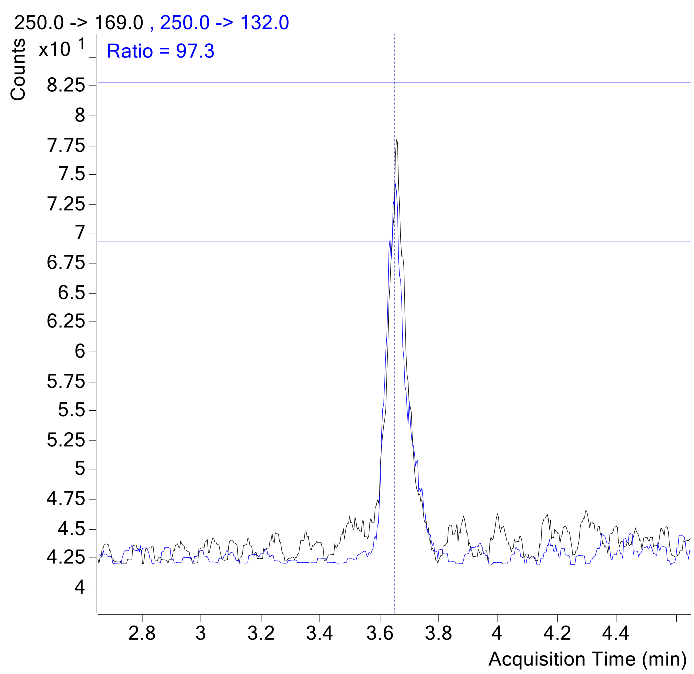


Figure 3. Chromatogram of CLO standard (0.53 ppb) showing peak retention time and ratio of quantifier and qualifier daughter ions

3.2 Levels of TMX and CLO in the sediment from Stroubles Creek

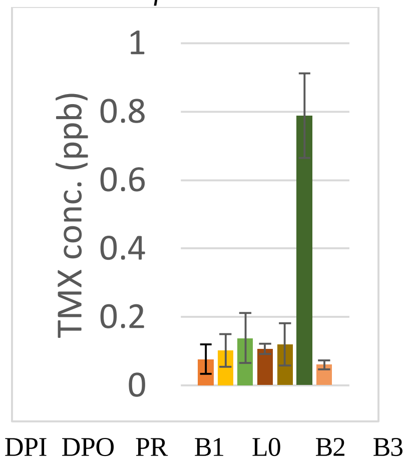
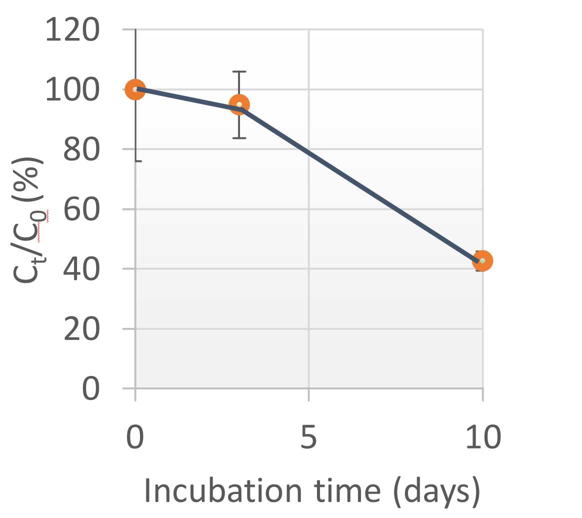


Figure 4. TMX concentration (ppb) at designated locations The locations shown here correlate with the locations on the sample map (Figure 1). Sediment at locations DPI and B3 were below detection limit, while locations DPO, PR, B1, and L0 were between 0.1 ppb and 0.16 ppb. Sediment at B2, adjacent to the cornfield, was 0.788 ppb.

The highest mean concentration of TMX was 0.788 ppb (Figure 4), found in the sediment samples collected from Stroubles Creek at the second bridge (designated as B2). Sediment samples from all other locations along Stroubles Creek had concentrations that were, at most, 0.16 ppb. The concentrations in those sediment samples were either under or very close to the detection limit of 0.1 ppb. The sediment samples had concentrations of CLO that were all below the detection limit of 0.1 ppb. Because the concentration of TMX in Stroubles Creek was found to be the highest at the location directly below the cornfield (Figure 1), it can be concluded that TMX may mobilize readily from the soil in the cornfield to the sediment in the creek. Additionally, the presence of the cornfield impacts the accumulation of TMX found in Stroubles Creek at that location. CLO is present in various locations along Stroubles Creek, though it is unclear what specific events along the stream would cause an accumulation of the compound.

3.3 TMX and CLO Transformation Rate in Sediment



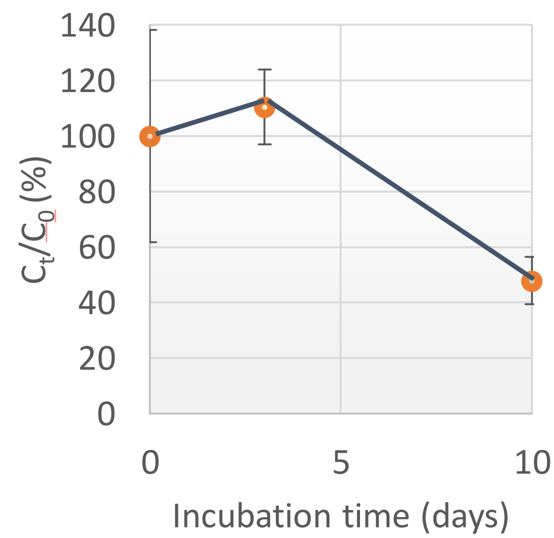


Figure 5. Graph showing the transformation rate of TMX in sediment collected from Stroubles Creek. The half-life of TMX in this sediment was found to be about 8 days.

Figure 6. Graph showing the transformation rate of CLO in sediment collected from Stroubles Creek. The half-life of CLO in this sediment was found to be about 9 days.

The half-life of TMX in sediment in this study was 8 days and the half-life of CLO in the sediment used in this study was 9 days. Over the course of 10 days, no concentrations of CLO were detected in the samples where TMX was transforming. Because the concentration of CLO in Day 3 is higher than it is in Day 0, one of these sets of data is incorrect. This may be due to uneven distribution of the compound in the jars, either just within the sediment or between the water and sediment portions. This is especially suggested as one jar's sediment sample showed an increase from 0.3 ppb to 26.7 ppb from Day 0 to 3.

3.4 TMX Transformation Rate in Soil

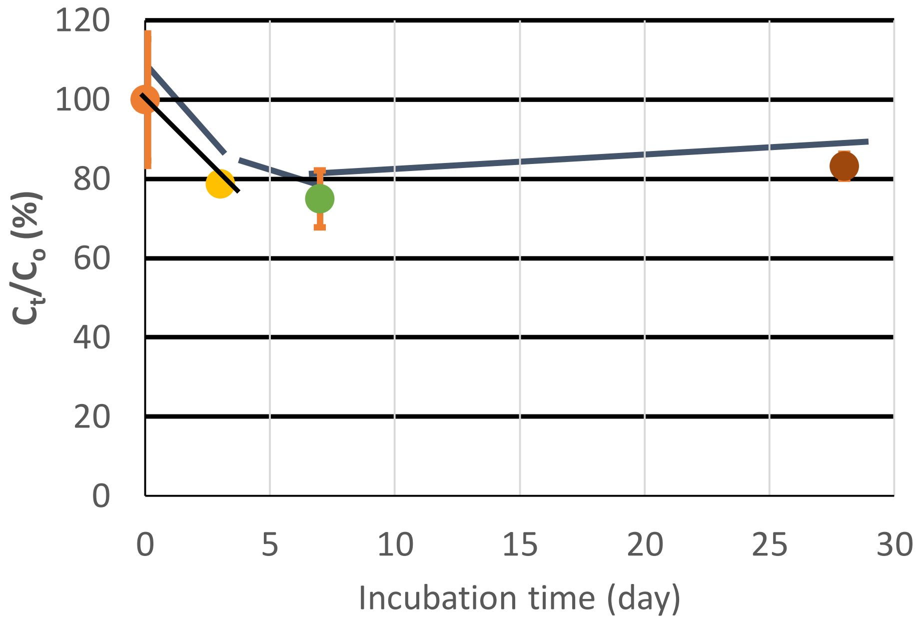


Figure 7. Graph showing the transformation of TMX in soil collected from the VT Ag. Exp. Station. The concentration of TMX in the soil decreased 25% over

The TMX concentration in this study decreased by 25% over the first 7 days. For the next 3 weeks, to day 28, the concentration of TMX in the soil was relatively stable. At the day 28 time point, the concentration of CLO contained in the soil was also analyzed. Of the 25% of transformed TMX, only 0.8% of that concentration transformed into CLO.

4. Conclusions

In the results obtained from the sediment samples collected along Stroubles Creek, the location of sampling adjacent to the cornfield had the highest concentration of TMX, 5 times larger than the next highest concentration. Based on this data, it can be stated that TMX has the ability to mobilize from the cornfield to the creek. Because the concentration of TMX was below the detection limit at the next downstream location, it is assumed that TMX does not mobilize much through the creek itself. The transformation rates of TMX in sediment from Stroubles Creek were comparable to those found in previous aerobic water studies (Hladik et al., 2014), while the transformation rate of CLO, which does not have much literature on it, was similar to that of TMX. The transformation rate of TMX in soil was also comparable to that of previous studies (Maienfisch et al., 2001) as the half-life of TMX in soil was at least double that of TMX in sediment. The lack of high concentration of CLO found in the day 28 soil samples was unexpected. This possibly contradicts a previous study, as the analysis was not performed on other days for comparison and the low concentration could be due to other reasons such as CLO degradation, which had stated CLO as a main transformation product of TMX (Nauen et al., 2003). The analysis of CLO concentrations in comparison to decreasing TMX concentrations is a possible topic of further study.

5. Acknowledgements

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I thank Dr. Kang Xia and Hanh Le for their continuous help and support throughout my research.

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Effects of Flow Rate on Turbidity and Microbial Growth in Premise Plumbing Systems

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Abstract

Opportunistic pathogens (OPs) are the leading cause of water-borne disease in developed countries. Water- and energy-conserving plumbing system designs with reduced flow rates can increase OP growth by fostering sediment accumulation, biofilm development, and disinfectant residual decay. A simulated water faucet experiment was constructed, testing four flow rates (1.6-6.5 L/min) in duplicate. Hot (50° C) and cold (<20° C) water was mixed, targeting 37° C at each faucet. The lowest flow rate had 22-28% more turbidity and 22-32% more bacterial cells than the highest flow rate, confirming that lower flow rate faucets have an increased potential to facilitate growth. In a parallel bench-scale plumbing rig operated at four flow rates (0.2-9.8 L/min), and flushed with a 50 NTU solution of natural organic matter, 3.5 times more turbidity accumulated in the lowest flow rate pipe than the highest flow rate pipe. Chlorine residual disappeared in the lowest flow rate pipe 7 times faster than a stable chlorine residual control and 5.5-6.3 times faster than the higher flow rate pipes when 5 mg/L free chlorine was introduced. This parallel work confirms that lower flow rates create favorable conditions for microorganism regrowth. Future work will investigate the effects of low flow on OPs.

Keywords: particle entrainment, premise plumbing, turbidity, flow rates, opportunistic pathogens

1. Introduction

Water-borne diseases caused by opportunistic pathogens (OPs) are a major public health challenge. OPs can naturally colonize premise (i.e., building) plumbing systems, which are beyond the jurisdiction of water treatment authorities and are the leading cause of waterborne disease in the United States (Yoder et al., 2008; Brunkhard et al., 2011). While field surveys have identified risk factors for colonization of or disease occurrence from building plumbing systems (e.g., Straus et al., 1996; Alary and Joly, 1991; Borella et al., 2004), they do not provide cause and effect relationships between water quality, plumbing design, and complex microbial ecologies that may limit the effectiveness of engineering controls. For instance, sampling for *Legionella* occurrence at taps with limited information about the system components, temperature, or disinfectant residual stability makes concrete conclusions difficult to make.

A better understanding the conditions in premise plumbing systems that promote the regrowth of OPs can inform the design of building plumbing systems, but discrepancies exist in the published research regarding the effect of common engineering controls on regrowth. Hydraulic conditions, such as flow rate and flow frequency, are critical design aspects of green building design. Low flow and stagnation can stimulate microbial proliferation, as can hands-free water conservation faucets (Chaberny et al. 2004), resulting in their removal shortly after installation in high profile incidents (Sydnor, 2011). However, sometimes the opposite effect is observed, with continuous and/or turbulent flow facilitating more regrowth (Liu et al. 2006; Moore et al., 2006; Mathys et al., 2008). We hypothesize that such differences are driven by flow rate due to sediment accumulation, biofilm development, and disinfectant residual decay.

No literature specifically connects the effects of the combination of sediment accumulation, biofilm development, and disinfectant residual decay to microbial growth; however, these factors are a product of low flow that can create conditions that promote microorganism growth, potentially including OPs. Decreased flow velocities in pipes allow for the accumulation of sediment in drinking water from a variety of sources, including pipe corrosion and soil runoff. The settling of sediment can detract from water quality in premise plumbing by providing an environment for microbial growth and by consuming disinfectant residual. When sediment accumulation leads to the development of a biofilm, built up organic matter can make maintaining a disinfectant residual in chlorinated or chloraminated water difficult due to quick reactions between chlorine and organic matter. Maintaining a chlorine residual is the last line of defense against microbial growth in building plumbing after water treatment. Understanding the flow conditions and related factors that avoid these outcomes has the potential to reduce microbial growth and limit the proliferation of OPs in premise plumbing systems.

1.1 Experimental Objective

Turbidity and chlorine concentrations from both a simulated premise plumbing rig and parallel bench-scale experiments were examined to determine the influence of flow rate on the development of favorable circumstances for microorganism growth.

2. Research Methods and Experiment Setup

2.1 Experimental Methods

Two experimental rigs were built for the purposes of this study: a full-scale model plumbing rig ("faucet rig") and a bench-top plumbing rig ("turbidity rig").

2.1.1 Faucet Rig

A full-scale model plumbing rig was constructed featuring eight faucets operating at four different flow rates (0.44 gpm, 0.7 gpm, 0.96 gpm, and 1.2 gpm) in duplicate (Figure 1). Each faucet was connected to 15' of cross-linked polyethylene (PEX) piping (Sharkbite, Atlanta, GA) for both hot (50° C) and cold (<20° C) influent water. Influent water was well-flushed (7 minutes at Y L/min), granular activated carbon (GAC) (Pentek, Upper Saddle River, NJ) filtered Blacksburg, VA tap water. The GAC filters removed 83% of the total influent chloramine, reaching 0.50 mg/L as Cl_2. Hot water was supplied by a 75.7 L (20 gallons) household water heater. The system was programmed using an automated timer (Chrontrol, San Diego, CA) such that 6.50 L (1.70 gallons) flowed from each faucet, reaching a target temperature of approximately 37° C. The faucets operated sequentially, with a ten-minute period between each faucet to provide adequate temperature recovery time for the water heater after each water draw. Samples were collected into autoclaved (i.e., sterile) 1 L containers (Thermo Fisher, Waltham, MA). The first 250 mL released from each faucet was collected at the start of the flush of each faucet (i.e., first flush sample) in addition to a 1 L sample taken at the end of the programmed flush. Samples for biological analysis were immediately aliquotted to 1.5 mL tubes.

2.1.2 Turbidity Rig

Three phases of this experiment with the turbidity rig (Figure 2) were conducted in order to understand mass transport, settling, and re-entrainment in premise plumbing.

Phase 1. The critical velocities at which model natural organic matter (NOM) particulates settle and are re-entrained in flowing water pipes were determined experimentally. Three diameters (3/8", 5/8", and 3/4") of Tyvek tubing (DuPont, Wilmington, DE), each 500 mL total volume, were seeded with NOM by recirculating 150 NTU water for approximately one hour. Water was recirculated using a sump pump (Superior Pump, Minneapolis, MN), outfitted with a gate flow control valve, at a flow rate that qualitatively allowed larger NOM particles to settle and accumulate. This flow rate was recorded for each diameter of tubing as the maximum velocity than NOM particulates settled in the pipes, v_{max}. The pump was then turned off and the particles were allowed to settle for four to ten hours. The 150 NTU seed water was replaced with 0 NTU reverse osmosis (RO) influent water. Water was flushed through the tubing at incrementally increasing flow rates. At each flow rate, consecutive samples were collected until no more NOM was being re-entrained. Turbidity was measured in each consecutive sample and the flow velocities at which 50%, 90%, and 100% of the accumulated NOM was re-entrained were recorded for each pipe diameter.

Phase 2. The effect of flow rate on NOM accumulation was then determined using flow velocities that spanned the critical velocities determined in Phase 1. A pipe rig was constructed with four 500 mL Schedule 40 3/4" polyvinyl chloride (PVC) pipes (Charlotte Pipe, Charlotte, NC), each with a different flow rate (0.23, 0.76, 2.27, 9.84 L/min). 1.5 L of continuously mixed 50 NTU influent water was flushed through each pipe and then allowed to stagnate for one day. The effluent from each pipe was collected in incremental samples up to 1.5 L. This experiment was repeated in a "rinse" trial by pumping 0 NTU RO water through each pipe and collecting incremental samples until no or very few visible NOM particles could be seen in the effluent. In a final "blast" trial, the flow rates in each pipe were increased to the maximum flow rate possible from the pump (9.84 L/min) using 0 NTU RO water to force all accumulated mass to exit each pipes. Incremental samples were collected until no or very few NOM particles were visible in the effluent water from each pipe. At the end of each trial, all incremental samples were measured for turbidity.

Phase 3. Phase 2 was repeated with additional seeding with 50 NTU to test the effects of NOM accumulation on disinfectant residual decay. To accomplish this, an additional "rinse" trial was conducted with chlorine and chloramine disinfectant residuals The system was seeded with 50 NTU water five times over three days at varying flow rates (0.23, 0.76, 2.27, 9.84 L/min) in order to accumulate sediment in each pipe. After this seeding period, 0 NTU RO water was flushed through the plumbing rig in a rinse trial in which incremental samples were collected until no NOM particles were visible and measured for turbidity. A second rinse trial was performed at the lowest flow rate possible in the system with 0 NTU RO water dosed with 5 mg/L; 10 mL samples were collected from each pipe and measured for total chlorine over a two-and-a-half hour period every 10-30 minutes until trends were established or the residuals had fully decayed. A "blast" trial followed in which 0 NTU RO water was pumped through the plumbing rig at the maximum flow rate possible in each pipe (9.84 L/min) to remove all of the accumulated NOM. Incremental samples to be measured for turbidity were collected from each pipe until no NOM could be seen in each sample.

2.2 Analytical Methods

2.2.1 Natural Organic Matter "Seed" Solution

Particulate natural organic matter (NOM) was used to simulate particle transport, settling, and re-entrainment. Approximately 5 kg of commercially-available peat moss (Pro-Mix, Quakertown, PA) was added to 4 gallons of RO water to create a stock solution NOM. The NOM was wetted, well-mixed, and allowed to settle overnight. The fraction of NOM that settled overnight was re-suspended in 4.5 gallons of RO water, and allowed to settle for 15 minutes. The fraction that did not settle in 15 minutes (but had settled overnight) was used as the stock solution of NOM, which was diluted to the desired turbidity. Although the conditions in the transport, settling, and re-entrainment portion of the experiments are exaggerated, they are useful to inform the relationship between flow rates in premise plumbing and sediment accumulation.

2.2.2 Physical and Chemical Analytical Methods

For both experimental rigs, turbidity measurements were performed using a HACH turbidimeter (Loveland, CO). Disinfectant residual was measured with a “Pocket Colorimeter” (HACH, Loveland, CO).

2.2.3 Biological Analytical Methods

Stagnant and well-flushed samples from the low-flow model plumbing rig were examined using traditional heterotrophic plate counts (HPC) and flow cytometry techniques. HPC were performed according to Standard Method 9215. A BD Biosciences Flow Cytometer (San Jose, CA) analyzed samples from each faucet.

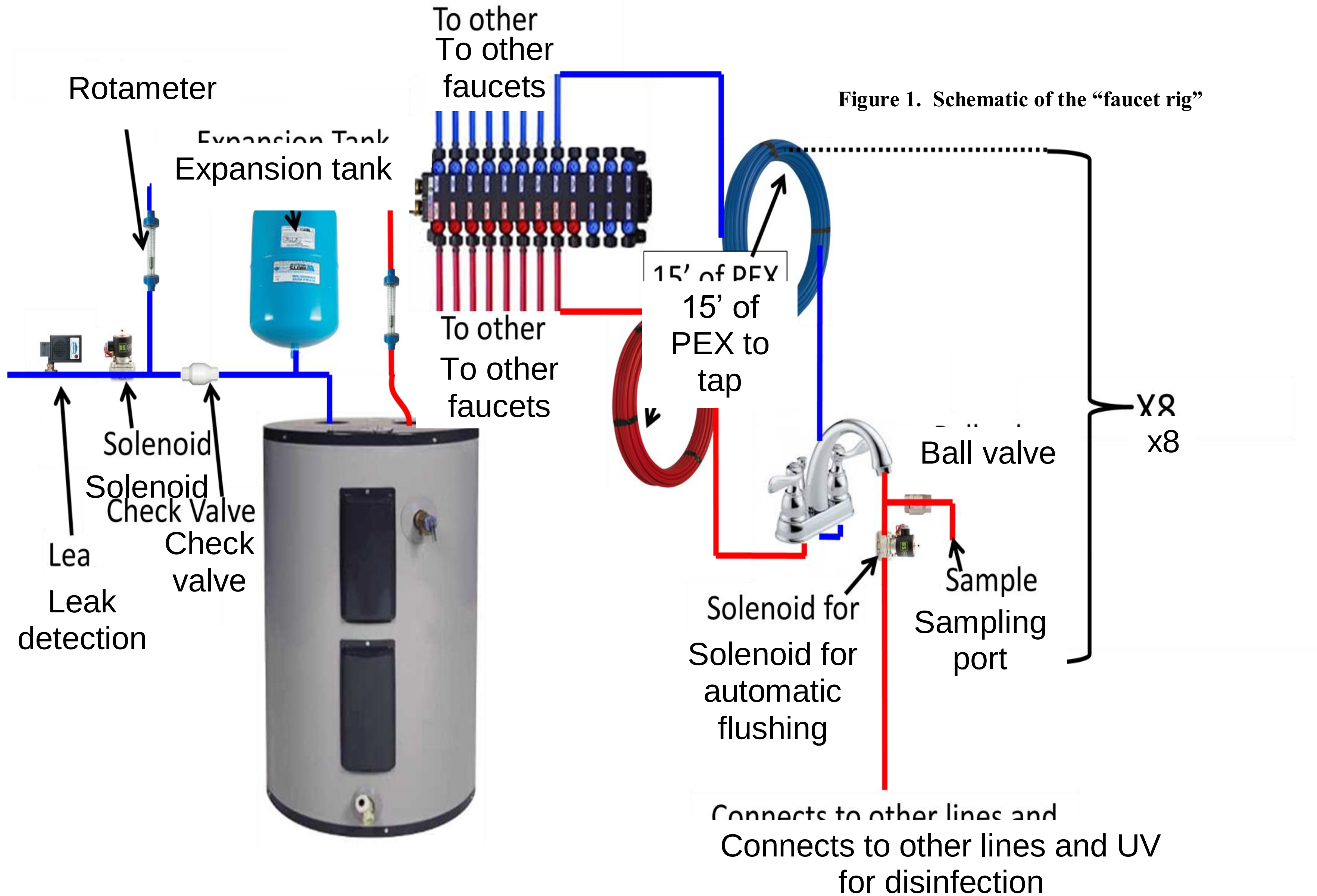

Figure 1. Schematic of the “faucet rig”

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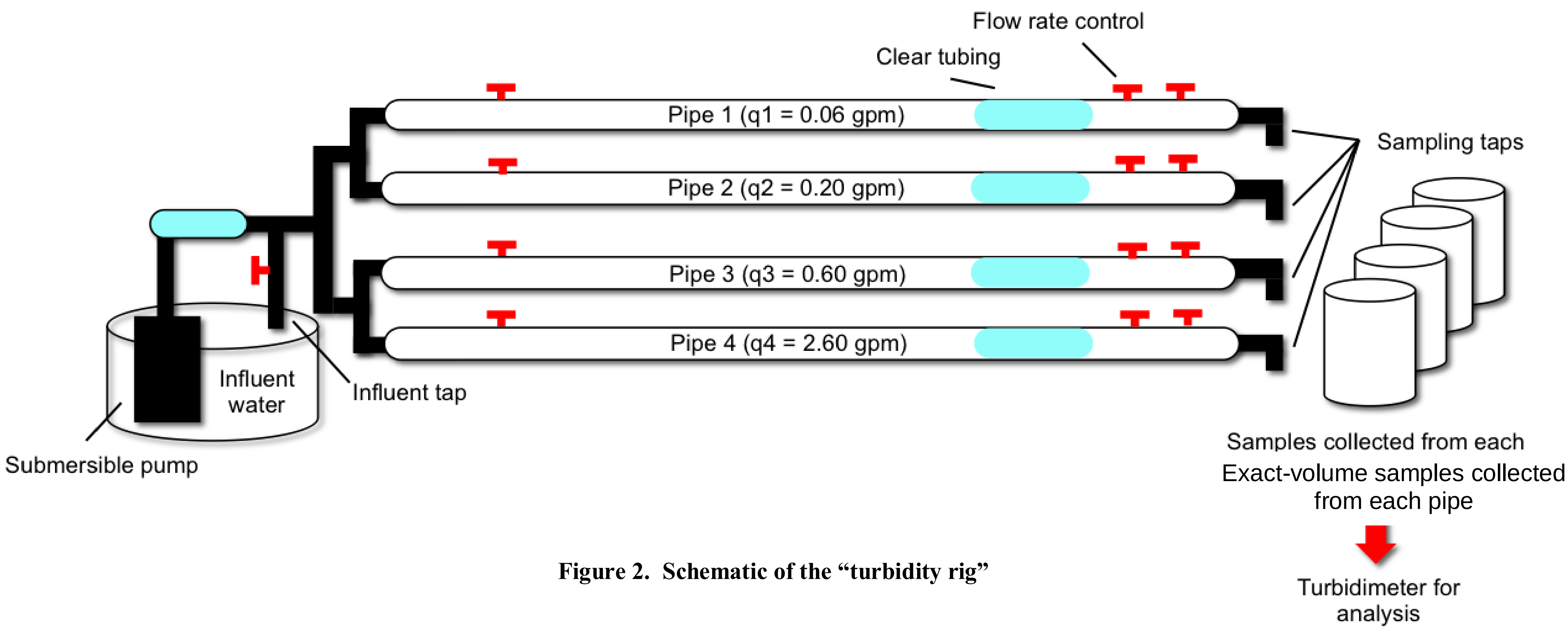

Figure 2. Schematic of the "turbidity rig"

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3. Results and Discussion

3.1 Faucet Rig

Microbial regrowth was measured as the difference in cells or colony forming units (CFU) per unit volume between first flush and well-flushed samples. Preliminary results show that the lowest flow rate (0.44 gpm) had 27% more cell regrowth and measured 54% more bacterial regrowth as measured by flow cytometry and culturing, respectively (Figure 3).

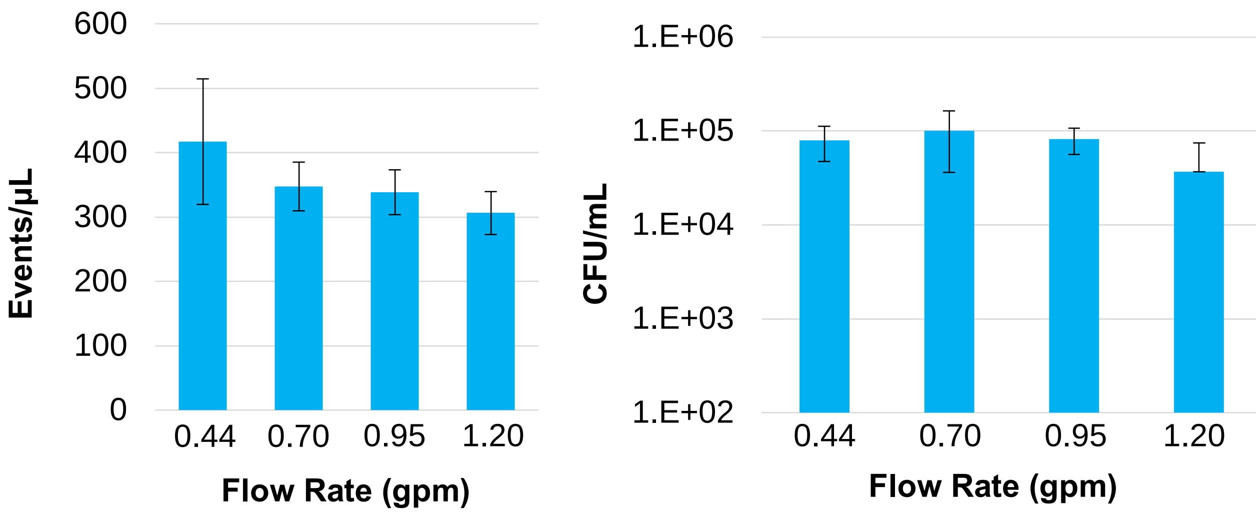

Figure 3. Regrowth in each faucet as measured by flow cytometry results (left) and heterotrophic plate count results (right)

There were no significant differences in temperatures, chlorine, or total organic carbon among the faucets in the same samples taken from throughout the flush, indicating that these physical conditions stayed consistent (Figures 1-3, Appendix). However, turbidity for each flow rate co-varied with both the HPC and flow cytometry data—the lowest flow rate faucets displayed 22-28% more turbidity in comparison to the to the highest flow rate faucets in stagnant and flushed samples (Figure 4). Though turbidity decreased in the order the faucets were flushed, influent turbidity in the hot and cold influent water did not follow this same pattern. These data suggests that low flow rates have an impaired ability to flush debris from the pipes, and may facilitate microbial regrowth. Although there is circumstantial evidence from the literature that flow rate contributes to regrowth (e.g., Sydnor et al., 2012; Chaberny et al. 2004), there are no controlled laboratory studies exploring impacts on water quality. Therefore, proof of concept is needed to further explore these observations.

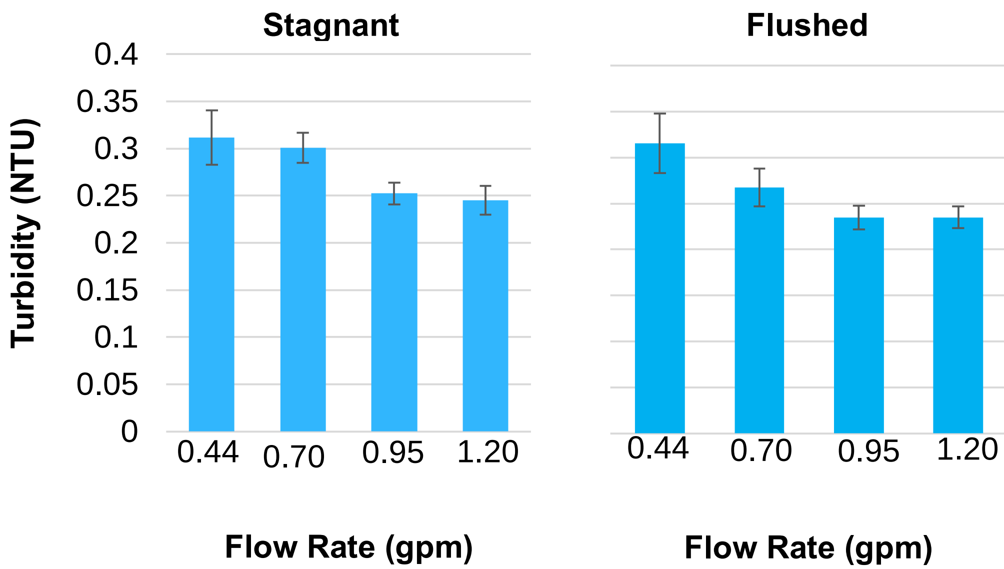

Figure 4. Side-by-side comparison of stagnant and well-flushed turbidity measurements from the faucet rig.

3.2 Turbidity Rig

Three phases of work established that particle deposition can be minimized by maintaining internal pipe velocities above a critical value, that low flow can facilitate the accumulation of sediment, and that sediment accumulation can exert an instantaneous chlorine demand.

3.2.1 Phase 1

The relationship between NOM particle accumulation, flow rates, and pipe diameter was assessed using a mass balance approach. An experimental unit of mass was defined (Equation 1). The mass balance was constructed according to a system defined around each pipe (Equation 2-4).

Mass (NTU-L) = Turbidity (NTU) x Volume (L) [Equation 1]
Mass In = Turbidity Influent x Volume Influent [Equation 2]
Mass Out = $\sum_{i=1}^{n}$ (Turbidity$_i$ x Volume$_i$) [Equation 3]
Mass Accumulated = Mass In – Mass Out [Equation 4]

Despite the use of 150 NTU water to seed each tubing diameter, every trial accumulated a different total NOM mass due to differences in each tubing diameter and differences in flow rate during the seeding procedure before each trial (flow was not measured during the seeding process).Accordingly, an incremental fraction of mass remaining in the pipes can be calculated to normalize the results relative to the influent mass during each trial (Equation 5)

Fraction of Mass Re-Entrained = Mass Out/Mass In [Equation 5]

As the internal velocity in each pipe diameter was increased, more of the accumulated mass was re-suspended and flushed out of the pipe (Figure 5) Yet, similar internal flow velocities were required to remove all the accumulated mass, regardless of pipe diameter.. For instance, the velocity at which all particles in the smallest tubing diameter (3/8") were ejected was approximately 1.67 ft/s (Figure 5); for the largest tubing diameter (3/4") this critical velocity was 1.78 ft/s. However, because the shear stress associated with water flow through pipes is proportional to the internal velocity divided by the pipe radius, the 3/8" pipe experienced 1.9 times more shear stress to release all of the accumulated mass. Though this is directly contrary to the conventional knowledge that it is easier to remove particles from smaller diameter pipes, the flow rate required to achieve higher pipe velocities, and therefore higher shear stresses are lower in smaller diameter pipes. This poses a particular challenge for buildings seeking to install low flow devices because the minimum pipe diameter is specified by the number of fixtures a supply line needs to supply. As the number of fixtures increases, supply line pipe diameter increases, and flow velocity and shear stress decreases.

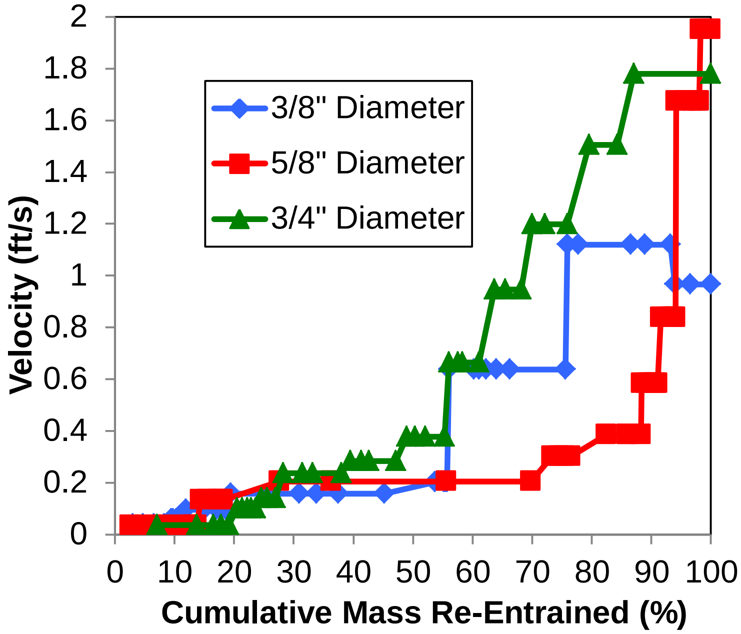

Figure 5. Increasing mass re-entrainment with increasing flow velocities.

3.2.2 Phase 2

A mass balance was conducted on 50 NTU water being flushed through pipes with different flow rates (0.23, 0.76, 2.27, 9.84 L/min)._ While the none of the flow conditions exhibited 100% mass recovery, total mass recovery was 1.5 times higher in the highest flow rate condition compared to the lowest flow rate (Figure 6). This result is expected because the lowest flow rate had an internal flow rate of 0.23 L/min. Therefore, it is not expect that the lower flow rates in this experiment would be able to re-suspend the particles given the results obtained in Phase 1.

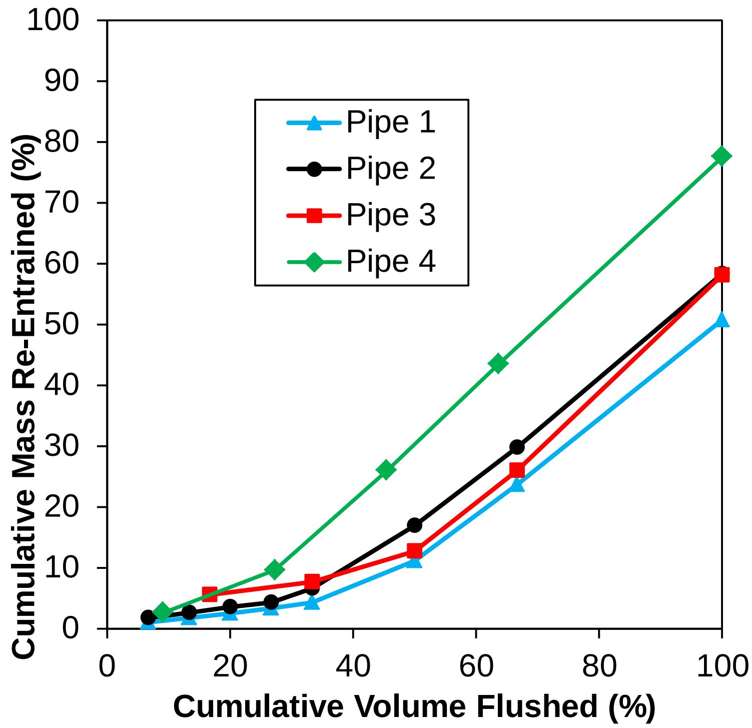

Figure 6. Increasing mass recovery with increasing flow rates by pipe.

When the system was flushed with 0 NTU RO water at the same flow rates as the 50 NTU condition above, it was expected that, again, the most mass would be recovered from the pipe with the highest flow rate. Approximately 6 times as much mass was released from Pipe 4 than Pipe 1 (Table 1). With decreasing flow rates, less mass was re-entrained and released from each pipe in terms of total NOM mass in experimental NTU-L units.

Table 1. Comparison of mass recovery in rinse and blast trials from the turbidity rig.

Pipe	Rinse Flow Rate (L/min)	Rinse Mass Recovery (NTU-L)	Blast Mass Recovery (NTU-L)
1	0.23	5.42	20.0
2	0.76	6.49	29.1
3	2.27	13.9	21.4
4	9.84	33.3	2.55

Finally, a high flow rate flush with 0 NTU was conducted. The internal velocity achieved was much higher than the critical velocities determined in Phase 1, and was designed to remove all remaining accumulated NOM. It was expected that less total mass would be recovered from the highest flow rate pipe compared to what would be released from the lowest flow rate pipe because the highest flow rate pipes were operated at internal flow velocities that were higher than the critical velocities. Nearly 8 times more mass was recovered from the pipes that originally had the lowest flow rate than the highest flow rate (Table 1). For the lowest flow rate pipe, little mass was released (5.42 NTU-L) during the low flow rate rinse at 0.06 gpm, but a a large amount of mass was released (20.0 NTU-L) during the high flow-rate rinse at 2.60 gpm. This indicates that lower flow rates in pipes facilitate the accumulation of sediments in pipes.

3.2.3 Phase 3

Phase 2 of the turbidity transport, settling, and re-entrainment experiment was repeated, with an additional rise step in which a 5 mg/L chlorine solution was introduced. The stability of the disinfectant residual was then monitored as a function of time. The initial rinse step (same as in phase 2) and high flow rate flush at the end of the experiment exhibited the same pattern as the rinse in Phase 2 (Table 1, Appendix).

In the lowest flow rate pipe with the most sediment accumulation, the initial chlorine concentration was 0.30 mg/L; in the highest flow rate pipe, the initial chlorine concentration was 3.2 mg/L (Figure 7). This indicates there was an instantaneous chlorine demand associated with NOM, and the more NOM that had been accumulated, the higher the initial demand was. In fact, the lowest flow rate pipe consumed X% of the original 5.0 mg/L that was introduced before the first measurement could be taken. As samples were taken incrementally over time, chlorine decayed at a similar rate in each pipe as it did in the influent solution that was not exposed to NOM.

Phase 3 of the turbidity transport, settling, and re-entrainment experiment demonstrates that chlorine decays more rapidly in pipes with higher amounts of NOM accumulation due to lower flow rates than pipes with lower amounts of sediment accumulation and higher flow rates. As previously established, the absence of a disinfectant residual can facilitate the growth of OPs.

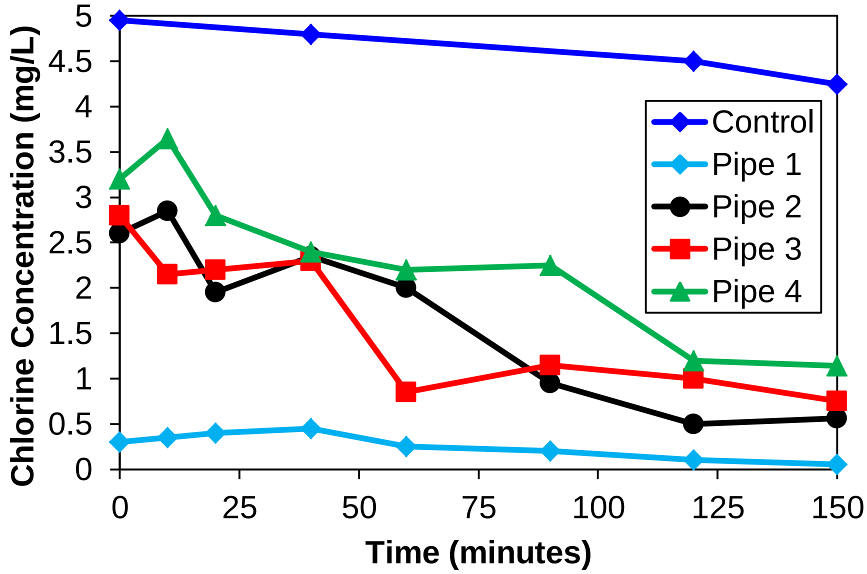

Figure 7. Chlorine decay by pipe as a function of time in the chlorine experiment.

4. Conclusion

This study experimentally established a relationship between low flow rates and organic matter/sediment buildup in plumbing systems at lower flow rates. The accumulated organic matter could serve as a nutrient source for bacteria and also accumulated removal of disinfectant. In parallel tests with disinfectant free drinking water, increased microbial regrowth was observed in lower flow rate faucets compared to higher flow rate faucets on the low-flow model plumbing rig. Further work will focus on OPs detection and will then examine effects of disinfectants at different flow rates.

5. Acknowledgements

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Appendix A

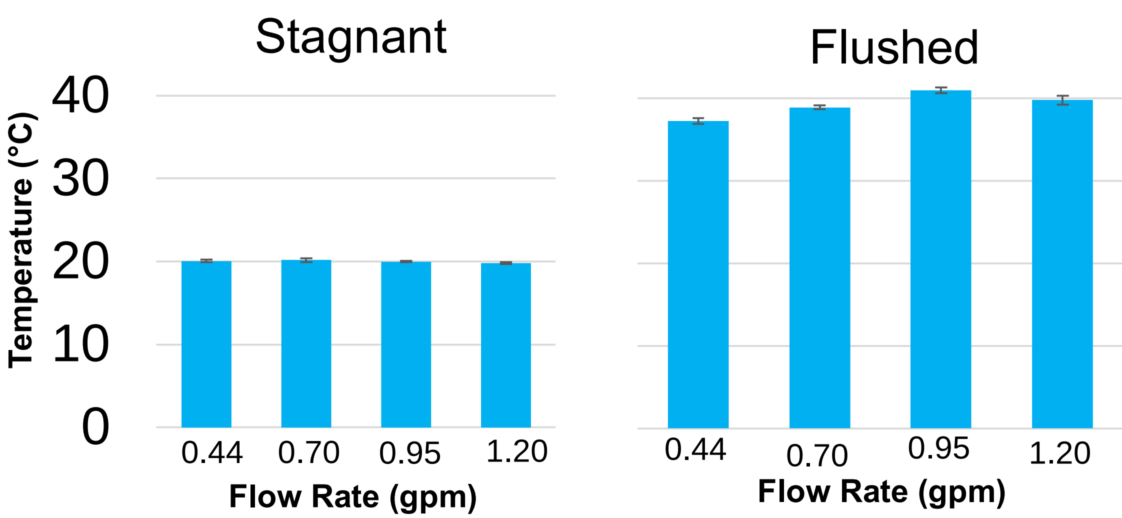

Figure 1. Temperature measurements from the faucet rig.

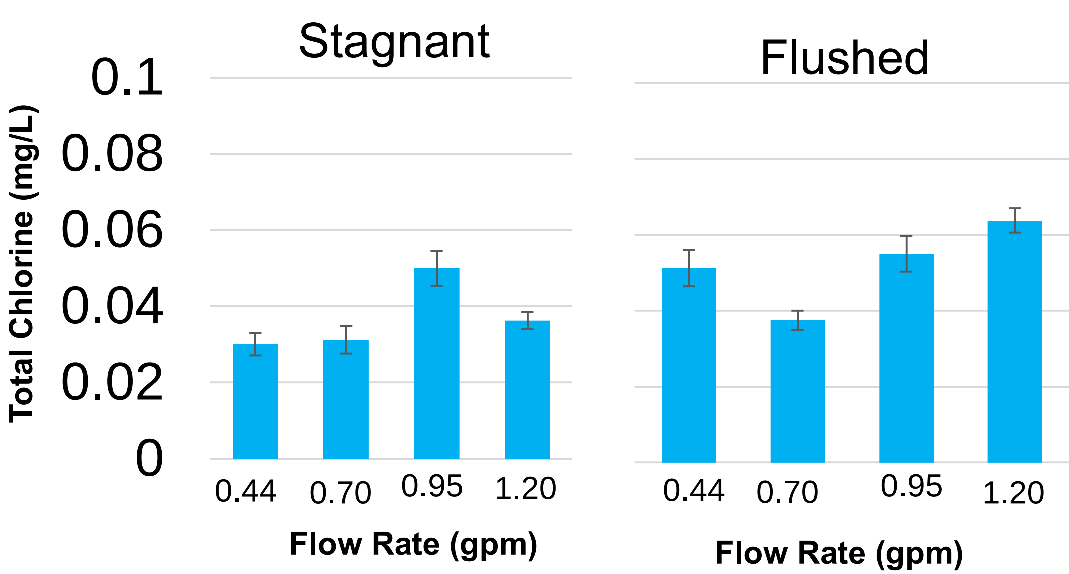

Figure 2. Total chlorine measurements from the faucet rig.

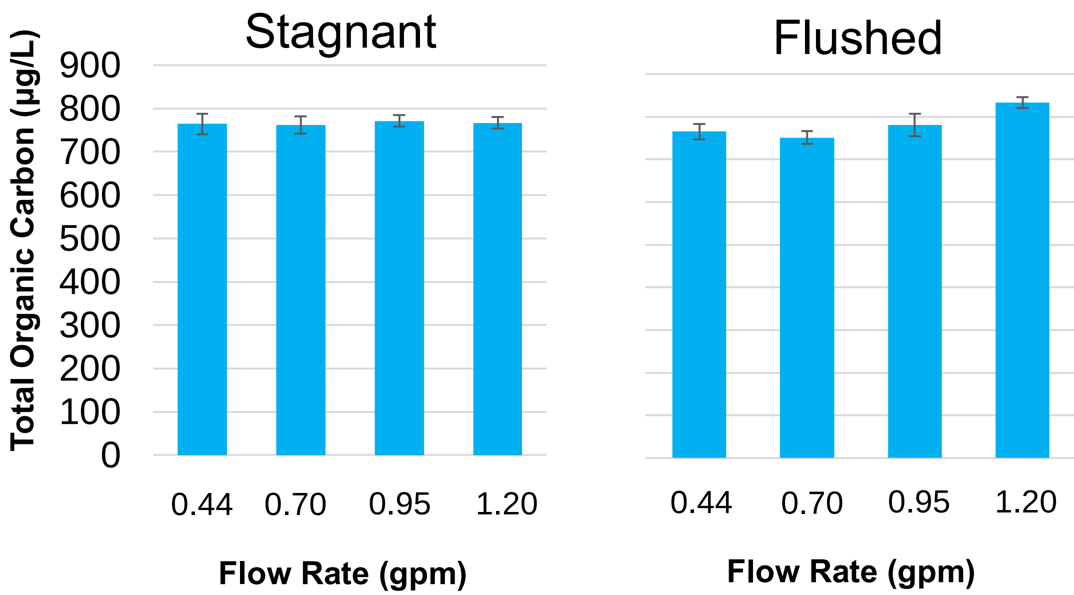

Figure 3. Total organic carbon measurements from the faucet rig.

Table 1. Rinse and blast mass recovery from chlorine rinse trial (Phase 3).

Pipe	Rinse Flow Rate (L/min)	Rinse Mass Recovery (NTU-L)	Blast Mass Recovery (NTU-L)
1	0.23	2.07	101
2	0.76	4.43	50.0
3	2.27	26.0	34.2
4	9.84	39.4	6.36

Nanoparticle Reactivity from Water Consumption throughout the Human Digestive System

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Abstract

Although the amount of consumer products containing nanoparticles is increasing, research data on the toxicity and reactivity of these nanoparticles is not readily available. The objectives of this research were to: (1) to evaluate the amount of dissolution of copper and iron nanoparticles in different digestive fluids: saliva, gastric, and intestinal; and (2) determine reactivity of common nanoparticles: nano- iron, silver, copper, and silicon dioxide, in the human digestive system by quantifying lipid oxidation using a TBARs assay. Dissolution results show that gastric fluid most readily dissolves copper and iron nanoparticles as compared to other digestive fluids. Since ferrous and cuprous solutions are known to induce lipid oxidation, they were the controls in the TBARs experiments. It was found that all nanoparticles induced lipid oxidation in at least one digestive fluid. Nanoiron caused the most lipid oxidation in all digestive fluids. However, lipid oxidation results varied for copper, silver, and silicon dioxide nanoparticles. Results show nanoparticles' reactivity significantly differed among each other and among each digestive fluid. These results suggest that nanoparticles exhibit a capability to react in human digestive fluids, which may lead to health concerns and exposure limits.

Keywords: nanoparticles, lipid oxidation, reactivity, digestive

1. Introduction

Every day, nanoparticles are becoming incorporated into more commercial and consumer products due to their unique and beneficial properties. Nanomaterials are regarded as having a measurement in at least one direction on the scale of 1-100 nanometers, and possessing a unique property, which differs from the bulk material (Albanese et al., 2012). For instance, nanoscale silver has been used in multitude of products for its antimicrobial property, while bulk silver does not exhibit this ability. Due to characteristic properties like this, many industries are using nanoparticles to improve current products and increase their efficiency. In 2009, it was reported that there were already upwards of 600 products containing nanomaterials, and by now that number has risen (Xia et al., 2009). However, these products may pose a health concern to humans and other animals as they accumulate in the environment. The Food and Drug Administration (FDA) does not require testing of nanoparticles when the bulk material is already known to be safe (Trafton, 2014). Currently, this is the problem since many believe that if the material of the nanoparticle at the bulk scale is safe, then so is the nanoparticle itself, which is not always the case. Nanoparticles frequently exhibit enhanced reactivity as compared to their bulk counterparts. It has been shown that nanoparticles can easily penetrate cells because of their size and cause damage to DNA (Trafton, 2014). In depth research about nanoparticle toxicity and exposure limits need to be conducted to ensure products are officially safe for use. As nanotechnology and nanoparticles become more incorporated into every day products, it is important to acknowledge the risks they may pose to the environment and human health. This study focuses on several commonly used nanoparticles, such as iron, silver, copper, and silicon dioxide, and their potential health concerns when introduced to the human digestive system.

1.1 Consumer nanoparticles

Several nanoparticle-containing products today pose a risk of being accidentally ingested. Common sources are cosmetics, food, and clothing products (Fröhlich et al., 2012). Most consumers do not even realize that nanoparticles are present in their life as sunscreen, toothpaste, and food packaging. Silicon dioxide nanoparticles have been used as food additives, while silver nanoparticles have been used in food packaging to improve shelf life (Fröhlich et al., 2012). **Table 1** below shows some of the most common nanoparticles being used in commercial products, healthcare, and water treatment.

Table 1: Common nanoparticles currently used in different industries, including cosmetics, food, water remediation, and healthcare (Shilling, 2015)

Nanoparticle	Common Uses
Iron	Groundwater remediation
Silver	Food packaging, bandages, clothing, toothpaste
Copper	Coatings on plastic
Silica	Food additives, drug delivery techniques

Previously, the amount of nanoparticles being used was low enough that there were no signs of impact on the environment or human health. However, with nanotechnology emerging and nanoparticle use increasing, the levels of nanoparticles in the environment are starting to become more significant (Nowack et al., 2007). Environmental nanoparticles levels need to be monitored and exposure limits need to be researched and identified to ensure the correct remediation protocols are being followed (Nowack et al., 2007).

1.2 Lipid oxidation

Lipids are ubiquitous in the human body and are one of the four basic organic compounds which make up life. Lipids are insoluble in water and other polar solvents; they make up cell membranes as well as provide long term energy storage. It has been shown that transition metals degrade and oxidize lipids. The extent of lipid oxidation, also known as lipid peroxidation, depends upon the nature of the lipid itself; it is dependent upon whether it is saturated or unsaturated. Unsaturated lipids are oxidized because of the presence of carbon-carbon double bonds. The lipid oxidation reaction is separated into three sections: initiation, propagation, and termination (Sevanian et al., 1985). Fatty acids, a subsection of lipids, are common in biological systems and take part in lipid oxidation. During initiation, an adjacently bonded hydrogen atom to the double bond is removed by an initiator, such as a transition metal like iron (Sevanian et al., 1985). This creates a fatty acid radical, which means it has unpaired electrons (Reaction 1). This fatty acid radical proceeds to react with stable oxygen and creates a lipid peroxy radical; this is known as propagation (Reaction 2, 3) (Sevanian et al., 1985). Radicals are known to be unstable and reactive. When radicals react with stable molecules, another radical forms and a chain reaction occurs. The termination portion occurs when one of these radicals reacts with another radical to form a one of many possible byproducts which ends the chain reaction (Reaction 4, 5, 6) (Sevanian et al., 1985). A few of the prevalent byproducts of lipid oxidation are malondialdehyde (MDA) and n-hexanal (Ömür-Özbek et al., 2012). The lipid peroxidation stages are shown below, where R represents a carbon chain of the lipid and the symbol · represents a free electron (Sevanian et al., 1985).

$$RH + \text{Initiator} \rightarrow R\cdot \quad (1)$$
$$R\cdot + O_2 \rightarrow RO_2\cdot \quad (2)$$
$$RO_2\cdot + RH \rightarrow ROOH + R\cdot \quad (3)$$
$$RO_2\cdot + RO_2\cdot \rightarrow ROOR + O_2 \quad (4)$$
$$RO_2\cdot + R\cdot \rightarrow ROOR \quad (5)$$

$$R\cdot + R\cdot \rightarrow RR \qquad (6)$$

Lipid peroxidation is quantitatively measured by using the thiobarbituric acid reactive substances (TBARs) assay to determine the amount of MDA produced. TBARs is a standard test used in quantifying lipid oxidation in tissues, fluids, drugs, and food; although, it is tedious and results vary due to lacking reactive aldehyde characterization (Phetxumphou, 2014). MDA alone is colorless; however, with the presence of thiobarbituric acid (TBA), these two bind together to form a product with a pink color. This color is analyzed by a UV-VIS spectrophotometer using a wavelength of 532 nm. **Figure 1** below shows the MDA and TBA reaction complex.

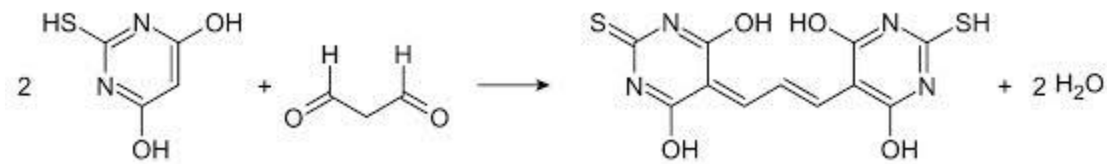

Figure 1: Reaction of the main byproduct of lipid peroxidation (MDA) and thiobarbituric acid to form a pink colored complex which is quantitatively measured using UV-VIS spectrophotometry.

Oxidative stress is damaging to human health and may contribute to disease pathogenesis (Xia et al., 2009). With increase lipid peroxidation, cell membranes become damaged and the cell becomes unable to regulate ion and water exchanges, eventually leading to cell death. Also, byproducts of this reaction are able to cause mutations in DNA that may lead to cancer (Trafton, 2014). It has been proven that trace metal ions increase lipid peroxidation. Since nanoparticles' reactivity is higher than their bulk counterparts, it raises the concern that nanoparticles have an enhanced effect on lipid peroxidation, causing even low concentrations to trigger health problems. The goal of this research was to evaluate the reactivity of iron, silver, copper, and silicon dioxide nanoparticles throughout the human ingestion and digestion systems. Two specific objectives were: (1) to evaluate the amount of dissolution of copper and iron nanoparticles in artificial saliva, intestinal, and gastric digestive fluids; and (2) to quantitatively determine lipid oxidation in artificial saliva, gastric fluid, and intestinal fluid induced by nano- iron, silver, copper, and silicon dioxide using the TBARs assay.

2. Research Methods

2.1 Preparation of digestive fluids

Each artificial digestive fluid was prepared fresh before each day of experimentation since proteins as well as lipids degrade with time. However, inorganic salt solutions were kept for weeks at a time. Soybean oil was chosen as the lipid source for its oxidative stability, since other lipids, like linoleic acid, oxidizes easily in air and would be difficult to work with (Phetxumphou, 2014). Artificial saliva consisted of an inorganic salt solution, proteins, and soybean oil; this solution is comparable to human saliva (Phetxumphou, 2014). The inorganic saliva salt solution was based on saliva's salt characteristics and included: NaCl, 0.126; KCl, 0.964; KSCN, 0.189; KH_2PO_4, 0.655; Na_2SO_4, 0.337; NH_4Cl, 0.178; $CaCl_2$, 0.155; $NaHCO_3$, 0.568 grams, and dissolved in 1000 mL Nanopure® water (TDS=0 mg/L) (Phetxumphou, 2014). The artificial saliva fluid consisted of: 30 mg soybean oil, 0.216 g mucin protein, 0.541 g α-amylase protein, and 100 mL of the inorganic salt solution. The artificial intestinal fluid was made up of 100 mL inorganic intestinal salt solution and 30 mg soybean oil. The inorganic intestinal solution included: KH_2PO_4, 6.805; NaOH, 0.896 grams dissolved in 1000 mL Nanopure® water, and the pH was 6.8 (Stippler et al., 2004). The pH of this fluid was adjusted accordingly with NaOH and/or HCl. Artificial gastric fluid contained no salts or proteins. The artificial gastric fluid imitated the conditions of fasted state simulated gastric fluid with a pH of 1.4-2.1 (Aburub et al., 2008). This fluid was prepared by adding 1 mL 99.9% HCl to 99 mL Nanopure® water. The pH was adjusted with water or HCl depending on the initial reading. Once desired pH was achieved, 30 mg of soybean oil was added to the fluid to act as the lipid source.

2.2 Preparation of metallic and nanoparticle solutions

2.2.1 Preparation of metallic ions

The metallic ions ferrous (Fe^{+2}) and cuprous (Cu^{+1}) were used for this study. The targeted total concentration of each metallic ion was 10 mg/L. The ferrous solution was prepared by diluting 0.010 g $FeSO_4 \cdot 7H_2O$ (Fisher Scientific, CAS #7782-63-0) into 200 mL Nanopure® water. The cuprous solution was prepared by diluting 0.008 g CuCl (Sigma-Aldrich, CAS #7758-89-6) into 500 mL Nanopure® water. Solutions were acid digested with 5% HNO_3 by volume and ran on the Atomic Absorbance Spectroscopy (AAS) (Perkin-Elmer, 5100PC AAS, Waltham, MA, USA) to confirm the targeted concentrations of 10 mg/L.

2.2.2 Preparation of nanoparticle solutions

Only copper and iron nanoparticles were used for dissolution testing. The targeted concentrations of copper and iron nanoparticles were 100 mg/L and 25 mg/L, respectively. The copper solution was prepared by diluting 0.008 g Cu nanoparticles in 80 mL Nanopure® water. The nZVI solution was prepared by adding 130 µL to 80 mL Nanopure® water.

For lipid oxidation experiments, nanoparticles copper, silver, silicon dioxide, and nanoscale zero-valent iron (nZVI) were used. The targeted concentration of nanoparticles was 10 mg/L for lipid oxidation studies. Average human exposure to nanoparticles has been reported to vary from 0-112 mg/individual/day, so an environmentally relevant value of 10 m/L was chosen for the TBARs study (Fröhlich et al., 2012). Copper and silver nanoparticles exhibited poor mixing abilities, so an increase in particles was necessary to achieve a AAS reading of approximately 10 mg/L. Copper nanoparticles (Sigma-Aldrich, CAS #7440-50-8, Size 40-60 nm) were prepared at a concentration of 15 mg/L, and silver nanoparticles (Sigma-Aldrich, CAS #7440-22-4, Size <100 nm) were prepared at a concentration of 50 mg/L. Silicon dioxide nanoparticles (Sigma-Aldrich, CAS #7631-86-9, Size 10-20 nm) were prepared at a concentration of 10 mg/L.

The nanoparticles: silver, copper, and silicon dioxide, arrived in the powder form, and proper precautions and personal protective equipment were needed to ensure safety. In the powder form, nanoparticles were weighed and handled in a fume hood while wearing a laboratory coat, nitrile gloves, and safety glasses to minimize exposure. Nanopure® water was used to suspend the nanoparticles in solution. Once in solution form, the nanoparticles were able to be handled with gloves outside of the fume hood. Lastly, nZVI (provided by from Nanoiron Ltd., Rajhrad, Czech Republic, EU, Size <50 nm), which was already in a slurry form, was handled with gloves and safety glasses to minimize possible exposure. The targeted concentration was 10 mg/L and was prepared by adding 50 µL to 60 mL of Nanopure® water. All solutions were acid digested with 5% HNO_3 by volume and ran on the AAS except silicon dioxide nanoparticles, which were ran on the inductively coupled plasma mass spectrometry (ICP-MS), to confirm concentrations of the ions and nanoparticle concentrations.

2.3 Measuring dissolution

Two sets of dissolutions tests were conducted. The first test exclusively used a copper nanoparticle solution targeted at 100 mg/L. The second used an nZVI solution targeted at 25 mg/L. Artificial saliva, intestinal, and gastric fluids were prepared aforementioned. A one to one ratio of digestive fluid and copper nanoparticle solution, 5 mL each, was prepared in a 15 mL propylene conical tubes. A one to one ratio of Nanopure® and copper solution acted as the control. Four time periods were selected at which AAS readings would be taken: 0, 15, 30, and 60 minutes. A total of 16 conical tubes were needed for each dissolution test, four per fluid and the control. The 15, 30, and 60 minute tubes were placed in a 37ºC water bath to mimic body conditions.

2.4 Measuring lipid oxidation

2.4.1 Thiobarbituric Acid Reactive Substances (TBARs) Assay

The Spanier TBARs method (1991) was modified to measure lipid oxidation in aqueous samples by allowing low MDA concentrations to be read (Wang, 2002). MDA standards (0.0313, 0.625, 0.125, 0.250, 0.500, 0.750, 1.00, 2.00, 4.00, and 10.0 µM) were prepared to create a standard curve, Figure 2, using the UV-VIS spectrometer set to read at 532 nm. The best fit line was determined and shown with Figure 2. The TBARs samples consisted of equal volumes of digestive fluid and metallic or nanoparticle solutions, 5 mL each, in 15 mL propylene conical tubes. Control samples were 1) Nanopure®; 2) Nanopure® and digestive fluid mixture; 3) digestive fluid only; and 4) Nanopure® and metallic/nanoparticle mixtures. All samples were done in triplicates. Once prepared, the tubes were placed in 37ºC water bath for 15 minutes to imitate body temperature. After incubation, samples were analyzed for lipid oxidation using the TBARs method. This method measures the oxidative stress caused by each metallic and nanoparticle solution. Once measured on the UV-VIS spectrometer, absorbance values were averaged and converted to MDA concentration per mg of total metallic ion or nanoparticle using the standard curve.

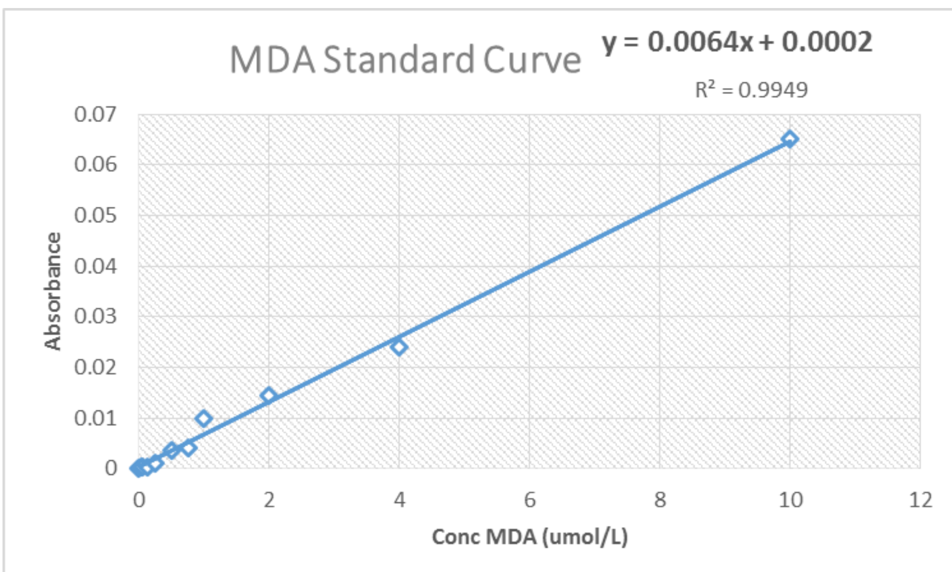

Figure 2: MDA standard curve.

3. Results and Discussion

3.1 Dissolution in digestive fluids

3.1.1 Dissolution of copper nanoparticles

For this dissolution, the copper nanoparticle solution was targeted at 100 mg/L. Since samples were prepared with equal volume of digestive fluid and metal solution, the maximum dissolution which could be achieved was 50 mg/L. The pH of the intestinal fluid was 6.8, and the gastric fluid pH was 1.43.

The amount of dissolution in gastric fluid increased with time. After 60 minutes of incubation, gastric fluid had the highest dissolution with 47.6%, then saliva with 14.2%, intestinal with 9.6 %, and lastly, Nanopure® with 9.0%. Gastric fluid considerably differed from the other test fluids. Saliva, intestinal, and Nanopure® fluids yielded comparable results with each other. **Figure 3** is a graphical representation of the dissolution of copper nanoparticles in digestive fluids over time.

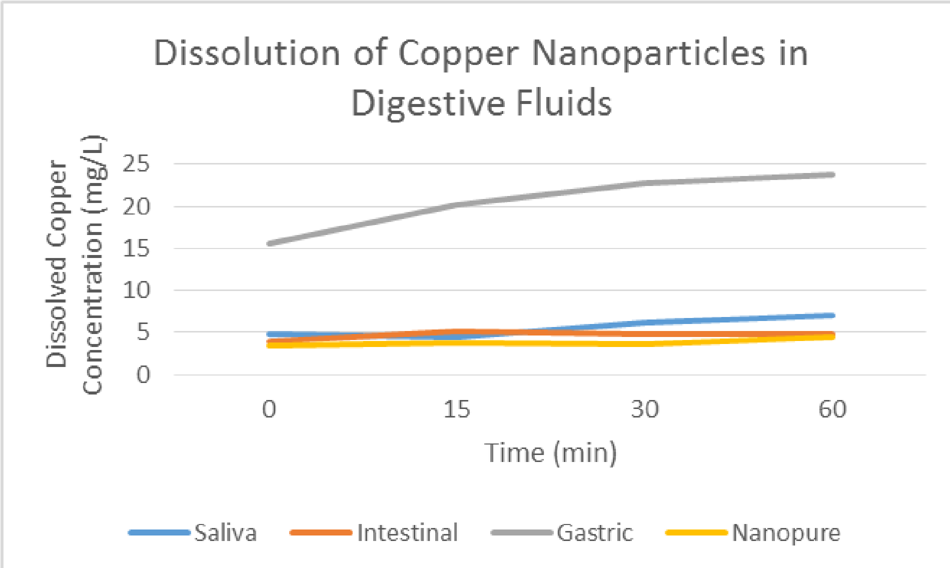

Figure 3: The dissolution of copper nanoparticles in the artificial digestive fluids of saliva, intestinal, and gastric. Nanopure® water was used as the control fluid.

The exhibited high dissolution of copper nanoparticles in gastric fluid was proposed to be because of the fluid's acidity. Nanopure®, saliva, and intestinal fluids all had pH values of relatively neutral, while gastric was acidic. Hydrochloric acid has been reported to corrode and react with metals (Zhang et al., 2004). However, metal copper does not readily react with hydrochloric acid; it is a relatively slow reaction (Crundwell, 1992). Although bulk metal may not quickly react with hydrochloric acid, copper nanoparticles may increase the rate of reaction because of the increased surface area and reactivity, which nanoparticles are known for.

3.1.2 Dissolution of nZVI

The nZVI solution for this dissolution test was targeted at 25 mg/L, meaning the maximum dissolution concentration would be 12.5 mg/L due to the samples diluted as an equal volume mixture. The pH for the intestinal fluid was 6.8, and the gastric fluid pH was 1.51. Similar to the copper nanoparticle dissolution, gastric fluid exhibited the greatest dissolution of nZVI. After the 60 minute incubation period, gastric exhibited the highest dissolution of nZVI with 94.4%, then intestinal with 57.5%, saliva was 54.7%, and lastly, the Nanopure® control with 53.2%. All fluids showed a slight increase in dissolution over time as expected. By looking at the graphical results in **Figure 4** gastric results differ noticeably from the Nanopure® control results, as compared to the other digestive fluids used.

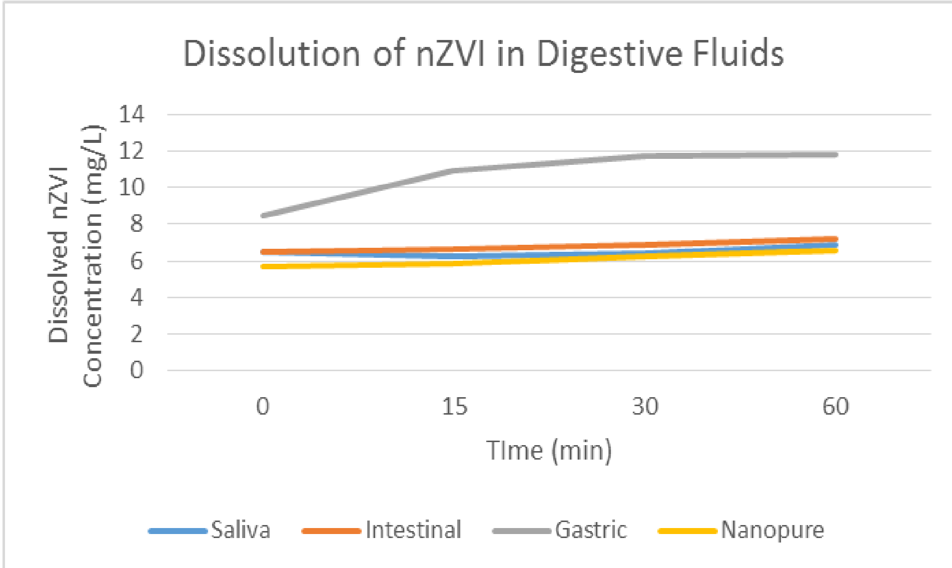

Figure 4: The dissolution of nZVI in the artificial digestive fluids saliva, intestinal, and gastric. Nanopure® water was used as the control fluid.

Similar to the copper dissolution, the proposed reason for gastric having increased dissolution for nZVI is the acidity. In this dissolution test, results were closer to the projected maximum. The nZVI particles were better suspended because they are in a stable slurry instead of powder form, like the copper nanoparticles. The slurry was nearly a year old, and the iron nanoparticles were capable of dissolving with time. This was verified by the results. Nanopure® exhibited an over 50% dissolution result. If Nanopure® water were to dissolve nZVI this well, the end dissolution should have been near the maximum 12.5 mg/L. However, since Nanopure® dissolution neared 50%, the initial slurry was suggested to contain a mix of nZVI particles and dissolved iron ions. Unlike copper, iron readily reacts with hydrochloric acid (Chetouani et al., 2004). It is proposed that gastric fluid neared the maximum nZVI dissolution because of the considerable amount of dissolved iron in the initial nZVI slurry and hydrochloric acid's ability to corrode and dissolve iron. These results indicated that if certain nanoparticles were ingested, lipid oxidation may increase. The increased oxidation leads to more reactive oxygen intermediates, which are associated with oxidative stress and cellular damage (Mittler, 2002).

3.2 Lipid oxidation using TBARs

With nanoparticles increasingly incorporated into consumer products, like food packaging, it is essential to evaluate their reactivity in case of accidental consumption. In all artificial fluids, nZVI samples did not significantly differ from the ferrous controls samples, which were known to induce lipid oxidation. nZVI samples showed higher increases in lipid oxidation than any other solution used, as seen in Figure 5. Cuprous, copper nanoparticles, and silicon dioxide nanoparticles exhibited lower increases of lipid oxidation. Silver particles were shown to have a similar increase in lipid oxidation as to the cuprous solution. In the silver nanoparticle intestinal testing, an outlier was present, which was taken out. The outlier affected the average increase of lipid oxidation and misconstrued the results. The silver nanoparticles were difficult to suspend and readily aggregated on either the top or bottom of the solution. For the outlier silver sample, it was believed that a clump was present. Therefore, it caused an increase in the concentration of silver nanoparticles, which impacted the resulting average MDA concentration. This silver sample outlier made the end result of MDA per milligram in intestinal fluid much higher than expected. Copper nanoparticles did not readily dissolve in solution. This made getting homogenous and repeatable samples for copper and silver nanoparticles problematic. For further testing, it would be ideal to use stable slurries for all nanoparticles, like the nZVI samples.

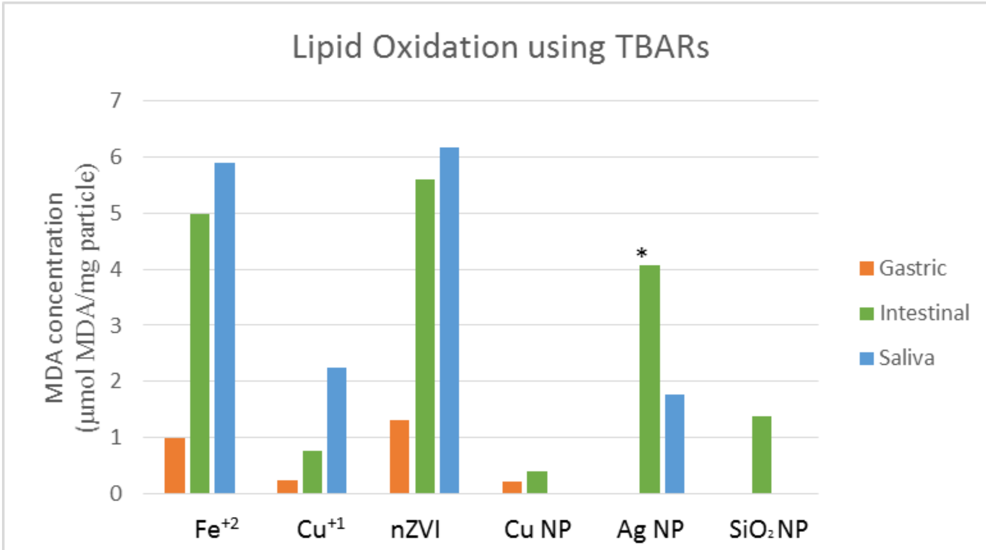

Figure 5: The increase in lipid oxidation in different artificial digestive fluids when subjected to ferrous, cuprous, nZVI, copper nanoparticles, silver nanoparticles, or silicon dioxide nanoparticles. *An outlier sample was removed.

Through the use of a two-way Anova statistical test, lipid oxidation between digestive fluids significantly differed with p-value of 0.005, and lipid oxidation significantly differed between tested metallic/nanoparticle solutions with a p-value of 0.011. It was proposed saliva showed the highest lipid oxidation since the soybean oil was better dispersed due to the salts and proteins that were present in saliva. In gastric fluid, the soybean oil stayed primarily at the top of the fluid in one or two main clusters. The lipid source for saliva dispersed more evenly into smaller clusters when mixed. When the lipids are more dispersed, there is more surface area to react, which may be the cause of difference in lipid oxidation between the digestive fluids. For future testing, an addition of an emulsifier would be encouraged to disperse the lipids more consistently between fluids. Overall, it is important to realize that all nanoparticles increased lipid oxidation, in at least one fluid. Lipid oxidation is harmful to the human health, and any amount of increase may be concerning (Harris, 2013). Out of all of the nanoparticles tested, nZVI exhibited consistently the highest reactivity, and is the highest concern for human health. Further tests using stable slurries of these nanoparticles with a better dispersed lipid source is encouraged to expand upon current findings.

4. Conclusion

For the dissolution tests of copper nanoparticles and nZVI, artificial gastric fluid was the only digestive fluid which noticeably differed from the Nanopure® control. Gastric fluid had dissolution results of 47.6% and 94.4% for copper nanoparticles and nZVI, respectively, while the results of Nanopure® control were 9.0% and 53.2%, respectively. The gastric fluid's increased dissolution results were proposed to be due to the acidity of this fluid. The nZVI's increase in dissolution was because of the stable slurry it was in.

Ferrous and nZVI consistently yielded the highest increase in lipid oxidation throughout the digestive fluids. The other solutions: cuprous, copper nanoparticles, silver nanoparticles, and silicon dioxide nanoparticles, exhibited lower increases in lipid oxidation in comparison. Since not all nanoparticles form stable solutions when prepared, stable and fresh slurries should be used for future testing. Silver and copper nanoparticles readily aggregated at the top or bottom of the solution, making precise, 10 mg/L samples difficult to attain. Nevertheless, lipid oxidation between digestive fluids significantly differed. Lipid oxidation between nanoparticle samples significantly differed. In conclusion, nanoparticles exhibited an increase in lipid oxidation in at least one digestive fluid, if not all. Lipid oxidation can be a harmful reaction, which oxidizes lipids that are present everywhere in the human body. With nanoparticle use in consumer products increasing, it is crucial to monitor the increase of nanoparticles present in the environment as well as further studying the effects of nanoparticles on human health.

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Drought Evaluation in the Northern Shenandoah River Valley

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Abstract

Water supply planning in the Northern Shenandoah Valley (NSV) requires a careful evaluation of the region's resources, climate, and projected demand, in order to create a more versatile drought response contingency plan for the upcoming water supply plan update. This project studied the availability of local drought indicator data, including precipitation, stream discharge, and groundwater levels for the NSV. The spatial distributions and timeframes of the available data were represented on an interactive map, which provided a simple way to useful relationships between the data stations. Furthermore, the drought indicator levels were analyzed using the Standardized Precipitation Index (SPI) and the Standardized Streamflow Index (SSI), allowing the comparison of station data across watersheds. To consider recent changes in climate, the SPI and SSI over the period of record were compared to those evaluated over the latest 15 years, and demonstrated that most watersheds' climatological patterns were consistent with the historical levels. However, a few watersheds demonstrated recent SPI and SSI z-values varying from historical values, calling for a closer analysis on changing conditions. Using the historical patterns of the SPI and SSI, a definition of drought was created for the region, which can be used for drought forecasting purposes in the water supply plan.

Keywords: water supply planning, drought indicators**,** Standardized Precipitation Index (SPI), Standardized Streamflow Index (SSI), Shenandoah valley, drought, forecasting

1. Introduction

The sustainable management of worldwide fresh water supply has become an increasingly pressing concern over the last few years. As the global climate continues to change due to increased greenhouse gases and higher temperatures, the risk of drought increases along with water demand. These conditions require a more serious consideration of drought monitoring all over the world, in order to ensure a sustainable water supply for years to come (Govindaraju, 2013).

1.1 Northern Shenandoah River Valley Region

The Commonwealth of Virginia is taking preemptive measures to monitor the state water supply and plan for a changing climate and increased population. The 2003 Code of Virginia mandated local and regional committees to submit a water supply plan to the State Water Control Board every 5-10 years (Virginia Department of Environmental Quality, n.d.). These plans require an evaluation of existing water supply, a projected need estimate for the next 30-50 years, and a drought response contingency plan. This drought response plan requires a statement of conservation actions, an alternatives analysis, and an assessment of deficits. This calls for a broad analysis of regional climate, a definition of drought stages, and a comprehensive consideration of the ecological, economical, and social effects a drought could induce (Virginia Department of Environmental Quality, 2015)

The Northern Shenandoah Valley (NSV) is one such region. It encompasses the counties of Clarke, Frederick, Page, Shenandoah, and Warren; the towns of Berryville, Boyce, Edinburg, Front Royal, Luray, Middletown, Mount Jackson, New Market, Shenandoah, Stanley, Stephens City, Strasburg, Toms Brook, and Woodstock; and the city of Winchester (Virginia Department of Environmental Quality, 2015). By 2040, the region expects a 23% increase in population growth- an additional 60,000 people in

25 years (Northern Shenandoah Valley Regional Commission, 2011). If not planned properly, this population surge could place a strain on the water supply of the region and make the onset of a drought a cause for significant alarm.

In addition, the economy of the NSV is largely agriculture based, with 39% of land used as farmland and pasture (Virginia Department of Environmental Quality, 2015). This creates an even greater demand of water resources when faced with a drought. It is then critical that the regional committee formulates a conscious and well-informed plan to ensure a constant, adequate, and sustainable water supply for years to come.

1.2 Characteristics of Drought

Drought is described as a shortage of precipitation over a sustained period of time (Zargar, Sadiq, Naser, & Khan, 2011). Droughts are infamous for their prolonged effects on society and the environment, due to their slow creeping approach, extended timespan, and their capability to extensively impair natural processes (Zargar et al, 2011). There are a few widely accepted types of drought:

- *Meteorological drought* occurs when indicators such as precipitation and cloud cover fall below the normal level
- *Agricultural drought* occurs when agriculture in the region is negatively impacted – when indicators such as soil moisture content fall below necessary levels
- *Hydrological drought* occurs when there exists a depletion in long term water supplies, such as surface reservoirs and groundwater (Zargar et al, 2011)
- *Socioeconomic drought* occurs when water supply fails to meet the water demand required by society to thrive (Soľáková, De Michele, & Vezzoli, 2014)

All four forms of drought can occur simultaneously, but often occur as a result of one another. . For example, a socioeconomic drought caused be anthropogenic factors may lead to an agricultural and hydrological drought because of the increased demand placed on long term supplies. Nonetheless, socioeconomic drought is the most relevant to the creation of complete water supply plans, as these plans involve consideration of water supply and demand for not only private consumption but for the regional economy. It is important then to minimize water consumption and wastage when faced with increased demand and changing climatological conditions.

1.3 Drought Indices

A major concern in drought forecasting is providing a valid definition of drought. Conditions which constitute a severe drought in one region may be normal somewhere else. Therefore, it is crucial to use standards local to the area of interest- global or even national standards are not sufficient. Pinpointing the exact onset and resolution of a drought event also proves a challenge as droughts often exhibit a slow onset and commencement (Soľáková et al, 2014). Various drought indices have been developed in an attempt to identify, classify, and ultimately standardize regional drought. Most drought indices compare current levels of specific indicators to their historical values to determine the possibility of an oncoming or existent drought.

The two drought indices used in this project are the Standardized Precipitation Index, developed by McKee et al. (1993) and the Standardized Streamflow Index, both of which rely on probabilistic measures to quantify the significance of a drought event.

2. Research Methods and Experiment Setup

2.1 Drought Indicators

Varying levels of precipitation are the inherent cause of wet or arid periods in a region's climatic history. However, as drought has far reaching effects into the ecosystem, there are many other indicators used to recognize and classify a drought. Some indicators commonly used in drought forecasting include surface reservoir levels, soil moisture, evapotranspiration, groundwater levels, stream discharge rates, and of course, precipitation.

The first objective of this project entailed searching records to determine the types of indicator data available for the Northern Shenandoah Valley Region, its spatial extent, and timescale. This data had to be spatially and temporally far reaching in order to provide a substantial summary of the region's climate and its normal fluctuations. After considerable examination of the data record, it was determined that the best measures for drought forecasting in the NSV were precipitation, stream discharge rates, and groundwater levels. Even the record of these measures proved to be oftentimes inconsistent, with many gaps in station records over time. The lack of substantial historical data became a major issue especially in the groundwater level record, allowing a spatially broad but historically inadequate record of groundwater data. A summary of the stations used for streamflow, precipitation, and groundwater is available in the appendix.

2.2 Data Visualization

After compiling the data record, the scope of the data demonstrated a need for a means of visualizing the information in order to understand intrinsic relationships between the indicators. Using the Google My Maps application, the station information and historical availability was mapped, to better recognize spatial relationships between the various measures. This visualization proved to be useful in identifying watersheds and creating an accurate representation of the data. It also provides a user friendly interface to easily find and use station data. Figures 1 through 4 show the information displayed by the Google My Maps application for all stations, precipitation stations, stream gaging stations, and groundwater wells, respectively.

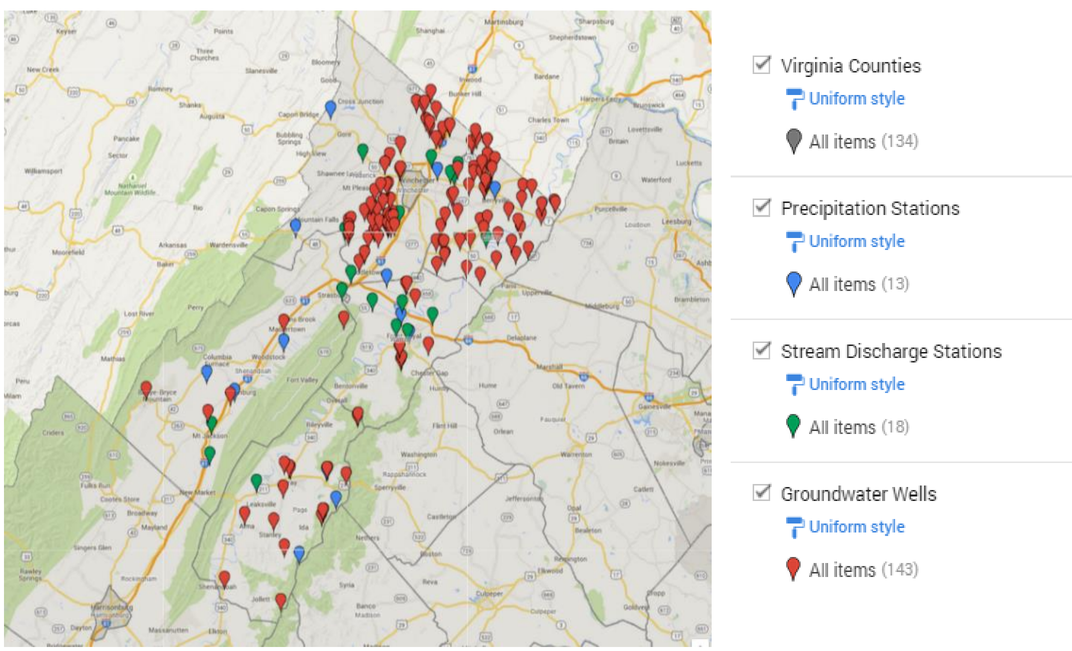

Figure 7. Screenshot of station map (left), and legend (right). Map data ©2015 Google.

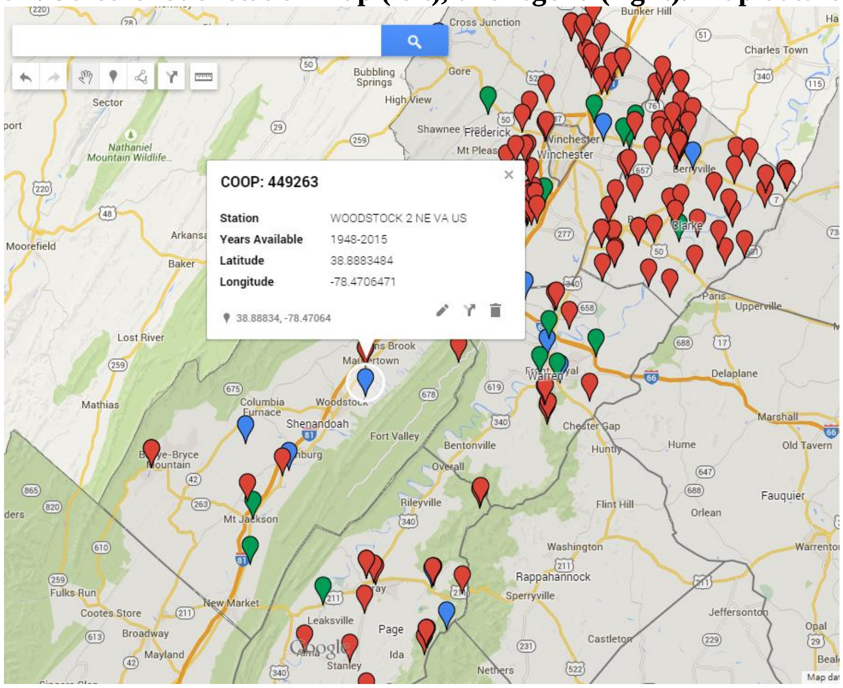

Figure 8. Example of information displayed for precipitation stations. Map data ©2015 Google.

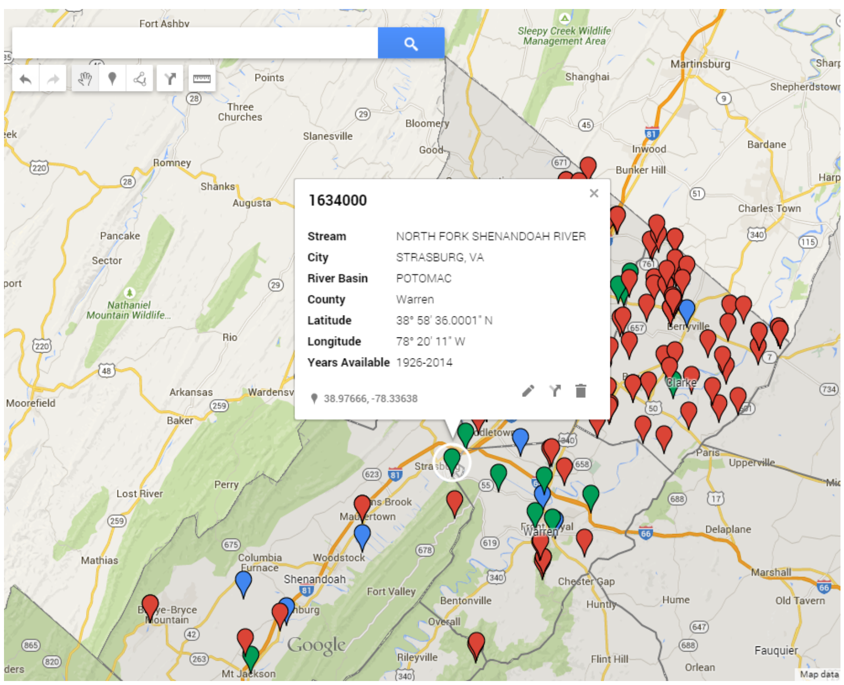

Figure 9. Example of information displayed for stream gaging stations. Map data ©2015 Google.

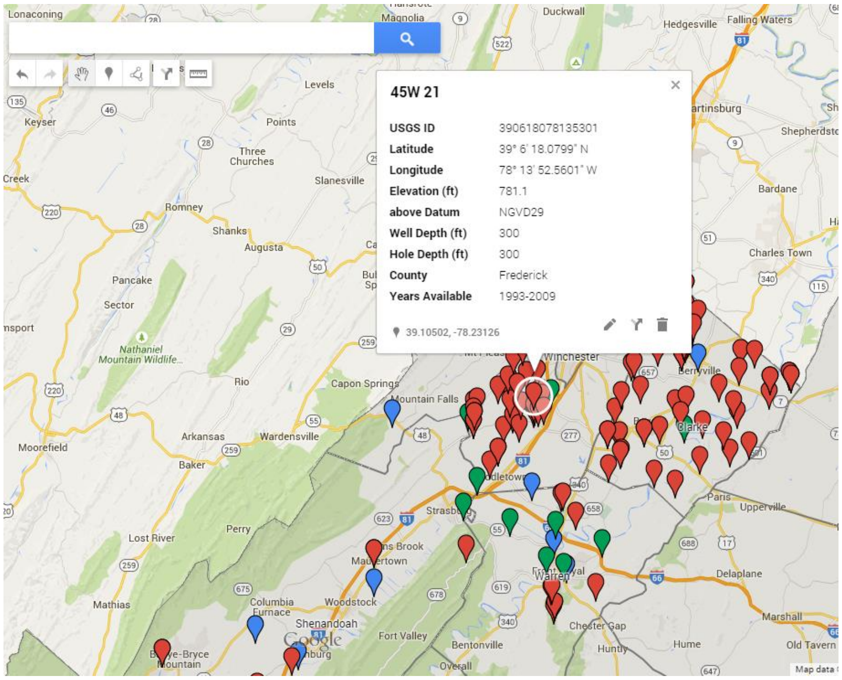

Figure 10. Example of information displayed for groundwater wells. Map data ©2015 Google.

2.3 Drought Indices

The next objective of this project was to analyze relationships between the various indicators that were considered in the course of this research. The most powerful way to consolidate the large amounts of data was to use the station map to pair stations along watersheds and evaluate the trends in the calculated drought index values. These pairings were determined by following the stream/river along its course and finding a stream discharge station downstream from a precipitation station. As an example of the watershed analysis, the relative locations of precipitation station COOP: 449263 at Woodstock, Shenandoah County, and the Strasburg stream discharge gaging station (Local ID: 01634000) in Warren Co., along the North Fork Shenandoah River, are shown below. The remaining watershed grouping are shown in **Table 3**.

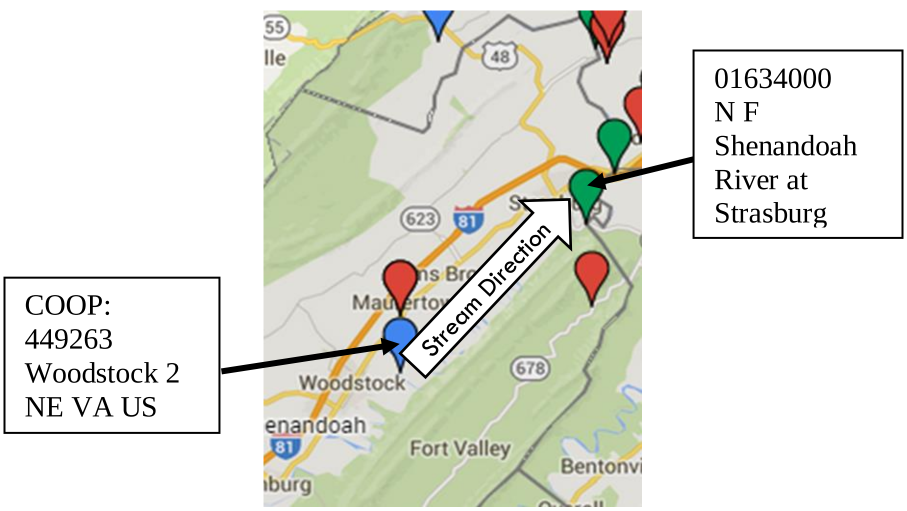

Figure *11*. Example watershed evaluation diagram for precipitation and stream gaging stations. Map data ©2015 Google.

Table 3 - Summary of Watershed Pairings (Isha Deo, 7/21/15)

Precipitation Station	***Streamflow Gaging Station***	***Groundwater Well***
COOP:449263 ***Woodstock 2 NE VA US***	**01634000** *N F Shenandoah (Strasburg)*	**40U 3 SOW 218**
COOP:448046 ***Star Tannery VA US***	**01613900** *Hogue Creek (Hayfield)*	**44W 20**
COOP:449186 ***Winchester 7 SE VA US***	**01615000** *Opequon Creek (Berryville)*	**46W 175**
COOP:440720 ***Big Meadows VA US***	**01629500** *S F Shenandoah (Luray)*	**-**
COOP:449263 ***Woodstock 2 NE VA US***	**01635500** *Passage Creek (Buckton)*	**-**
COOP:447254 ***Riverton VA US*** **COOP:443229** ***Front Royal VA US*** **COOP:443231** ***Front Royal VA US***	**01631000** *S F Shenandoah (Front Royal)*	**-**

2.3.1 Standardized Precipitation Index

A common drought index is the Standardized Precipitation Index. A relatively simple index, it allows a comprehensive and localized measurement of meteorological drought based on precipitation (Soľáková et al, 2014). In this study, the SPI was chosen over various other drought indices because of its simplicity, ease of analysis, and probabilistic nature, all of which make it a viable tool for creating the water supply plan. The SPI is based on long term monthly precipitation data series for a specific region. The series is adjusted for a specific time interval (i.e. 1 mo., 3 mo., 6 mo., 12 mo., etc.). The most applicable probability density function is then fitted to the data. The inverse Gaussian distribution function with a mean of zero and a standard deviation of 1 is then applied to the cumulative density function. This effectively yields a measurement of departure from the mean precipitation value, the SPI. Positive z-values indicate wetter than normal conditions, whereas negative values indicate drier conditions, and the possibility of a drought. (Guttman, 1999)

In this analysis, a two parameter gamma distribution function was applied to monthly and annual precipitation totals. The probability density function can be given by the equation:

$$g(x;\ \alpha,\beta) = \frac{\beta^{\alpha}x^{\alpha-1}e^{-x\beta}}{\Gamma(\alpha)},\ \text{where } x \geq 0;\ \alpha,\beta > 0$$

2.3.2 Standardized Streamflow Index

The Standardized Streamflow Index is similar to the SPI in that it relies on probability to create an overview of current regional climate conditions. The SSI is based on monthly streamflow data, which is fitted to a probability distribution. The cumulative probability density function is then translated to a normal distribution (X~N(0,1)) using the inverse Gaussian function (Telesca, Lovallo, Lopez-Moreno, &

Vicente-Serrano, 2012). In this analysis, the SSI was calculated using a lognormal probability distribution, given by the probability density function:

$$f_X(x;\mu,\sigma) = \frac{1}{x\sigma\sqrt{2\mu}} e^{-\frac{(\ln x-\mu)^2}{2\sigma^2}} \text{, where } x > 0$$

2.4 Analysis of Drought Indices and Watersheds

The z-values for the SPI and SSI were compared within watersheds and across the entire region. Using the trendlines, a valid definition of drought was established by studying the historical variations and previous drought events. Defining threshold values for each index creates a quantitative method to declare a drought event and prepare sufficient response.

Another consideration was the effect of recent climate changes on drought indicators in the NSV. In order to understand this, the SPI and the SSI were evaluated for the past fifteen years. This provokes an examination of instances in which the trends over the period of record are very different from the 15-year analysis.

The groundwater data record's inconsistency and its lack of historical scope made it difficult to apply groundwater levels to the definition of drought. However, in an effort to use the relationships between the other drought indicators and groundwater, the levels for specific stations were included in the watershed analyses. As the well depths and water levels varied widely, a normal distribution was assumed for the groundwater (for a lack of an equivalent drought index based on groundwater). This allowed the groundwater levels to be represented clearly with the SPI and SSI.

Lastly, multiple precipitation and stream gaging stations were analyzed to better comprehend the intrinsic relationships between properties of the stream and the watershed and their effects on the drought index values and the correlation between the two indices. The mean stream discharge, location of the stream gaging station along the Shenandoah River, and the distance between the precipitation and stream gaging station were variables used in comparison with the correlation coefficient between SPI and SSI.

3. Results and Discussion

The analysis of SPI and SSI for the six watersheds showed an inherent relationship between the precipitation and streamflow. The indices were first calculated for annual values, which showed a more exact trend in precipitation and streamflow (see **Error! Reference source not found.**). However, it was etermined that in order to successfully forecast a drought, monthly data would be necessary. This allows a necessary response time to declare the onset of a drought and take appropriate measures.

Group 1. Hogue Creek (Hayfield)/Star Tannery

Although the record including both stream discharge and precipitation dates only to 1995, the monthly SPI and SSI values for the stations show a correlation, with an R^2 value of 0.473. However, the SSI does not precisely reflect an extremely low precipitation month as readily as the SPI does. This implies SPI is more susceptible to changes in the climate than the SSI. The groundwater well 44W 20 does not have an extensive period of record, but where it is recorded, it shows a trend line similar to the SPI and SSI of this watershed.

Group 2. North Fork (N F) Shenandoah (Strasburg)/Woodstock

Group 2 was the most ideally situated in the watershed, as the precipitation station, Woodstock, was located directly upstream of the stream gaging station, about twelve miles apart. In the annual trend (***Figure 12***), the SPI and SSI z-values follow each other quite closely. In the monthly trend, the stream discharge shows a slight lag behind the precipitation. However, the correlation between the two is not as high as expected, especially for the monthly calculations, with an R^2 value of 0.449. (***Figure 13***).

A groundwater well, local ID 40U 3 SOW 218, was located near the SPI and SSI stations. Mapping this well through its period of record, 2006-2015, shows a close correspondence with the other drought indicators, especially precipitation (***Figure 14***).

The 15-year SPI trend closely follows the period of record SPI, showing that for this station, precipitation patterns have not changed in recent history. The SSI, on the other hand, approximately follows the period of record values, but on occasion can be seen to reverse the sign from the period record. For example, see the end of year 2007 in ***Figure 15***. The 15-year SSI indicated a drier than normal month whereas the period of record indicates an above average streamflow level for that time frame. This concept is reversed in 2012. These results can be explained by a slight variation in mean values for the period of record (607.72 cfs) and the 15-year span (620.50 cfs) but the reason for this variation is undetermined.

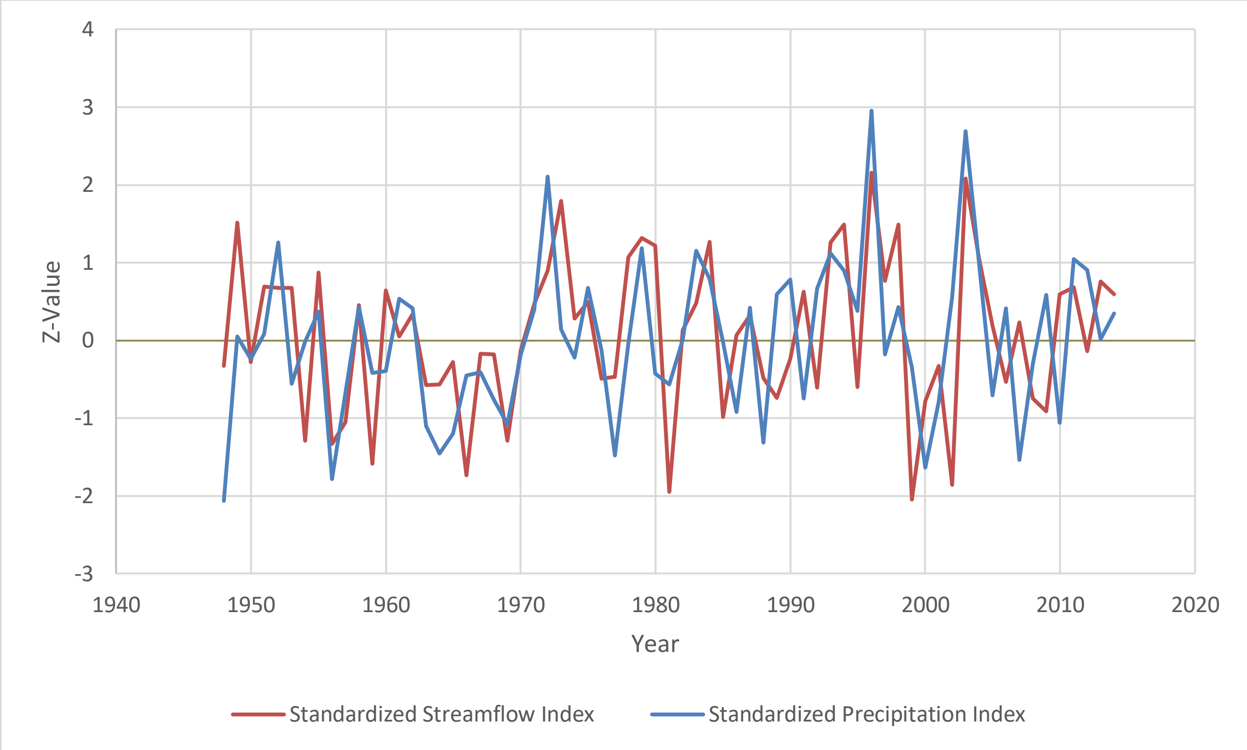

Figure 12. Annual SPI & SSI Trends for Woodstock/Strasburg over period of record

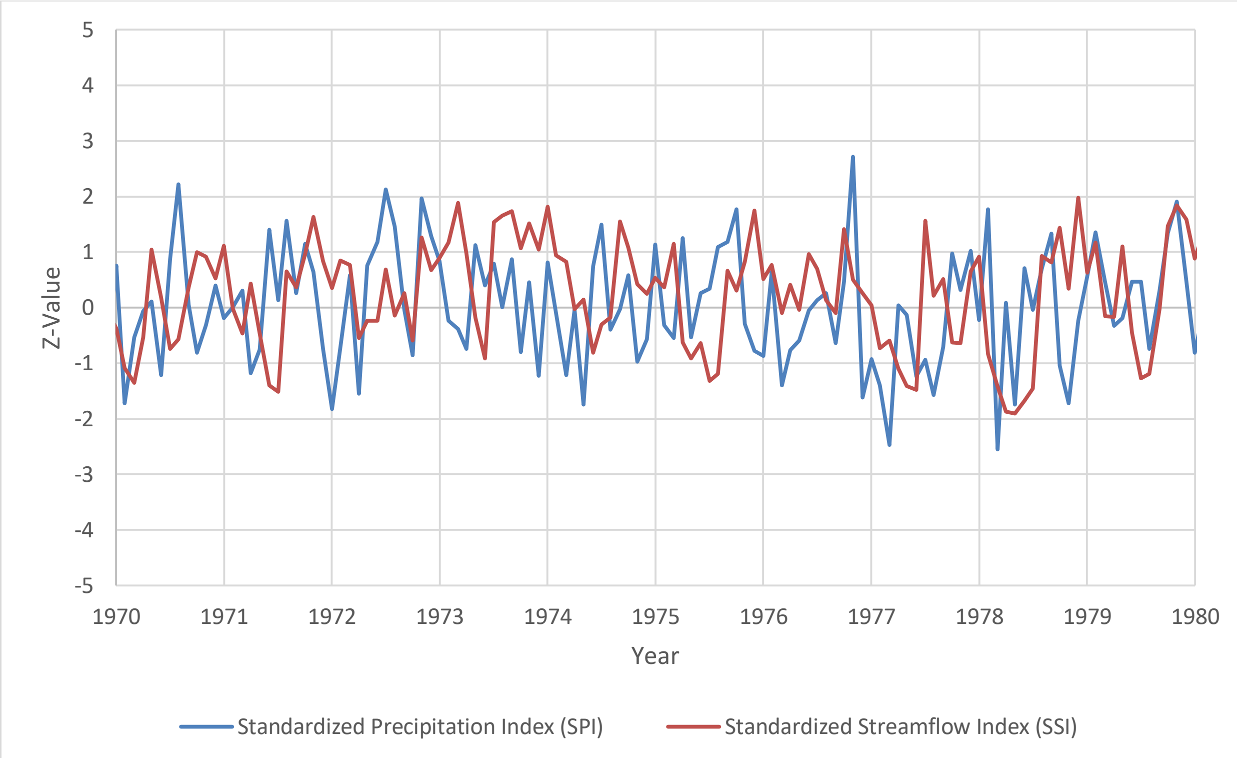

Figure 13. Monthly SPI & SSI Trends for Woodstock/Strasburg for 1970-1980

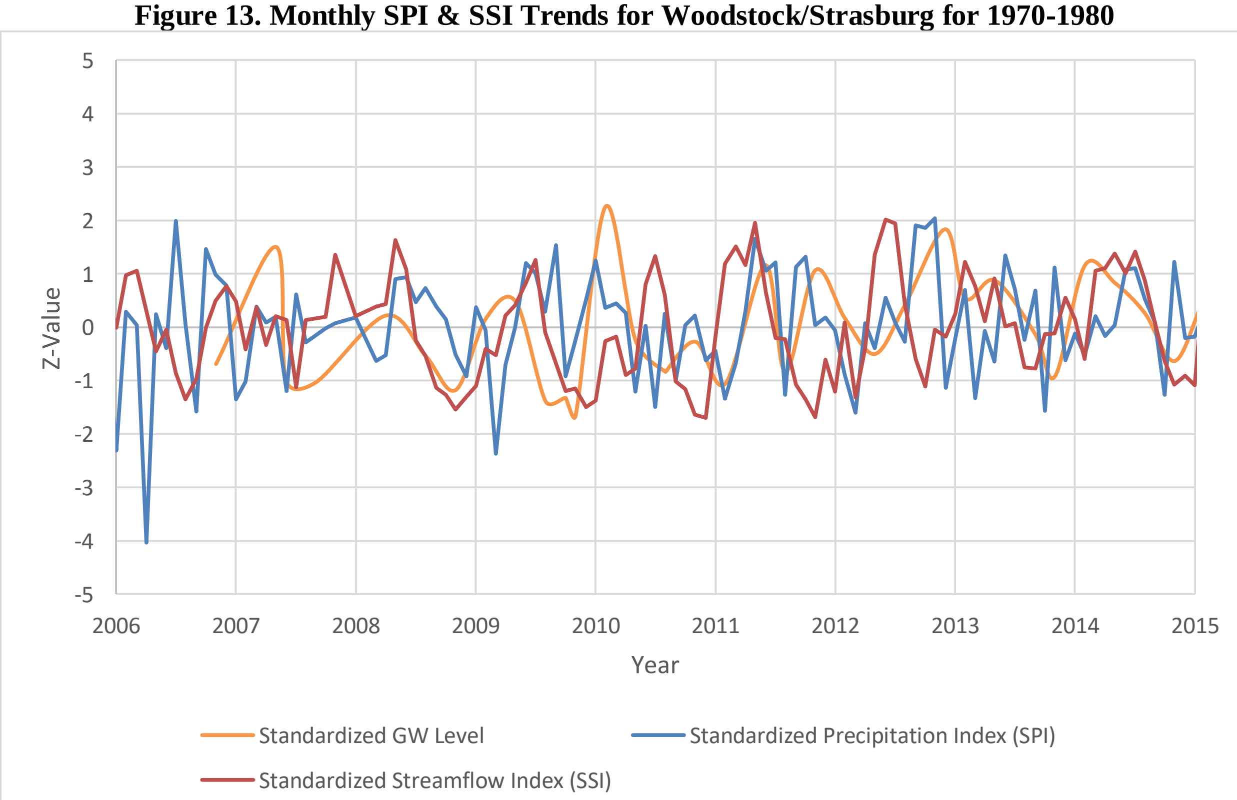

Figure 14. Monthly SPI and SSI with standardized groundwater levels for Woodstock/Strasburg

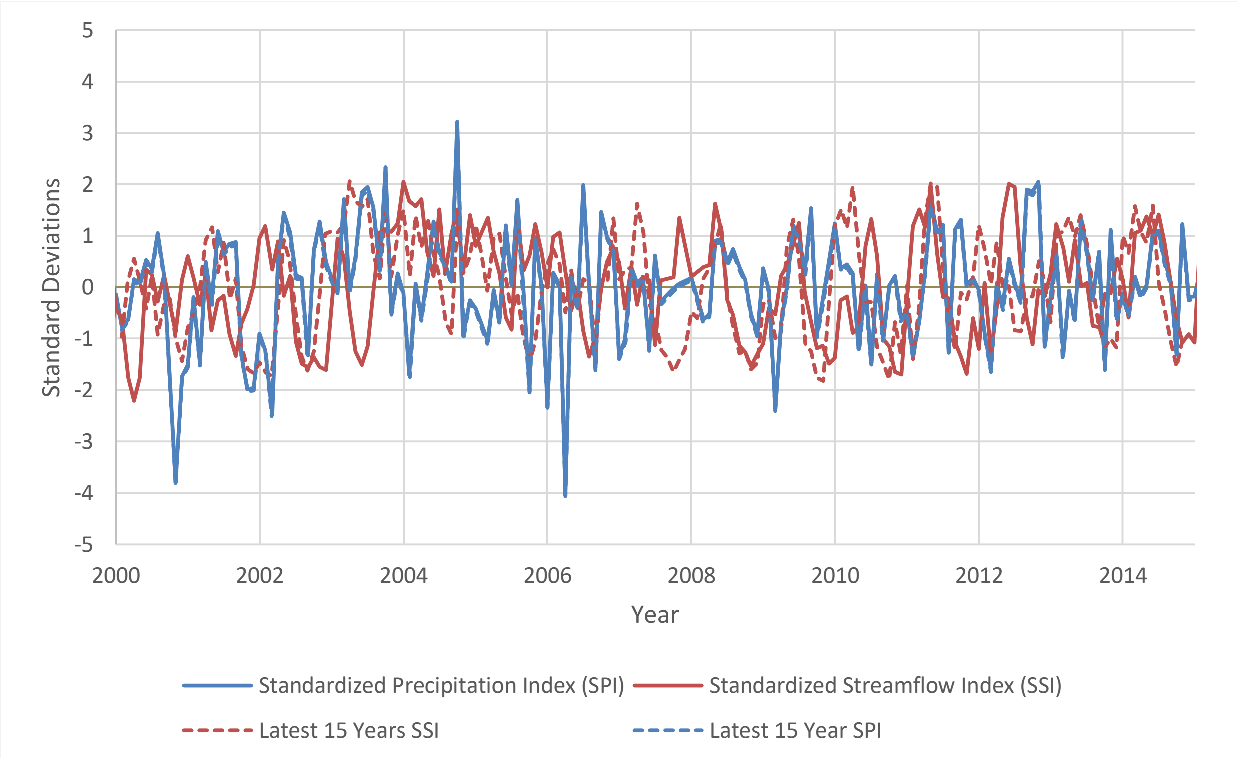

Figure 15. Monthly SPI & SSI w 15 yr comparison

Group 3. Opequon Creek (Berryville)/Winchester

The Berryville and Winchester stations were the most closely correlated, possibly because they were located a short 2.14 miles apart. The SPI and SSI z-values for the stations demonstrate an obvious relationship.

The stations were near to groundwater well 46W 175, for which the period of record is the most comprehensive, from 1987 to 2015. This well was the most useful in understanding the severity of droughts during its period of record, as groundwater deficiencies indicate a long-term water deficiency as opposed to rapidly changing measures such as streamflow (***Figure 16***).

The 15-year SSI and SPI z-values for this station group closely follow the values for the period of record. The 15-year z-values tend to be more susceptible to changes in precipitation and streamflow but that is expected because of the smaller sample size of monthly records. However, the rainfall and streamflow pattern for the recent years seems to be in line with the historical data.

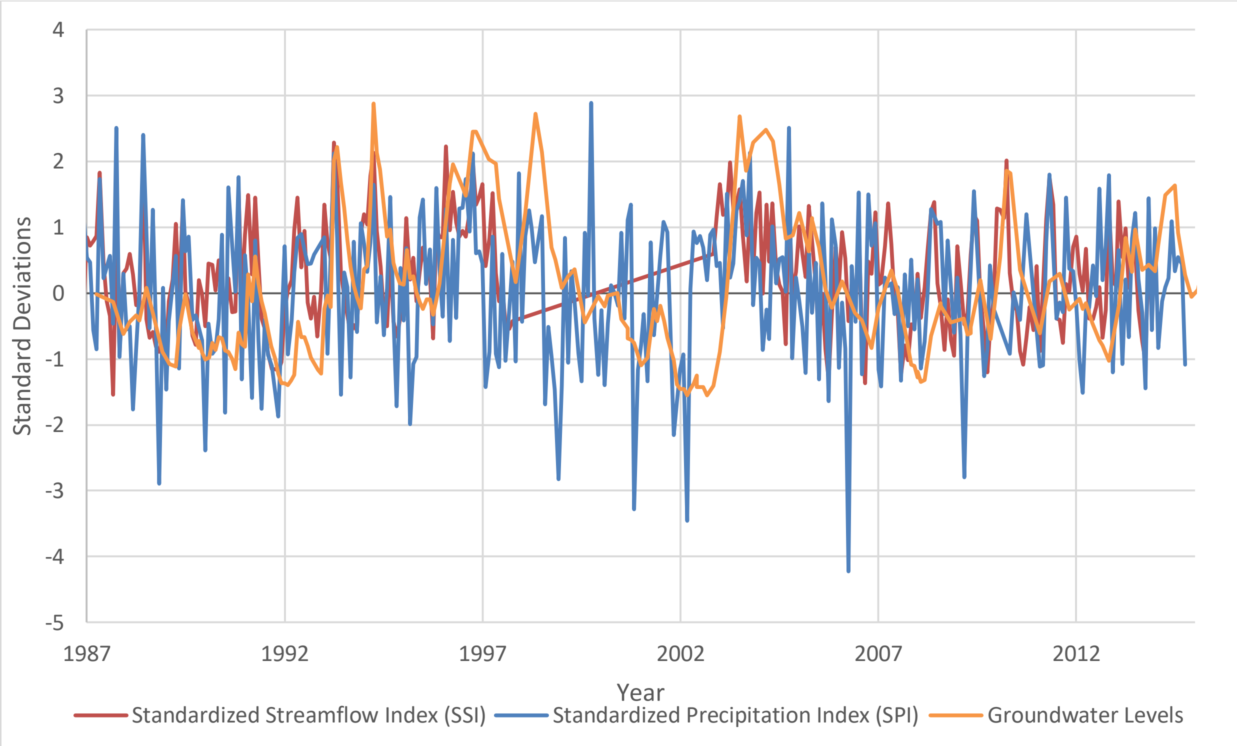

Figure 16. Opequon Creek (Berryville)/Winchester/46W 175 from 1987-2015

Group 4. Passage Creek (Buckton)/Woodstock

The Passage Creek (Buckton) and Woodstock stations had similar timeframes and so provided a historically broad comparison of SPI and SSI. The two stations show a good correlation with an R^2 value of 0.394. The 15 year SPI and SSI match up nearly perfectly with the period of record drought index values, showing that recent trends in precipitation and stream discharge are in line with the trends over the period of record. There was no groundwater well analysis in conjunction with this pairing.

Group 5. South Fork (S F) Shenandoah (Front Royal)/Riverton/Front Royal 1,2

This grouping was the most complex to analyze because of the multitude of precipitation stations located near each other, but none with a broad period of record. In order to use this information, the S F Shenandoah (Front Royal) stream gaging station was paired with three precipitation stations in the watershed- two in Front Royal and one in Riverton. Even so, this did not allow for a complete picture of precipitation over the period of record, but allowed a broader comparison than would have been possible with a singular pairing. The R^2 value using the SPI across all stations and the SSI remained similar to the other large streams, at 0.377. However, because of the lack of extensive precipitation data, the 15-year SPI/SSI and groundwater level comparisons were not executed.

Group 6. S F Shenandoah (Luray)/Big Meadows

Although the period of record for these two stations did not overlap consistently, the years in which they did showed a good correlation with an R^2 value of 0.43. Even on a monthly level, the Luray and Big Meadows stations showed a clear relationship in SPI and SSI. The 15-year SPI trend line was consistently lower than the period of record trend line, showing that the mean precipitation over the recent 15 years was higher than that of the period of record. The SSI trend lines were extremely similar, implying that recent streamflow patterns were similar to historical ones. There was no groundwater well analysis in conjunction with this pairing.

Standardized Precipitation Index (SPI)

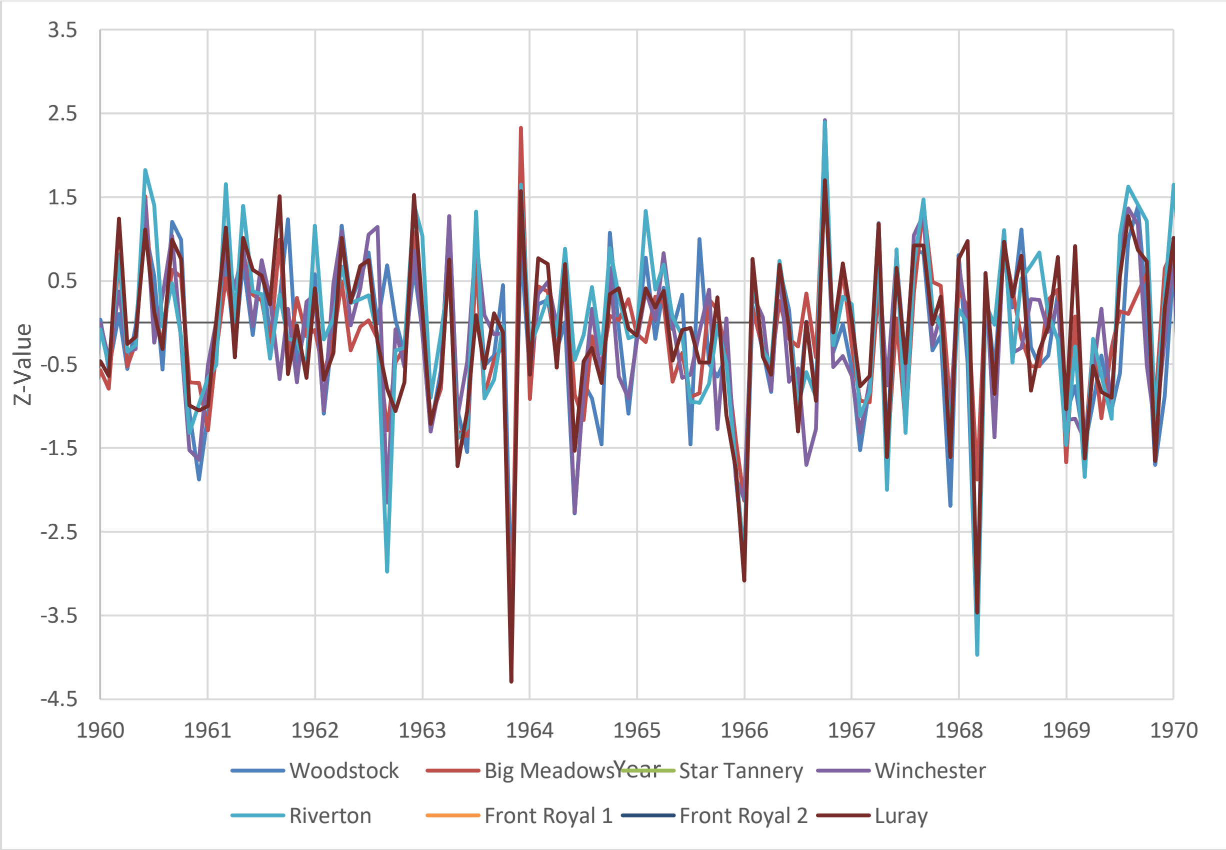

Figure 17. Standardized Precipitation Index (SPI) for 1960-1970

The close relationship of SPI values across the precipitation stations allows for a spatially broad analysis of changes in precipitation over time. Low and high precipitation events can be identified using the average SPI values at a specific point in time, as seen in **Figure 17**.

Standardized Streamflow Index (SSI)

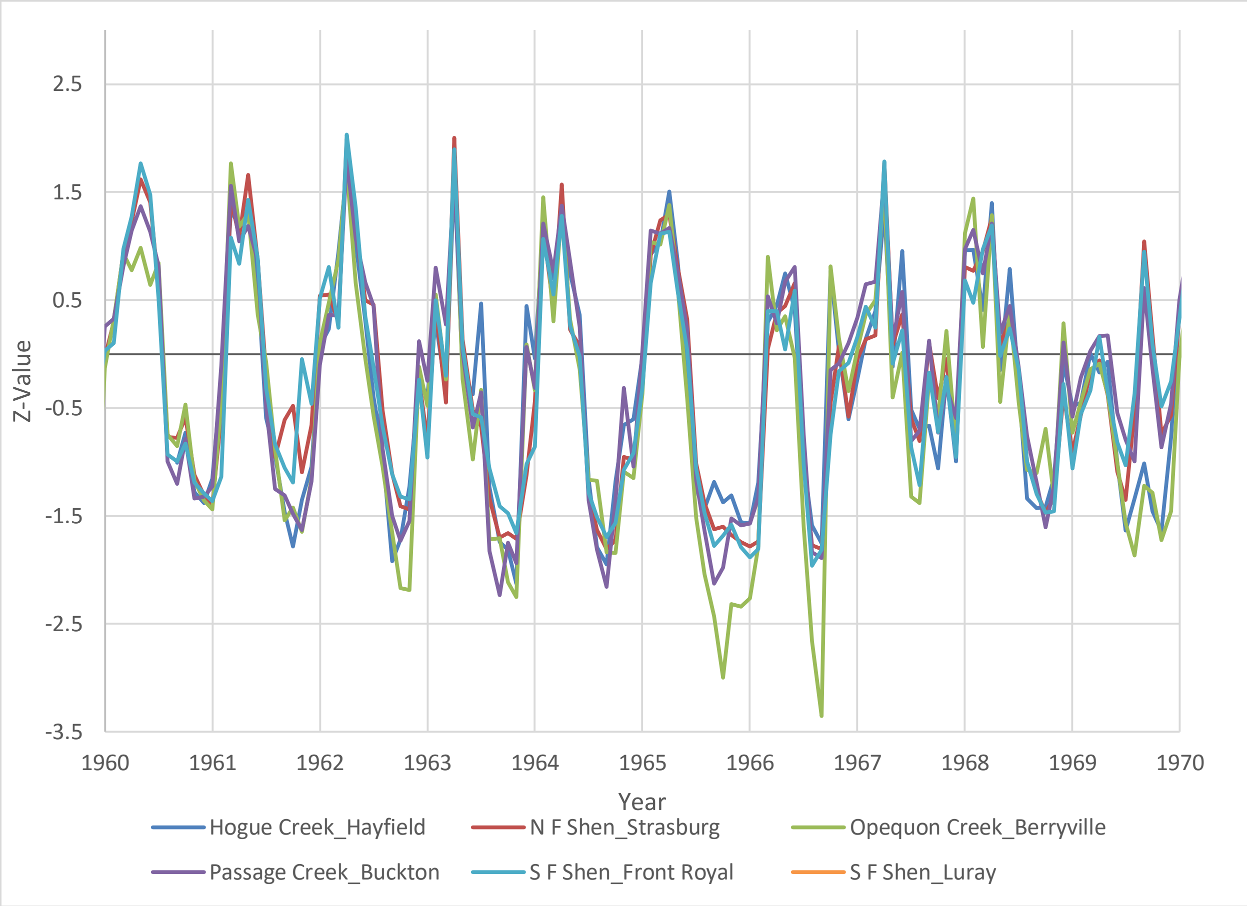

Figure 18. Standardized Streamflow Index (SSI) for 1960-1970

Similarly, the trend lines of SSI z-values across stream gaging stations can be used to locate historical anomalies in stream flow and quantify effects of low precipitation on the stream discharge in the region, as seen in **Figure 18**.

Definition of Drought

Using the historical trends, conditions for a serious drought event were defined. The SPI and SSI z-values were averaged across the stations for each month, giving an overall picture of index values across the region. A drought occurs when SPI/SSI drought definitions given below overlap over a time frame.

<u>Standardized Precipitation Index</u>

- Average monthly SPI value below -1 for six months without a drought resolution period in between
    - Drought onset: 1st month below -1
- Average monthly SPI value below 0 and drops below -3 within the time period
    - Drought onset: 1st month below 0
- Drought resolution: 3 consecutive months above 0

<u>Standardized Streamflow Index</u>

- Average SSI z-value remains below -1 for 6 months within any 12 month period, unless a drought resolution occurs in between
  - Drought onset: 1st month below -1
- Average SSI z-value remains below 0 and drops below -2 within the time period
  - Drought onset: 1st month below 0
- Drought resolution: 3 consecutive months above 0

Historical Drought Events

Using the definition of drought, the two most severe drought events across the period of record were identified in **Table 4**.

Table 4 - Historical Drought Occurrences (Isha Deo, 7/28/15)

Drought Period	***Lowest SPI***	***Highest SPI***	***Lowest SSI***	***Highest SSI***
August 1962 – April 1968	-3.799	1.591	-2.122	0.046
July 1998 – October 2002	-3.502	2.427	-1.991	0.668

Other Analyses

Although there were multiple analyses done on the variables affecting correlation between SPI and SSI, most did not show a consistent trend in the results. However, it was shown that the higher the mean stream discharge, the less of a correlation it has with changes in precipitation. This is important because of the use of stream discharge in supplying water and energy to the region- larger streams are less vulnerable to drought than the smaller tributaries (see **Figure 19**).

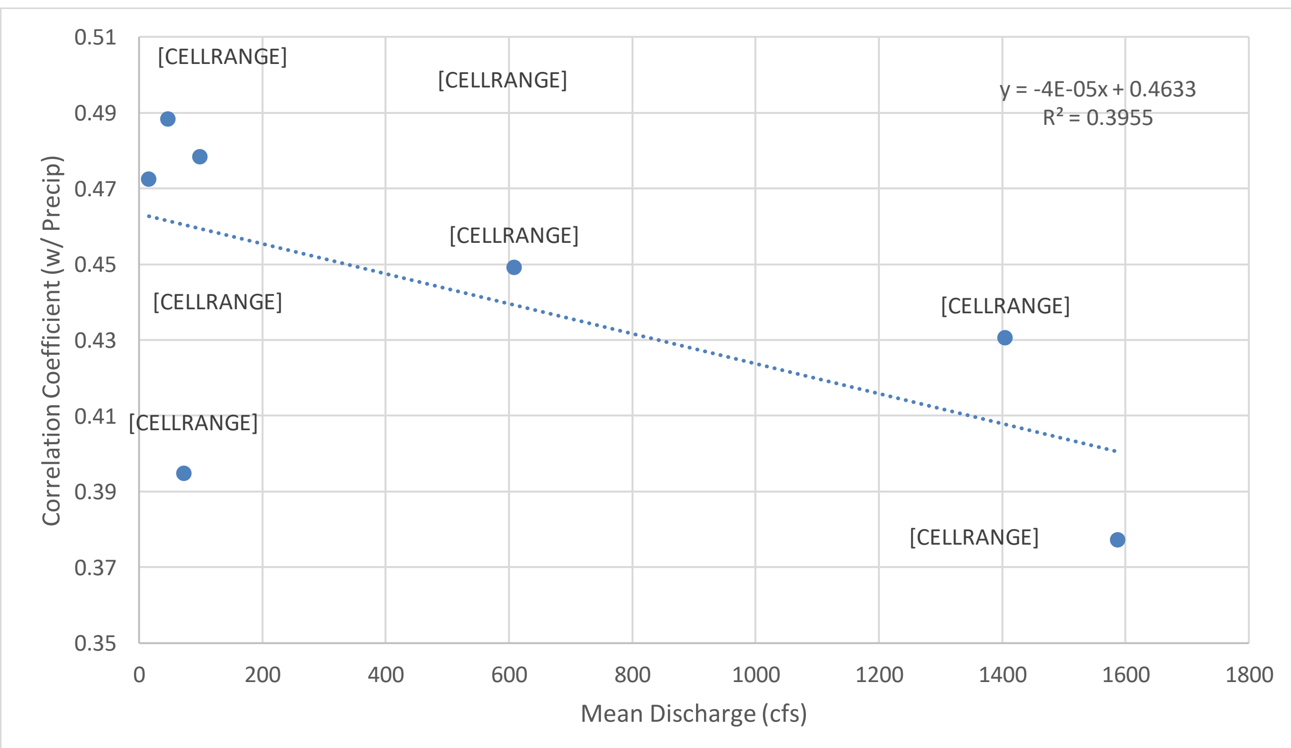

Figure 19. Correlation Coefficient vs. Mean Stream Discharge

4. Conclusion

Availability of Drought Indicator Data

The foremost goal of this project was to identify the spatial and historical availability of drought indicators for the NSV region specifically. Three indicators with a detailed record were identified-precipitation, stream discharge, and groundwater levels. However, upon deeper analysis, even the records of these indicators did not prove to be as extensive as previously considered.

The precipitation record provided a sufficient spatial coverage, with multiple stations in each of the five counties in the region. However, many of these stations did not have a lengthy period of record, rendering many of them impractical in considering drought on a long scale. The stream discharge stations afforded a broad all-around coverage, even though multiple stations did not have a long period of record. The considerable number of stations helped alleviate this concern. Lastly, the groundwater level record provided extensive spatial coverage in the northern counties, but a minimal number of wells in the southern counties. There was also nominal data pre-2002, which does not allow for a broad analysis of groundwater wells over a wide time frame.

SPI/SSI Trends and Definition of Drought

The second objective of this project entailed analyzing the available record of drought indicators and creating a working definition of drought for the NSV region. The various watershed grouping showed a consistent relationship between precipitation and stream discharge, along with a higher correlation between SPI and SSI with lower mean streamflow values. Groundwater levels, where available, matched the trends of SPI and SSI and could be used in future drought forecasting if more extensive records are recorded. In light of recent worldwide climate changes, the SPI and SSI were calculated for the latest 15 years. These values generally follow trends for the period of record, although a few watersheds show significant variation implying changing conditions in the region. Finally, using the averaged z-values of the SPI and SSI, a definition of drought was created that can be used in future drought forecasting and recognition.

Future Work

One of the primary considerations in creating a more comprehensive drought response contingency plan is in the availability of groundwater level data. The lack of a broad scope of data created difficulties in applying the indicator to the definition of drought, although it provides a better understanding of long term effects of low precipitation in the NSV.

A possible application of this information would be in the creation of a program that can evaluate drought conditions on a regular basis. This would provide relief against human error and could be the first step in an automated drought response plan.

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The Impact of Livestock Exclusion from Streams on Greenhouse Gas (CO_2, N_2O, CH_4) Flux

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Abstract

Recent climate changes are suggestive of the negative impact of increased anthropogenic greenhouse gas emissions. The agricultural sector is responsible for about 7.7 percent of these total emissions in the United States, with a large portion attributed to livestock. The purpose of this research was to determine correlations between greenhouse gas (CO_2, CH_4, and N_2O) emissions and cattle exclusion from streams, since this topic had not been previously explored enough to draw any significant conclusions. Appropriate research sites were determined based on the presence of cattle, with Docs Branch fenced off in 1997 and Holtan Branch remaining unfenced, allowing cattle to access the water. At both tributaries, greenhouse gas concentrations were measured at four transects with five points each, using a Picarro G2508 Gas Analyzer and the non-steady state static chamber method. Differences in the average greenhouse gas fluxes between the two tributaries were calculated to be as large as 450 kg ha^{-1} d^{-1} for CO_2, 5.34 kg ha^{-1} d^{-1} for CH_4, and 0.019 kg ha^{-1} d^{-1} for N_2O, at comparable distances from the center of the stream. The initial data suggests that the tributary where cows have access to the stream, produced higher emissions for all of the greenhouse gases in question, upland of the stream. This trend advocates that cattle should be excluded from streams and rivers to reduce greenhouse gas emissions.

Keywords: greenhouse gases, low-order floodplains, livestock exclusion, soil metabolism, climate change, stream fencing

1. Introduction

Humans create observable changes in the climate system, which in turn influence the human and ecological systems. Greenhouse gases (GHGs) are known to play a critical role in climate change, especially now with anthropogenic emissions recently reaching the highest levels in history. (IPCC, 2014) The principal greenhouse gases found naturally in the atmosphere are water vapor (H_2O), methane (CH_4), carbon dioxide (CO_2), and nitrous oxide (N_2O). Atmospheric concentrations of the latter three have increased substantially since the pre-industrial era. (IPCC, 2014) In the United States, 7.7% of greenhouse gas emissions were attributed to agricultural sources in 2013. Livestock constitute a great deal of the overall emissions from the agricultural sector. (EPA, 2014)

Cows, being one of the ruminant creatures of the world, have unique digestive systems that convert feed into a digestible product by means of microbial bacteria called methanogens. Ruminant animals are responsible for about 22% of global anthropogenic methane emissions as well as emissions of nitrous oxide and carbon dioxide. (EPA, 2012) Methane results from manure management procedures at 9.6% of total CH_4 anthropogenic emissions, and 74% of N_2O emissions in the United States are attributed to agricultural soil management practices. (EPA, 2014) In floodplains along rivers and streams cattle also cause erosion of banks, increased sediment loading, and waste pollution of streams. A safe management measure to reduce the disturbance of waterways in agricultural areas is the fencing off of streams to prevent livestock access. (EPA, 2012)

In the Town of Blacksburg in Montgomery County, Virginia, the Stroubles Creek watershed is partially situated on farm and vacant rural land. This creek drains to the New River which through the

Ohio River eventually meets up with the Mississippi to flow all the way down to the Gulf of Mexico. (Parece, T., et. al, 2010) In an attempt to "reduce sediment and nutrient loading to the stream and to improve biological integrity," about 1.3 miles of the stream was restored to varying degrees. (CWS, 2007) Along the entire restoration area, fences were built in 2009 to prevent cattle from accessing the stream. Several perennial tributaries connect with Stroubles Creek close to the StREAM Lab, or Stream, Research, Education, and Management Lab. One such tributary is Holtan Branch, located upstream of the restoration and currently unfenced allowing the cattle from neighboring farms to access the water. A tributary known as Docs Branch further downstream has been fenced off since 1997. These areas provide an opportunity to conduct research into the idea of livestock exclusion from streams. If cross sections from both of the varying tributaries are examined, comparisons can be made between them in terms of greenhouse gas emissions. The objective of this research is to determine any correlation between the fluxes of specific greenhouse gas emissions and the exclusion of cattle from streams. I hypothesize that implementing a fence to protect a stream, results in lower GHG emissions and less intense loading of waste and sediment.

2. Materials and Methods

The StREAM Lab is located on a restored portion of the second-order floodplain of Stroubles Creek in southwestern Virginia. Upstream, the headwaters flow through Virginia Polytechnic Institute and State University and urban sections of the Town of Blacksburg. This stream then enters agricultural land and forested regions. Stroubles Creek watershed is illustrated on a map in Figure 1 of Appendix A. As various sections of the stream and adjacent tributaries were fenced off in different years and some even left open, this is an ideal location for research into the impact of stream fencing on greenhouse gas emissions. Two tributaries in particular that were chosen for this research project are shown in Figure 2 of Appendix A and Photos 1-3 in Appendix B. In order to compile results and arrive at a conclusion stating whether or not the implementation of a fence affects fluxes in greenhouse gas emissions, several field measurements and calculations must first be completed.

2.1 Surveying the Floodplains and Determining Locations for Measurements

When dealing with streams of various flow rates and cross sectional areas, it becomes necessary to equalize the floodplains in such a way that measurements taken on the banks are of a comparable distance from the stream, given the differences in stream size. In other words, a ratio must be determined between the two locations based on the size and discharge of each, in order to collect data from points at proportionate distances from each stream. Determining these locations requires the use of a rating curve, which relates stage in feet and discharge in cubic feet per second. The two tributaries in question were lacking rating curves and therefore needed gaging. Stream gaging is a process used to determine the discharge of a stream at a particular point, but actually measures the velocity or stream stage. (Global Water, 2011) In the case of this project, stage was calculated using a laser receiver mounted on a measuring post, measuring tape, and a CST/Berger rotary laser level kit. (CST/Berger, Watseka, IL) Stakes were placed on either side of the stream, with the measuring tape running between as shown in Photo 4 of Appendix B. Vertical distances were recorded once every foot along the tape using the measuring post. The laser receiver attached to the post would beep when it was in line with the leveled laser, stationary on one bank, signaling that it was appropriately situated to take a reading on the post. Both the vertical and horizontal distances measured by this method are used to determine the flow rate of the respective stream.

Area and wetted perimeter of the stream channel were calculated using the measured distances. Manning's equation was then used to determine the discharge of each stream, where the slope and roughness coefficients were held constant at 1 and 0.03, respectively. Discharge was calculated for stage values in small increments from 0 to the maximum stage recorded during a recent flood event. Knowing both stage and discharge, rating curves for both tributaries were plotted and are provided in Figures 3 and

4 in Appendix A. From these rating curves, stage and the distance from the center of the stream to the edge of the floodplain were determined. The next step was to choose general locations for the measurements, given the floodplain area. It was decided that there would be four transects at each tributary on one side of the bank so that statistical tests could be run on the data. Each transect had five locations, all of comparable distances from the stream: in the stream, next to the stream, midway up the bank, near the edge of the floodplain, and upland outside of the floodplain. A diagram illustrating the general layout of the transects and locations is presented in Figure 5 in Appendix A.

2.2 Field Measurements

The actual data collection required a team of at least two people and various pieces of equipment. Collars were constructed out of 10 inch diameter PVC pipe, with one end sharpened for easier installment. At one site, a stake was placed in the estimated center of the stream and another marked the edge of the floodplain, with a measuring tape running between the two. The four collars were inserted into the ground at the aforementioned general distances from the stream. This technique creates a seal within the soil, limiting gas loss from the collar during the sampling period. The cap which fits over the collar, sealed off with a large rubber band, is illustrated in Photo 5 of Appendix B in its typical setup. Tubing runs from this cap to a Picarro G2508 Cavity Ring-Down Laser Spectrometry Greenhouse Gas Analyzer (Picarro, Santa Clara, CA), pictured in the field in Photo 6 of Appendix B. This device measures concentrations of CO_2, CH_4, and N_2O using the unsteady state static chamber method. Vegetation within the collars was cut to reduce the influence on the CO_2 flux via photosynthesis before measurements were taken. After five minutes the cap was removed and soil temperature, soil moisture, and collar headspace were measured using a digital thermometer, a Hydrosense meter (Campbell Scientific, Logan, UT), and a ruler, respectively. Elevation at each collar location was also determined using the laser level kit, measuring post, and laser detector. This procedure was followed for all five points measured along each of the four transects, totaling twenty measurements per tributary.

2.3 Laboratory Nutrient Extraction and Analysis

Soil samples were collected from the four points closest to the stream along one of the transects per site. A spade was used to remove about one kilogram of soil per sample. This soil was stored in polyethylene bags in a cooler. Nutrient extraction was performed in the lab within 24 hours of collection. Samples were broken up and mixed to ensure the soil used was a proper representation of the total collected. A 1:5 soil to water ratio was weighed out into a glass bottle. The samples were then mixed on a shaker table at 200 rpms for one hour. Pipettes were used to remove the top section, avoiding the soil settled at the bottom, to fill two centrifuge tubes per sample with about 45 mL each. The centrifuge ran for 10 minutes at 6000 rpms in order to separate the extractable nutrients and the clay. Finally filtering was done via a Geopump Peristaltic Pump (Geotech Environmental Equipment, Inc., Denver, CO) into three 20 mL scintillation vials (Fisher Scientific, Pittsburgh, PA) for each sample. These vials were stored in a freezer until further testing.

Solutions obtained from the soil samples were analyzed in the laboratory for various nutrients available for extraction via microbes and plants. A SEAL AutoAnalyzer 3 (SEAL Analytical, Mequon, WI) which “fully automates repetitive and complex sample analysis steps” was used to complete this task. These tests were performed colorimetrically with a segmented flow analysis technique which “reduce[s] inter-sample dispersion” by dividing the flow with air bubbles. (SEAL Analytical, 2014) Nitrate (NO_3^-), phosphate (PO_4^{-3}), and ammonia (NH_3) were all analyzed simultaneously, following this technique.

3. Results

With the coding software, R, fluxes for all of the greenhouse gas concentrations measured by the Picarro were calculated. These fluxes are depicted in box and whisker plots by site and gas. Each plot contains data from the five locations of varying distance from the stream: in the stream, next to the stream, midway up the bank, near the edge of the floodplain, and upland, outside of the floodplain. Also included on these graphs are the soil moisture, soil temperature, and elevation averages from each of these locations. These various parameters are presented as lines to illustrate the trends along the transect. The letters located either above or below each box plot indicate the results from the Analysis of Variance (ANOVA) of the data. This statistical test is used to determine differences between means by analyzing variance between the values. The Analysis of Variance was used here to compare all of the locations from the stream at both sites, in one test.

3.1 Fluxes of carbon dioxide, nitrous oxide, and methane

Fluxes in carbon dioxide emissions for Holtan Branch and Docs Branch are displayed in Figure 6 and Figure 7, respectively. Emissions of carbon dioxide include the respiration of soil organisms and plant roots. From general observation, the differences in the slope across the two floodplains is quite apparent. Holtan's channel is wide with a sharp increase in slope at the edge of the floodplain, whereas Docs has a more u-shaped channel and a steady increase in elevation with distance from the stream. Results from both tributaries demonstrate low concentrations of CO_2 in the stream. It is at the following four locations that variation between the sites is seen. At Docs Branch, the flux is much higher next to the stream and steadily decreases with distance from the stream. This follows the trend in soil moisture. However, the data from Holtan reveals lower fluxes with closer proximity to the water, where soil moisture is high. When soil moisture is around sixty percent, the area is considered saturated. The largest CO_2 flux was recorded in the upland region, about ten feet from the floodplain boundary. Temperature profiles at both tributaries remained fairly consistent along the transects, with Holtan having the slightly more drastic change of about five degrees Celsius, overall. The letters from the statistical test show significant difference between the means of the carbon dioxide fluxes from many of the locations from both sites.

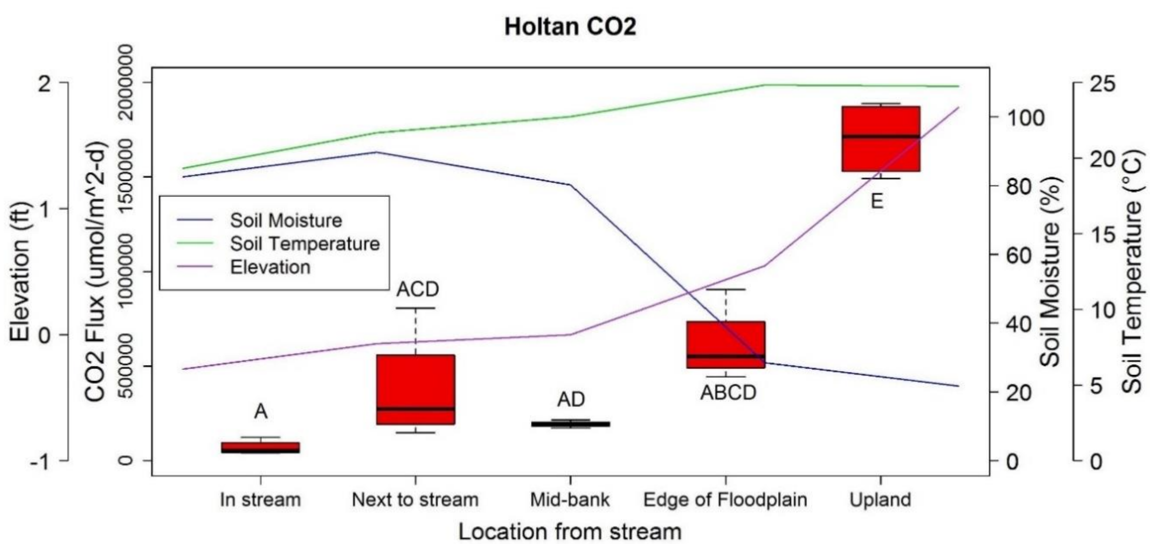

Figure 6: Carbon dioxide flux at Holtan Branch

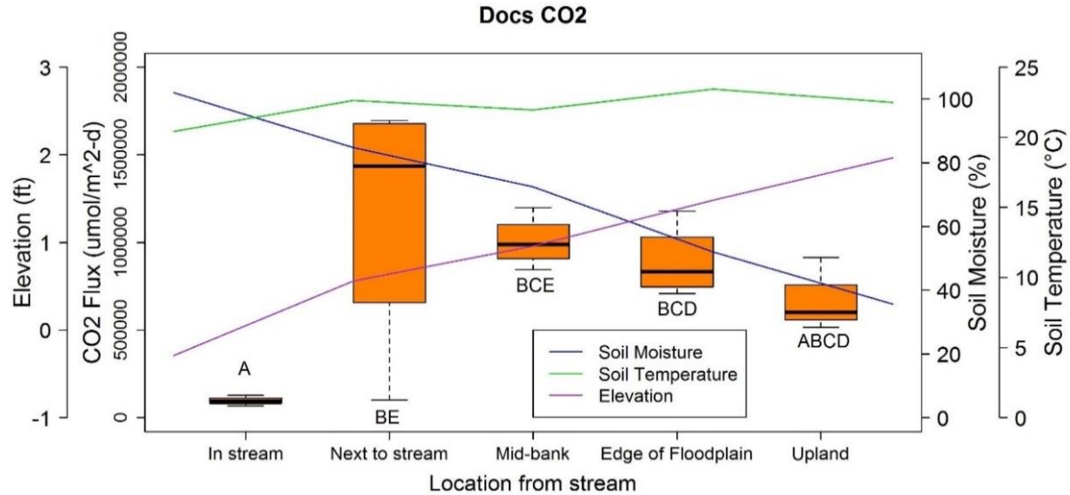

Figure 7: Carbon dioxide flux at Docs Branch

Figure 8 and Figure 9 provide the methane flux data from Holtan Branch and Docs Branch, respectively. Fluxes in methane, represented by the box and whisker plots, show a greater overall range from Docs where some values were negative and some were over 150,000 umol m^{-2} d^{-1}. At the Holtan tributary, however, there is more methane flux in general. Here, at the site with cattle, positive values of CH_4 flux are observed farther from the center of the stream, whereas at Docs, methane is quickly cut off with increased distance from the stream. The locations of higher soil moisture, such as in the water and where the cows trampled the bank at Holtan, are the ones that have higher methane flux. Proximity to the stream and soil moisture seem the deciding factors of the presence of methane in this case. No significant difference between any of the fluxes of methane were determined from statistical testing.

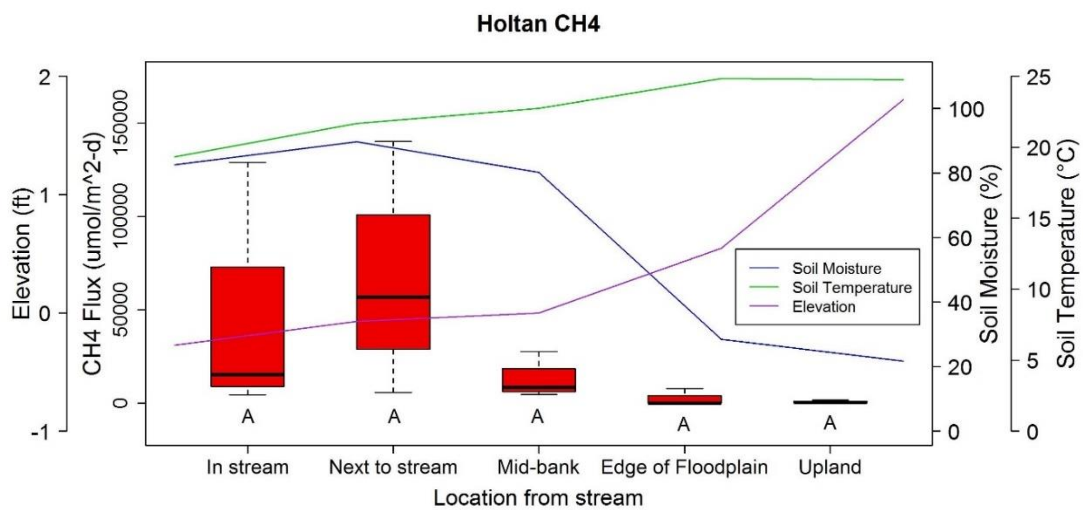

Figure 8: Methane flux at Holtan Branch

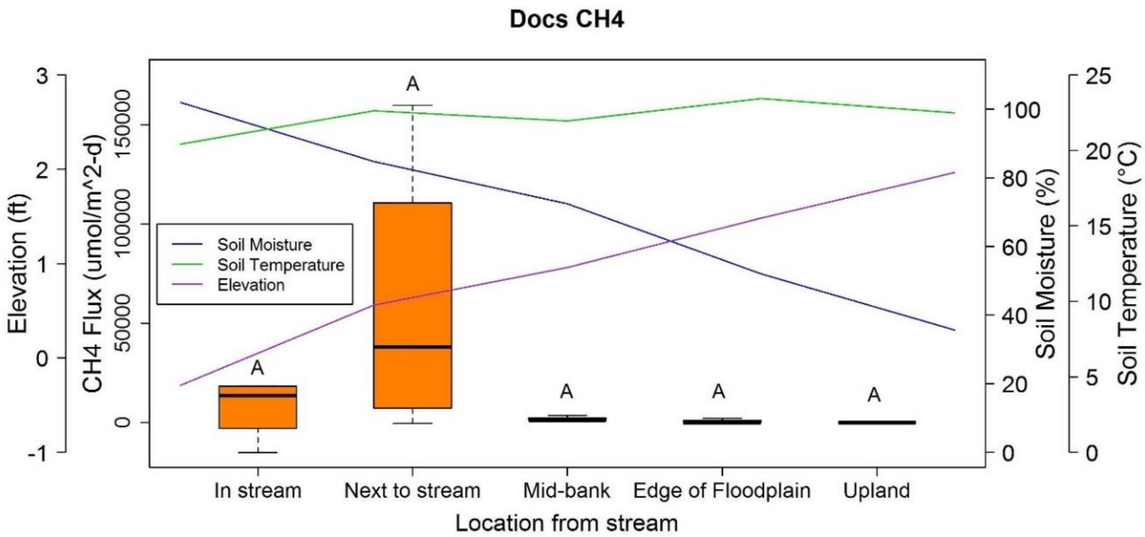

Figure 9: Methane flux at Docs Branch

Nitrous oxide fluxes for the tributaries, Holtan and Docs, are presented in Figure 10 and Figure 11, respectively. At the tributary with cattle, a larger range of fluxes with some higher values are observed. This differs from Docs Branch, where there is less range and more negative values of N_2O flux. Although there is not a great deal of significant variability between the locations at either tributary, there are notably higher ranges at a larger distance from the stream at Holtan, but higher ranges closer to the stream at Docs. Also, the mean flux values at each location somewhat follow the temperature trend along the transect at both sites. The Analysis of Variance test for nitrous oxide flux did not show any significant variance between any of the locations.

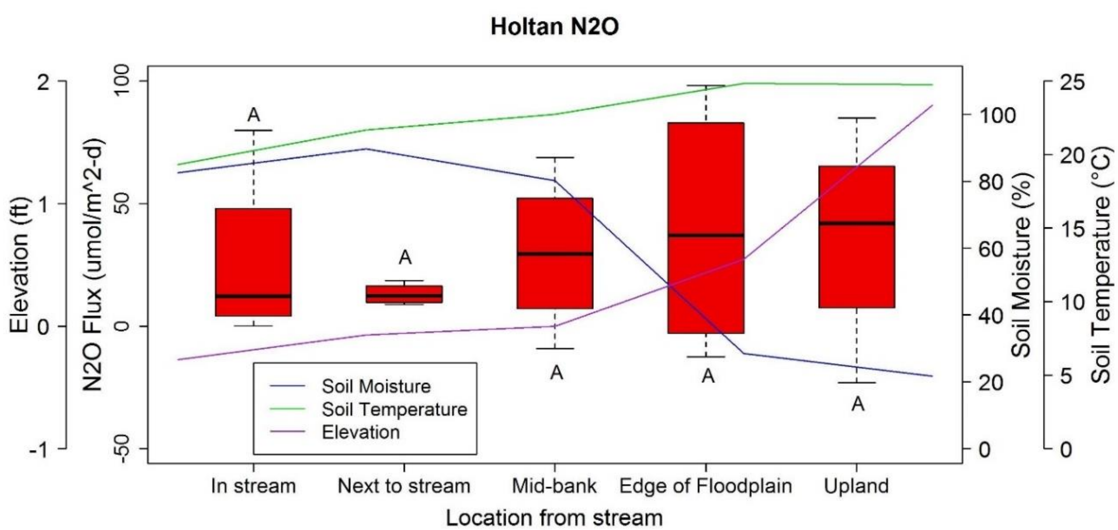

Figure 10: Nitrous oxide flux at Holtan Branch

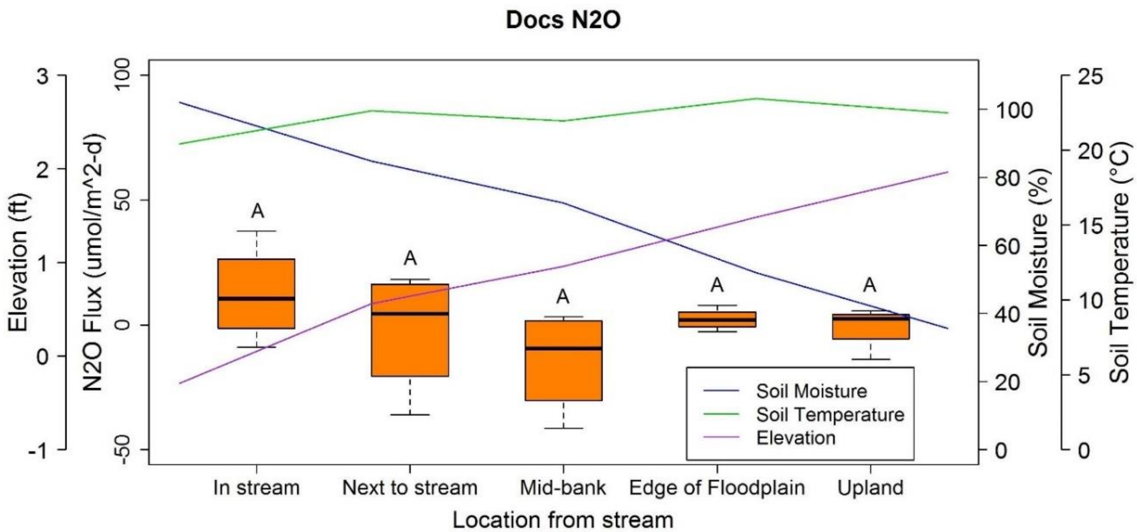

Figure 11: Nitrous oxide flux at Docs Branch

3.2 Global Warming Potential

Greenhouse gases insulate the Earth by trapping energy and therefore reducing how quickly that energy can exit the atmosphere. This concept is known as global warming. Every gas affects this warming differently, based on "their ability to absorb energy (their "radiative efficiency"), and how long they stay in the atmosphere (also known as their "lifetime")". (EPA, 2015) One way to compare the impacts of the various greenhouse gases is through the Global Warming Potential (GWP), which is a "measure of how much energy the emissions of one ton of a gas will absorb over a given period of time, relative to the emissions of one ton of carbon dioxide." (EPA, 2015) If a gas has a greater GWP, then it will have a larger impact on the Earth's warming. The Global Warming Potential was determined for CO_2, CH_4, and N_2O based on carbon dioxide equivalents for each location and each site as a whole. The results are presented in Figure 12 and Figure 13 of Appendix A, for 100 year lifetimes. H1 corresponds to the location in the stream, H2 the location next to the stream and so on until the upland region or H5. Overall, CO_2 dominated the graphs at both tributaries. At Holtan, however, methane was a much greater contributor overall than at Docs, with H2 even displaying a higher value of methane than carbon dioxide, based on the equivalents.

3.3 Soil Nutrient Analysis

Results from the soil nutrient analysis are provided in Table 1 of Appendix A. Nitrate, phosphate, and ammonia for each site were tested. The averages of the four soil samples per site were calculated. Although phosphate showed practically no difference between the two tributaries, the soil samples from Holtan Branch contained 1.17 and 5.5 times higher concentrations of NO_3 and NH_3, respectively, than Docs.

4. Discussion

The trends from this initial data vary. Differences in carbon dioxide flux between Holtan Branch and Docs Branch are quite significant. Low CO_2 concentrations at the in stream locations of both sites are likely the result of high water-filled pore space, which is known to limit CO_2 production. At locations closer to the center of the stream at Holtan, (including in the stream, next to the stream, and mid-bank) carbon dioxide fluxes were measured as much lower than at Docs. This could potentially be because the cattle at Holtan have trampled the bank, widening and causing increased saturation at a larger distance from the center of the stream. All three of these locations closest to the stream had standing water in the collars. The upland region at Holtan, however, is higher than that of Docs' upland. Cattle near the former, trample and graze the vegetation which results in reduced photosynthetic influence. Less vegetation, generally means more carbon dioxide. In Docs' upland region, the vegetation is quite dense, so the intense presence of photosynthesis causes reduced CO_2 emissions from the soil.

The statistical tests done on this data concluded that there were no significant differences between any of the locations for methane flux, which is believed to be because the data set was quite small (four points per location) and there was indeed less variation than with CO_2. Despite these results, there are still some notable variations between the two sites that can be observed. Overall, there were higher methane emissions measured at the tributary with cows. The "in stream" location shows greater fluxes at Holtan, which suggests that the cattle have some influence on the emissions from the stream water itself through increased sediment loading and waste pollution. Not far from the stream center, around four or five feet, methane fluxes drop to practically nothing at the site without cattle present. At Holtan where cattle have access to the water, however, there were slight CH_4 fluxes measured around nine feet from the center of the stream. The cows at this site have caused the stream channel to widen and therefore the floodplain area is larger. This greater floodplain is more saturated and trampled by the cattle which causes methane "burping" from compression of the soil. From general observation, the methane flux at Holtan follows the trend in soil moisture, so where the soil was more saturated there were higher fluxes of methane.

Fluxes in nitrous oxide measured for this research were, statistically, all similar between the locations. The values for the sites were comparable, possibly due to the fact that the land at both tributaries was used in the past, and is currently being utilized, for some type of agricultural purpose. There are some observable differences when comparing the data from the two tributaries, however. The site that allows cattle to access the water displays a larger range of N_2O flux with higher values than those at the fenced off site. This parallels the results from the soil nutrient analysis, where samples from Holtan Branch demonstrated an overall higher concentration of nitrogen than Docs Branch. The reason behind these results could be that the area around Docs and outside of the fence is mainly used for hay fields currently, whereas, at Holtan the area is still used as a cattle pasture. Manure from the cattle near the stream at Holtan is likely rich in nitrogen and other nutrients, which is a possible explanation for increased levels of nitrogen and N_2O emissions from the soil.

5. Conclusion

This research aimed to determine any correlation between fluxes in essential greenhouse gases and the exclusion of cattle from streams and floodplains. The data collected for the purpose of this research suggests that of the two tributaries, the one where cows have access to the stream resulted in higher fluxes for all of the greenhouse gases in question, upland of the stream. This trend advocates the exclusion of cattle from streams and rivers to reduce greenhouse gas emissions. Removing livestock from waterways and floodplains could cause a decrease in the amount of nitrous oxide, carbon dioxide, and methane produced by the agricultural sector. All three of these gases are contributors to global warming and are therefore inducing climate change.

As a continuation of this work, research could be done at these two tributaries and perhaps some other similar locations, temporally and spatially. To cover a greater area would provide more insight as to how far away from streams fences should be installed. Data collected throughout the year, would offer a chance to analyze how these initial results are altered by the various seasons.

6. Acknowledgements

I would first like to thank Dr. Vinod Lohani and those involved in coordinating this REU program for the opportunity to participate in research at Virginia Tech. The guidance, time dedicated, and encouragement from my mentor, Dr. Durelle Scott, was very much appreciated. To Breanne Ensor, my greatest gratitude for always being patient and assisting me in every step along the way. A thanks to Dr. Scott's research team for their wisdom, support, and assistance in introducing me to the research process and allowing me to feel like part of the team. I would like to thank the following individuals for their assistance in data collection and equipment preparation: Tyler Weiglein, Dumitru Branisteanu, Laura Lehmann, Kelly Peeler, and Dylan Cooper. To my REU fellows, thank you all for sharing in this experience, for your support, and for all of the memories we have made together this summer.

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Appendix A

Additional Figures and Tables

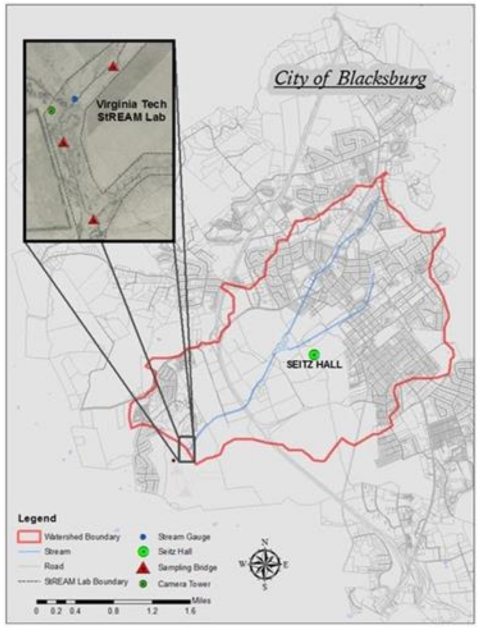

Figure 1: Stroubles Creek Watershed in Blacksburg, Virginia

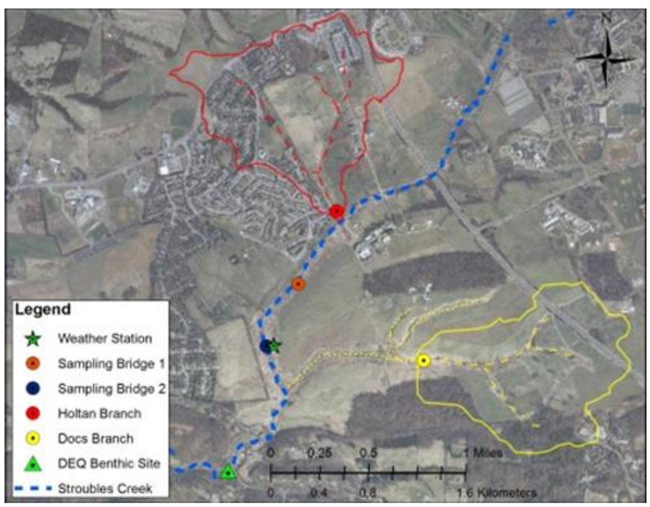

Figure 2: StREAM Lab including two tributaries, Holtan and Docs

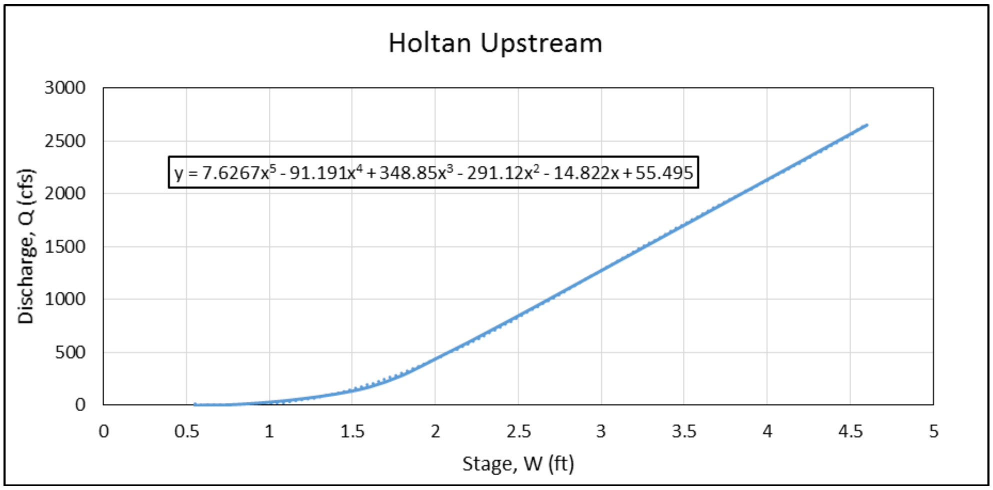

Figure 3: Rating curve for Holtan Branch

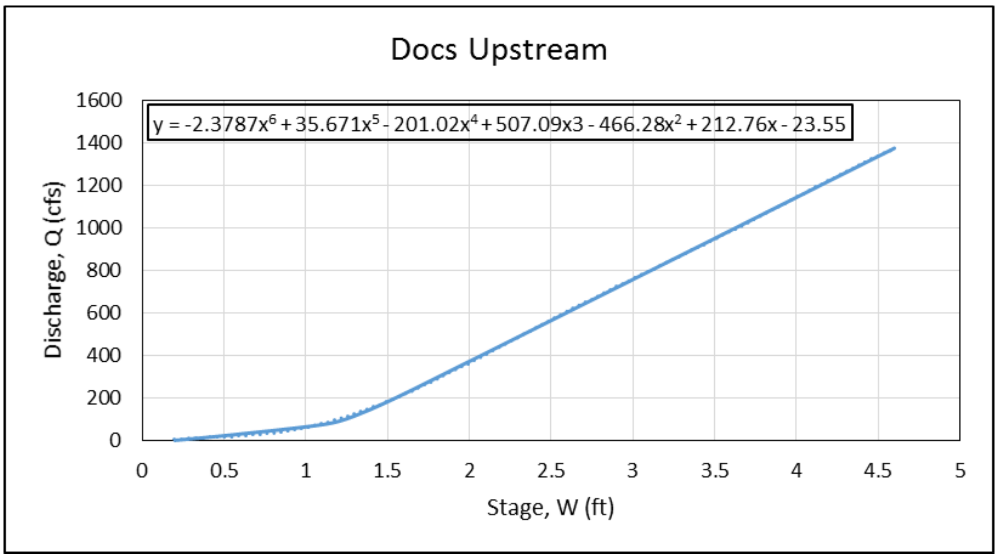

Figure 4: Rating curve for Docs Branch

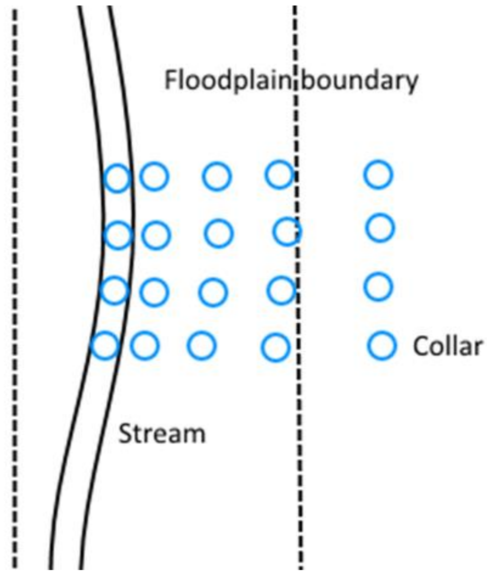

Figure 5: Diagram of general layout of locations for data collection

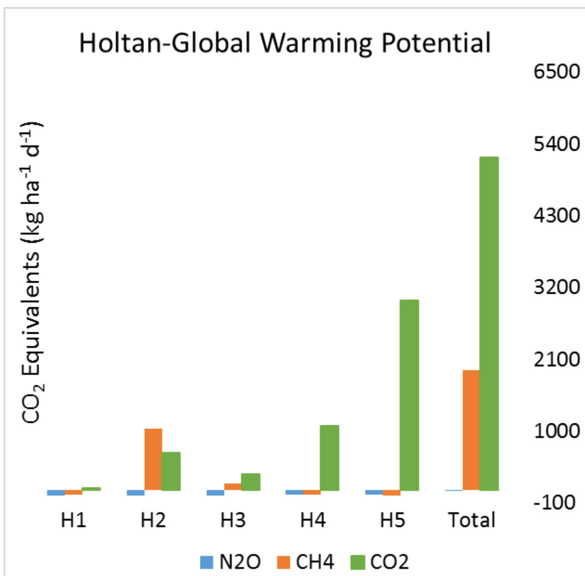

Figure 12: Global Warming Potential (100 year time horizon) for Holtan Branch

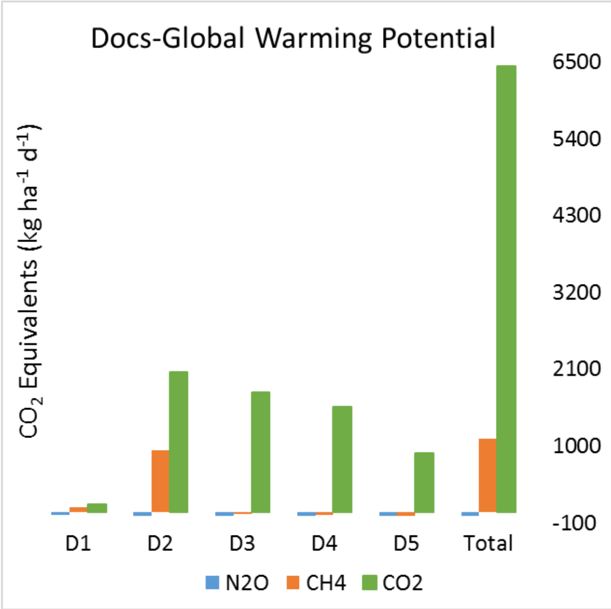

Figure 13: Global Warming Potential (100 year time horizon) for Docs Branch

Table 1: Results from soil nutrient extraction and analysis (nitrate, phosphate, and ammonia)

Site	Average NO_3-N(umol N/L)	Average PO_4^{-3}(umol PO_4^{-3}/L)	Average NH_3-N(umol N/L)
Holtan	30	0.21	47.1
Docs	25.7	0.21	8.57

Appendix B

Site Photos and Equipment

Photo 1: Trampled bank of Holtan Branch (with cattle)
(April Marsh, 6/15/15)

Photo 2: Holtan Branch
(April Marsh, 6/15/15)

Photo 3: Docs Branch (fenced off, without cattle)
(April Marsh, 6/15/15)

Photo 4: Surveying a cross section at Holtan Branch
(Breanne Ensor, 6/15/15)

Photo 5: Collars and cap measuring ghg concentrations in the field (Breanne Ensor, 3/26/15)

Photo 6: Picarro G2508 Greenhouse Gas Analyzer (Breanne Ensor, 4/23/15)

Continuous High Frequency Water Quality Parameters as Surrogates in an Urban Watershed

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Abstract

This study analyzes patterns in water quality parameters during storm events at two locations on the campus of Virginia Tech (VT), in the Webb Branch, which is an upland urbanized catchment of Stroubles Creek. Data for this study was collected using two Hach Hydrolab MS5 Sondes, and grab samples. The Sondes collect data in continuous high frequency (3 minute) intervals and measure various water quality parameters, including turbidity and specific conductance. The intent of the study is to find an empirical relationship between specific conductance and turbidity as measured by the Sondes, and the nutrients phosphorus and nitrogen, which are not measured by the Sondes. Two field sites for Sonde deployment and grab sample collection were selected for this study; the current outdoor field location of the Learning Enhanced Watershed Assessment System (LEWAS) lab, by West Campus Drive, and a second site upstream near Goodwin Hall. Water quality data from both base flow conditions and storm events were collected and analyzed to determine a relationship. This study was conducted during a ten week program called Research Experience for Undergraduates, funded by the National Science Foundation (REU/NSF) and supported by the LEWAS lab.

Keywords: High-frequency Data; Specific Conductivity; Phosphorous; Nitrogen; Hydrologic Data; Urban Watershed; Turbidity

1. Introduction

Found within the New River watershed in southwest Virginia flows Stroubles Creek, an urbanized stream which travels through Blacksburg, Virginia. Stroubles Creek is considered a sub-watershed as it is small in size (figure 1), only about 14,336 acres (5,802 hectares). The surrounding bedrock primarily consists of dolomite/limestone. The creek bed is characterized by bedrock, gravel and sand sized particles (Virginia Tech, n.d.). In the northern section of Montgomery County, three natural spring heads form the headwaters for Stroubles Creek. Stroubles creek is classified as a second order freshwater stream that is characterized into two different systems - Upper and Lower Stroubles Creek (Tammy Parece, 2010). The dam at the Duck Pond on Virginia Techs (VT) campus forms the divider between these two portions of the watershed. Lower Stoubles Creek is below the Duck Pond dam. This portion of the stream flows through many rural areas in Montgomery County, including agricultural farms owned by VT. Upper Stroubles Creek refers to areas of the watershed above the duck pond, which flow through parts of Blacksburg, and the main portion of Virginia Tech campus. Upper Stroubles Creek has been severely impacted from land use changes since it was first established in 1740. Most of the changes that have affected the watershed came from advanced land development as the Town of Blacksburg population increased and VTs student enrollment continued to advance (Tammy Parece, 2010).

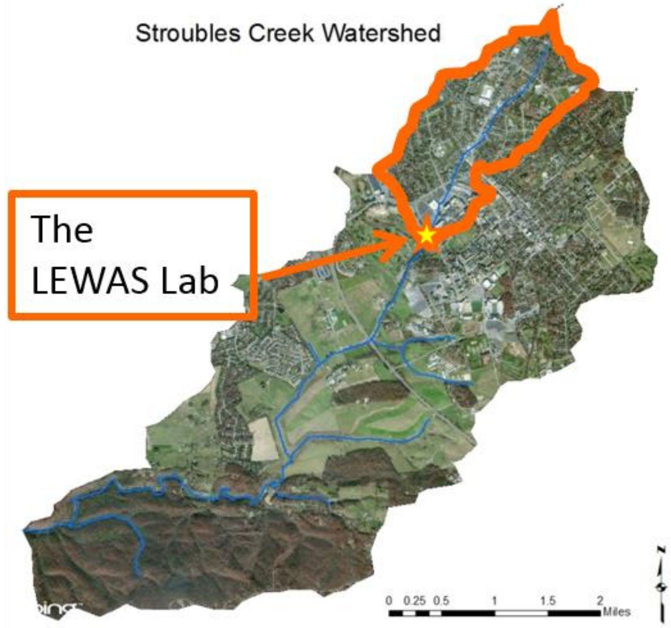

Figure 1. Stroubles Creek Watershed and LEWAS field site
Stroubles Creek is blue, Upper Stroubles Creek watershed defined in orange.

As urbanization from the Town and University progressed, the stream has been altered to travel underground. There are now only few places where the stream daylights, or is above ground. The majority of Upper Stroubles Creek travels through underground tunnels, and combines with runoff water channeled from roads and parking lots (Tammy Parece, 2010). The storm water runoff is often contaminated with roadside pollutants such as motor oil, and road salts which are then channeled into Stroubles Creek, causing stream pollution (Clark et al., 2015). The State of Virginia has recently established a new law requiring cities to monitor the quality of storm water released into nearby streams and riparian zones (State of Virginia, 2013).

Due to the increase population in this area, runoff storm water from roads and parking lots result in flash flooding at various locations within the watershed. This flash flooding is caused because the underground system is not capable of handling the copious amounts of runoff water that is channeled into the underground portions of Stroubles Creek, due to the large areas of impervious surfaces within the watershed. Flash flooding occurs most often at areas where the stream daylights.

Located within Upper Stroubles Creek in the Webb Branch Tributary, is the Learning Enhanced Watershed Assement System or LEWAS Lab. LEWAS is a high frequency, real time, water qualitiy monitoring site and weather mointioring station on VT's campus. The feild site is located in Stroubles Creek, just above the duck pond. The Lab was funded by several grants from the National Science Foundation for water quality research and continuing education. The Lab has several sensors that collect data in high frequency intervals or about every 1-3 minutes. This information is relayed to a database through a raspberrypi, where it is stored and can be accessed online. Acess to this data can be found through the user interface at http://www.lewas.centers.vt.edu/dataviewer/single_graph.html. The sensors include a real time weather station, which measures barametric pressure, tempature, and rain fall intensity; a tipping point rain gage which serves as a secondary measurement of precipitation; a Sontek Argonaut-SW flow meter to record the stream velocity and stage to estimate flow; an ultrasonic transducer to measure stage behind a weire for a second estimate of stream discharge; a water quality Sonde (Hydrolab MS 5), which measures for pH, specific conductivity, tempature, turbidity, oxidation/reduction potential and dissolved oxygen (Figure 2). A live camera monitors the site 24/7. This footage is also accessable on the LEWAS website. The LEWAS lab is fully powered by solar pannels and rechargeable batteries.

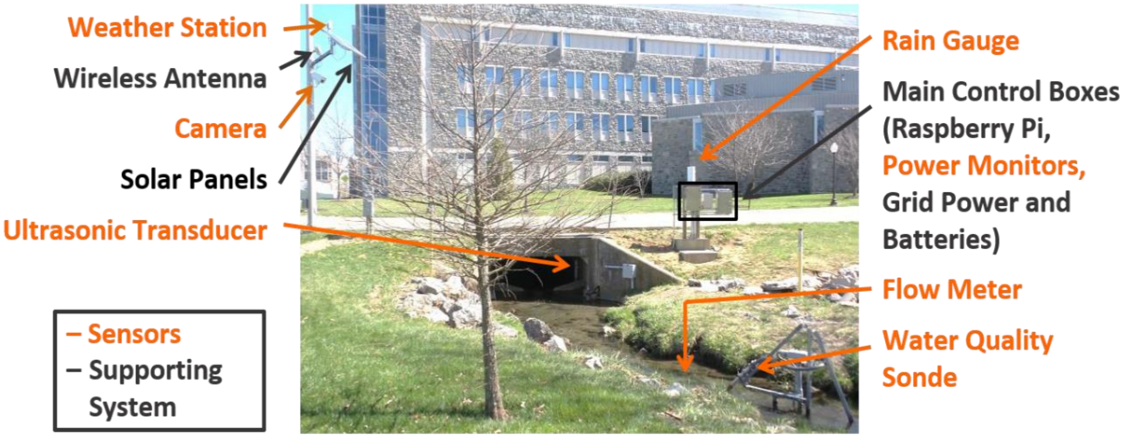

Figure 2. Field Site Instrumentation

The LEWAS Lab hosts a 10 week program called Research for Undergraduates, funded by a grant from the National Science Foundation (NSF/REU). This REU is on Interdisciplinary Water Quality Sciences and Engineering. Several departments from VT work together and host qualified students from different backgrounds to participate in this program. The Departments of Education Engineering, Civil and Environmental Engineering, Crop and Soil Environmental Sciences, Biology, and Geosciences are involved in this NSF/REU. This study was conducted by an undergraduate researcher from Western Carolina University during the summer of 2015. This study seeks to answer the following primary research questions:

1. Can a relationship could be established at the LEWAS site between nutrients (i.e., phosphorous, nitrogen, etc.) captured with grab samples and continuously sampled parameters (i.e., specific conductance, turbidity, etc.) captured with a Sonde?
2. What are the spatial and temporal patterns of nutrient concentrations at base flow conditions in the LEWAS watershed?
3. What are the spatial and temporal patterns of nutrient concentrations in storm water runoff in the LEWAS watershed?

The objectives as follows, were implemented in order that the overall research questions would be answered 1) Develop methodology to relate nutrients from grab-samples to continuous parameters from the Sonde; 2) Capture and analyze grab-samples from the LEWAS field site; 3) Develop regression relationship between nutrient grab-samples and continuous parameters from Sonde; 4) Deploy the secondary Sonde in an upstream location in the LEWAS watershed; 5) Capture and analyze grab-samples from the primary and secondary LEWAS sites; 6) Evaluate spatial and temporal patterns of nutrient concentrations in the LEWAS watershed

2. Methodology

2.1 Maintenance & Calibration

In order for the most accurate data to be collected from the water quality Sonde, the sensor must be regularly maintained (figure 4.) Sonde maintenance includes cleaning the Sonde and permanent frame two times weekly. This is done by using a handheld brush to brush off any allege, sediments, or any other items from the Sonde itself and the frame it is deployed in. The Argonaut flow meter also requires regular cleaning of sediment to maintain accurate readings. This process is generally accomplished before or after cleaning the Sonde. After each rain event additional cleanings are required. Often during storm flow, the

Figure 3. Flood Stage (Elizabeth Erwin 06/06/2015)

Figure 4. Sonde Maintenance After Flood Stage (Zac Fry 06/07/2015)

Sonde catches debris floating downstream and it must be removed. Occasionally the stream beds rocks are shifted during flood events and can end up on top or right in front of the flow meter which creates a false reading. Both the Sonde and the Argonaut require maintenance and site inspection after any rain event.

The Hydrolab MS 5 Water Quality Sonde must be calibrated every two-three weeks for most accurate readings. The calibration process requires about 1-2 hours to complete. The initial step is to retrieve the Sonde from the field site. From there it is taken into a lab and each individual probe is calibrated separately. The Sonde must be cleaned with a toothbrush and a small amount of toothpaste before calibration can begin. The Sonde connects electronically through cables and a power supply to a laptop computer. PH is calibrated first using three different levels of pH calibration fluid (pH 7, 10, and 4, in that order). The Sonde probes must be rinsed in a small amount of calibration fluid before being submerged in it. After the probe has been calibrated it must be thoroughly rinsed with deionized water (DI) before moving on to the next probe. The Specific Conductance probe is then calibrated using a conductivity standard solution. Turbidity is calibrated using DI water. The Oxidation/Reduction potential is calibrated next, followed by Dissolved Oxygen. After the calibration process is complete, the Sonde is redeployed at the LEWAS field site.

2.2 Data Collection –Water Quality Sonde

The Sonde that is permanently deployed at the LEWAS field site automatically records all data collected to an online user interface. This information can be accessed by anyone and downloaded on to any computer. The LEWAS Labs innovative design allows for specific time frames to be selected for data downloads. It is easy to log onto the website and download however much data is needed, from any specific date. Whenever a storm event occurs, the data can be downloaded as the Sonde collects information, or at a later date. All data is stored on a database since the Sonde was first deployed about three years ago. This system is called OWLS or Online Watershed Learning System. By using the OWLS data is easily picked by day and time, and even by parameter. The OWLS parameters include precipitation, flow velocity, as well as the parameters set by the Sonde.

The secondary Sonde however, is not implemented through the OWLS. The secondary Sonde is power supplied for short term deployment via rechargeable batteries, and can be deployed for up to one week. The secondary Sonde does collect data in high frequency, however it must be manually downloaded off the Sonde on to a lap top. The secondary Sonde is deployed before a rain event occurs and is retrieved when the stream returns to base flow. After it is retrieved the data is downloaded for analysis. This same process occurs during the base flow analysis.

2.3.1 Data Collection –Grab Samples at base flow conditions

The base flow conditions analysis occurred over a three day sample period between July 21st and July 23rd. On each day a grab sample was collected from both locations, once in the morning, and once in the afternoon. Stream water was collected in clean eight oz. bottles. These bottles were rinsed three times with stream water before sample was collected and the bottle was capped. The rinse insures riding the inside surface of the bottle of any impurities. Each bottle was labeled by site location and time. This information was also recorded in a field notebook. After collection was complete, the samples were taken to the lab for analysis.

2.3.2 Data Collection- Grab samples at storm flow conditions

When rainfall began grab samples were collected from both locations. In order to collect the grab samples at the same time, two people were needed; one person at each site. The collection would begin at the same time when the secondary Sonde was deployed, and would continue at five minute intervals until either all the sample bottles were used, or the stream returned to base flow. Most often this process started slightly before or right after rain fall began. The same rinsing procedure as mention in 2.3.1 was used when collection storm flow samples.

2.4 Data Analysis- Grab Sample

The Process for analyzing water samples for nitrogen is relatively simple. To perform this chemical analysis a Hatch Surface Water Test Kit was used (Figure 5). This specific kit comes

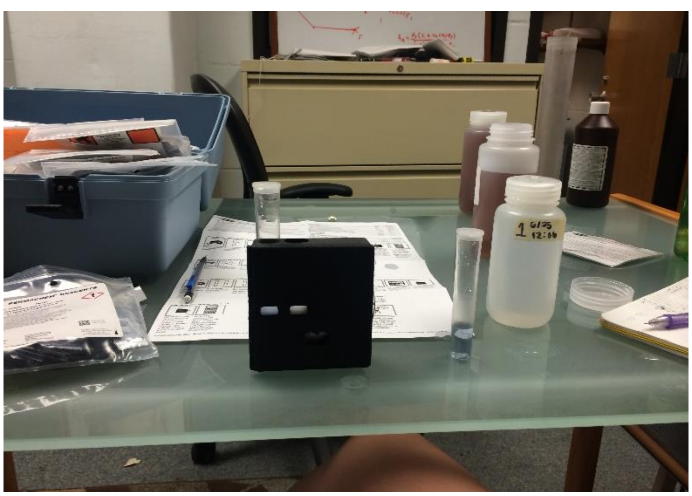

Figure 5. Phosphate test with color comparator from surface water test kit (Elizabeth Erwin 7/01/2015)
dfd

with the materials needed for testing of nitrate nitrogen, orthophosphate, dissolved oxygen, chlorine, and Nitrogen ammonia. For this study, the nitrate nitrogen and orthophosphate tests were used in order to analyze levels of nitrogen and phosphorus in mg/L. The nitrate nitrogen test requires 5 mL of sample water. First obtain the color comparator, which is a device that has an interchangeable color coded plastic wheel and two slots available for holding sample tubes. Take the colored disk for nitrate nitrogen that uses the nitraVer III method and place it inside the color comparator. About 1 mL of sample was poured into two test tubes provided in the kit. These tubes are marked with a fill line, which is around 1 mL of fluid. Insert one tube of sample into the left compartment side of the color comparator. A pillow powder packet of NitraVer 5 Nitrate Reagent was opened and added to the second sample. Then the tube was capped, and shaken vigorously for 1 minute. The sample must sit for one additional minute before inserting into the right side of the comparator. Then the device was held to a light source, and using the color wheel to change the color shade, the shade of the sample that has the reagent added was matched with the color on the wheel. The wheel has a numbering system that indicates how much nitrate nitrogen is in the sample in mg/L. This number was multiplied by 4.4 in order to obtain the amount of nitrate in mg/L. Low levels of nitrate nitrogen are a pale yellow color, while high levels of nitrate nitrogen turn a dark yellow to dark brown color. All samples were recorded in a field notebook. The following information was written down for each sample collected: weather during collection, sample tube ID, date collected, sample location, time collected, date tested, time tested, mg/L of nitrate nitrogen, mg/L of nitrate (x 4.4) and notes. This information was also recorded in an online spread sheet using google drive.

The test for orthophosphate is very similar to the test for nitrate nitrogen, however there are a few differences. First, the sample must be assessed for low-range (0-1 mg/L), mid-range (0-5mg/l), or high-range (0-50) mg/L. In order to do this, the test for low range levels of orthophosphate must be completed. If the resulting color is so dark that it reads off the high end of the scale, the process was repeated using the directions for mid-range, and if it continued to read darker than the high end of the scale, it was repeated a third time using the high range instructions. Each set of instructions vary slightly. Most of the variations include how much sample was added to a pillow powder packet of PhosVer III, the time it takes for the sample to react to the reagent, and how much the reading from the scale window is divided by. For example, for low-range samples the reading number must be divided by 50 while sampled for mid-range must be divided by 10 to obtain the amount of phosphate. All ranges of sample reads in mg/L of phosphate, and must be divided by three in order to obtain the mg/L value of phosphorus. For this study, only amounts of phosphate were analyzed.

All of the data collected was organized into an Excel file. Excel was used for organizing data and creating graphs. There were several data sets that were collected. In the first few weeks of June, two storm flow sample sets were collected. However these samples were collected about five days before they were tested. This time period was a result of not having the correct sample materials available. The storm flow samples aged for five days, allowing for microorganisms to consume amounts of phosphate and nitrate nitrogen. Both nutrients were lower than expected for storm flow. This is attributed to the aging of the sample. Uncertainty about if aging of the samples was the cause of deterioration or not arose. To address this, a sample set was collected. This sample set consisted of two samples of water from the LEWAS site during base flow. Both samples were collected at the same time. Two samples were collected at the same time at three different times during the day. One set of samples was tested immediately after collection, while the other set was allowed to age for five days. The nutrient levels significantly deteriorated in the samples that were allowed to age.

3. Results and Discussion

3.1 Base flow trends at both locations

The graphs as shown in Figure 6 and 7 show the four different parameters studied and how they varied over the three day base flow analysis. Fig. 6 demonstrates that there was little variation within the parameters studied. There was little to no change over the three day period for Specific Conductance, Phosphate, and Nitrate Nitrogen. Turbidity had a very slight change, however Turbidity can easily spike to the three hundred to five hundred range from a rain storm. Therefor the change that is displayed in turbidity in figure 6 is miniscule.

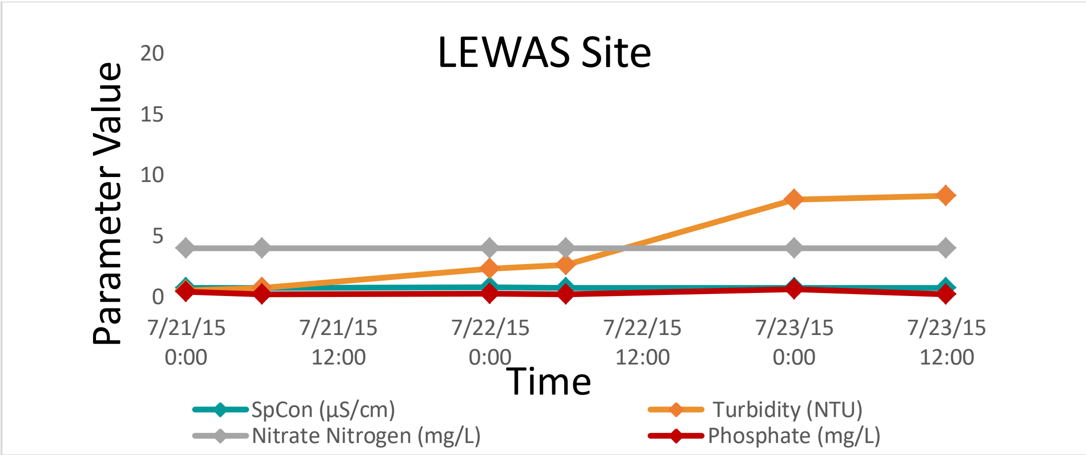

Figure 6. Base flow analysis at the primary LEWAS Site

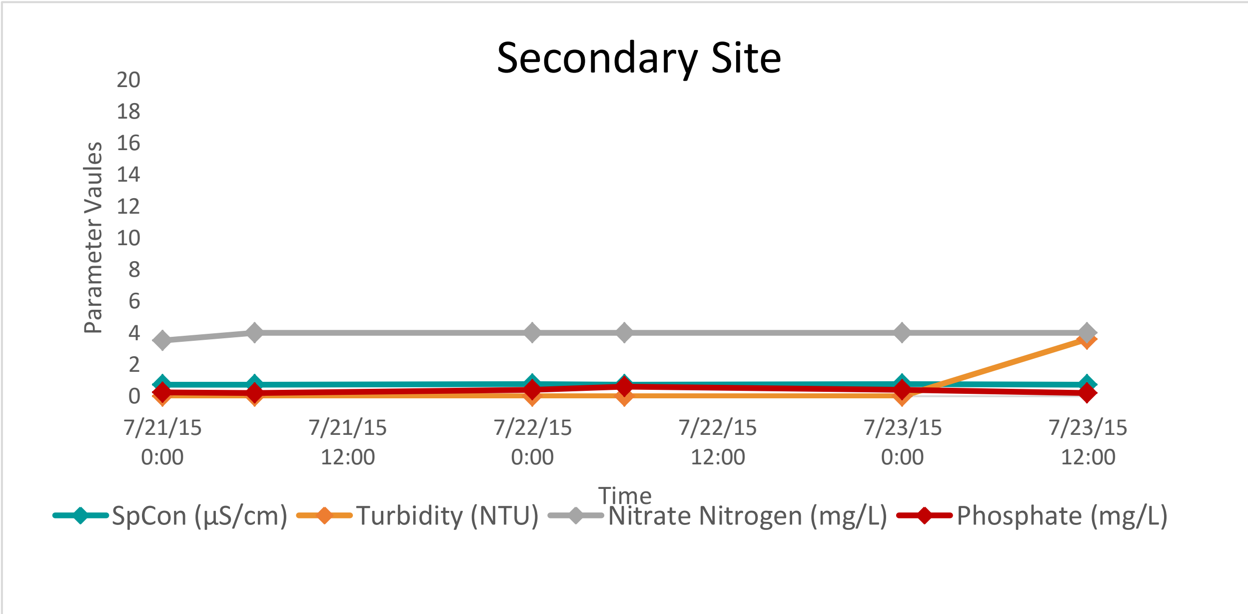

Figure 7. Base flow analysis at the secondary site

Figure 7 shows the parameters studied at base flow conditions from the secondary site. As the LEWAS site showed, the secondary site also shows little to no variation as well. Turbidity is the only parameter that shows any variation, and it is again such a small amount of change (less than 5 NTUs) that it is considered insignificant. At both locations the change in Turbidity may be due to the accumulation of Algae on the Sondes (see figure 8). The algae grows very quickly, even when the Sonde is well maintained.

Figure 8. Sonde at the LEWAS Site with algal

At base flow, there were only a slight changes in the phosphate values whereas the nitrate nitrogen values were overall a steady 4.0 mg/L. For this reason, nitrate nitrogen was not further analyzed in this study at base flow.

At the LEWAS Site during base flow conditions there does not appear to be any relationship between phosphate and specific conductance. The R^2 value is less than 0.1 which indicates that the relationship found explains less than 10 percent of the data values (shown below in figure 9). At the secondary site, the same parameters were plotted against each other to find a relationship. The shown in figure 10 below, clearly shows that there is no relationship as the R^2 value is again less than 0.1.

Turbidity and phosphate had a slightly higher R^2 values at base flow conditions than phosphate and specific conductance (see below figures 11 and 12). However this value was less than 0.2, which accounts for less than 20 percent of the data points.

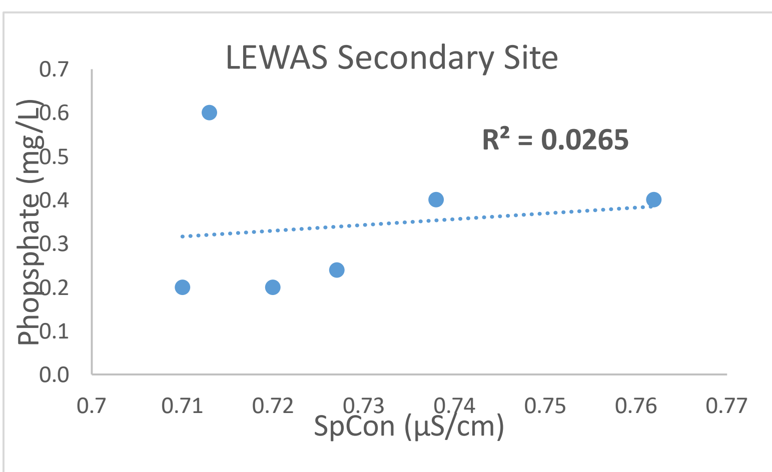

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Figure 9. Specific Conductance and Phosphate values from the LEWAS site during base flow conditions

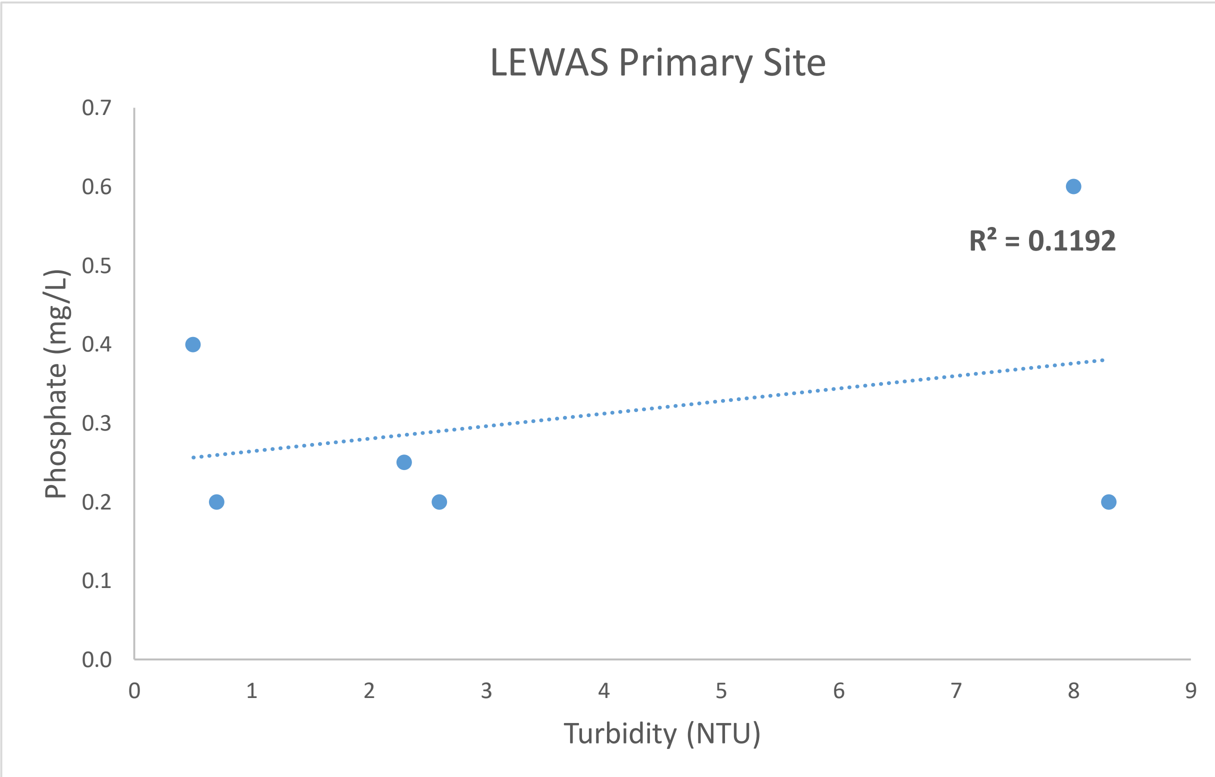

Figure 11. Base flow conditions of the LEWAS primary site with comparison of Turbidity and

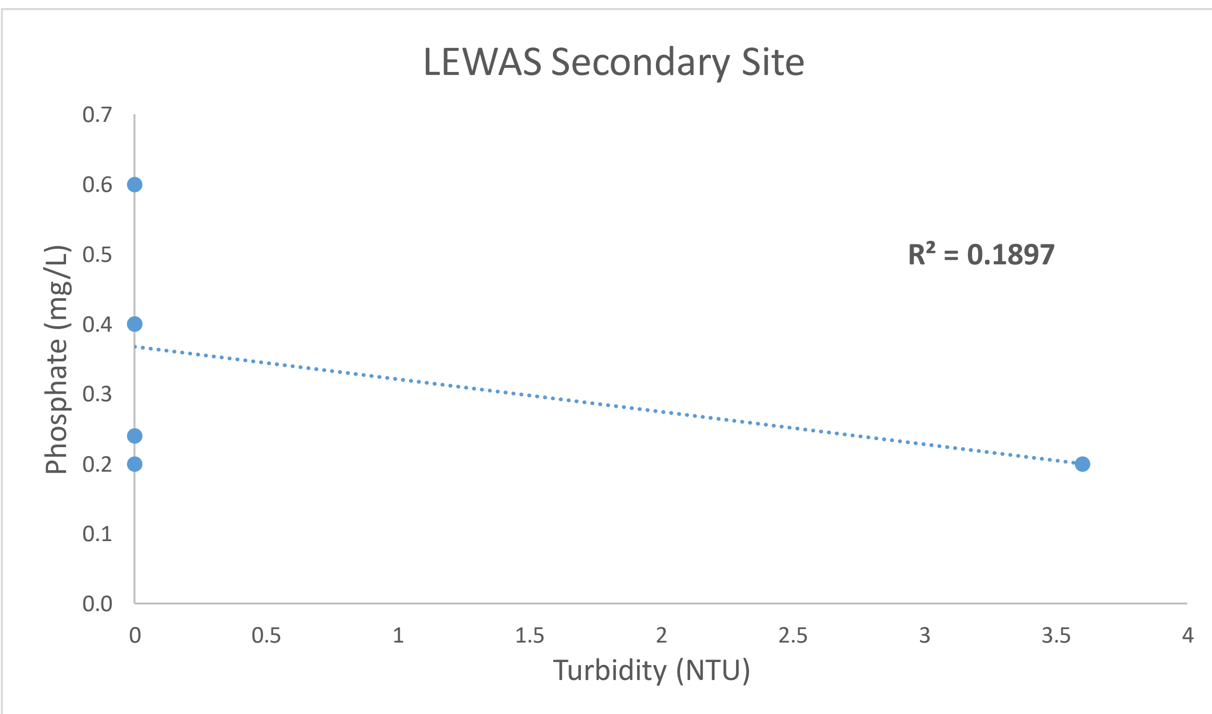

Figure 12. Base flow conditions at the secondary LEWAS sites comparing turbidity and phosphate

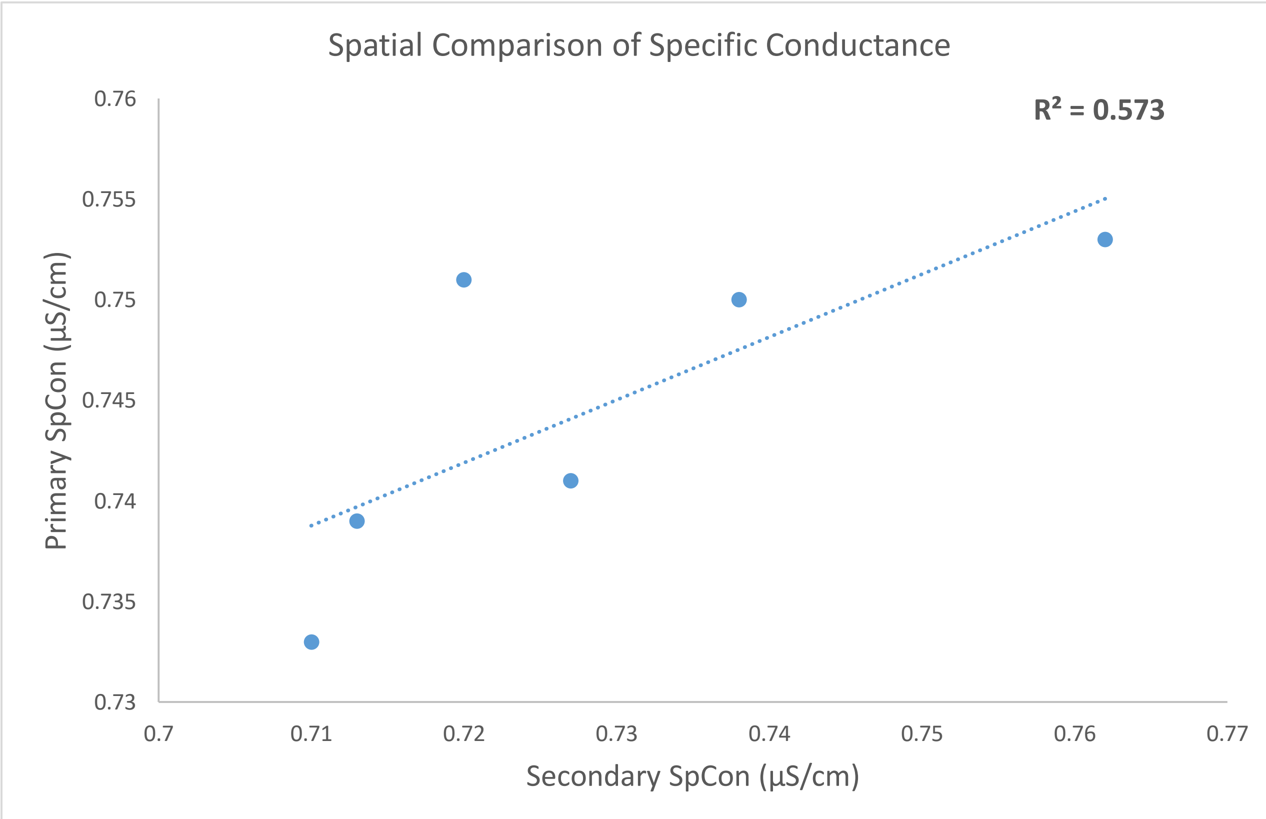

Figure 13. Comparison of both sites specific conductance values

It was discovered that the best R^2 value came from a spatial analysis between Specific Conductance. This value was slightly over 0.5 which relates to fifty percent of the data points. There may be a possible relationship between these locations and this parameter. There were no relationships found between the nutrient parameters.

There are several limitations in this study. The base flow analysis was only preformed for 3 days, resulting in a small sample size (n=6). Therefor further investigation is needed. There is a lack of variation in parameters due to base flow conditions. This study was very constricted by the weather. Storm flow is where the biggest variation is expected, however during the time allotted for this study, it did not storm when the stream could be properly analyzed and samples collected. At base flow, there is nothing new flowing into the stream. It is expected to see more variation at storm flow because of the first flush effect. Another limitation is instrument sensitivity and accuracy. There is some error involved with each sample analyzed for nutrients as well as the parameters measured by the Sondes.

On July 23rd 2015, The LEWAS alert system sent out an email indicating that the turbidity suddenly spiked to over 500 NTU. This alert allowed for a case study to be performed on the stream. The same procedure was taken as if it was caused by storm flow. Grab samples were taken in five minute intervals. The trends are displayed in figures 15 and 16. Figure 16 shows little to no change for phosphate specific conductance and nitrate nitrogen. There was a slight decrease in phosphorous at the beginning of the sample collection period. This is believed to be from dilution from the tap water flowing into the stream. When a rain event occurs we expect to see higher amounts of phosphorus with higher amounts of turbidity because phosphorus attaches to sediment and soil particles. However, during a rain event, the soil that is carried into the stream is primarily top soil coming from the O horizon. The O horizon contains mostly organic matter and higher amounts of phosphorus. The water main break occurred approximately 6 feet underground. The soil at this depth does not typically contain high amounts of phosphorus. Therefore the additional water being added to the stream from the break, did not add any phosphorus to what was already present, and diluted what was already in the stream. The Turbidity reading in figure 15 begins at 160 because by the time the first sample was collected, the stream had significantly cleared up. The nutrient values were analyzed and plotted against each other in figures 17 and 18.

Figure 14. LEWAS Site during water main break (LEWAS monitoring camera 7/23/2015)

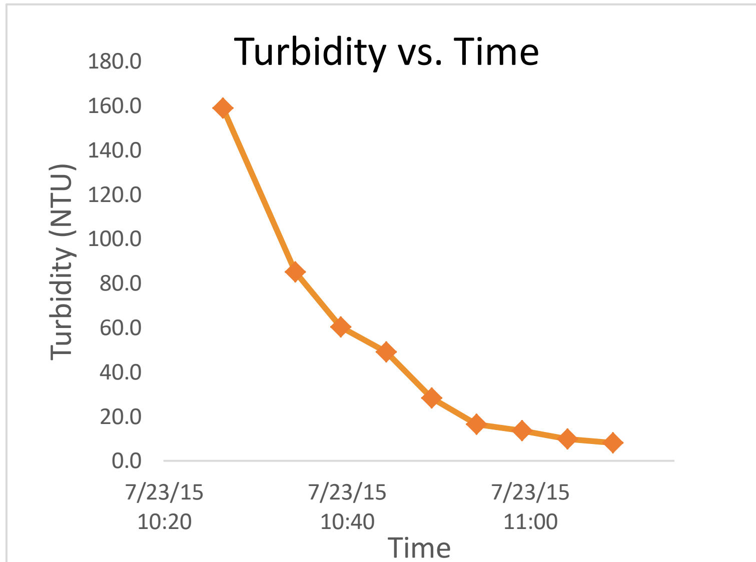

Figure 15. Line graph of Turbidity during water main break

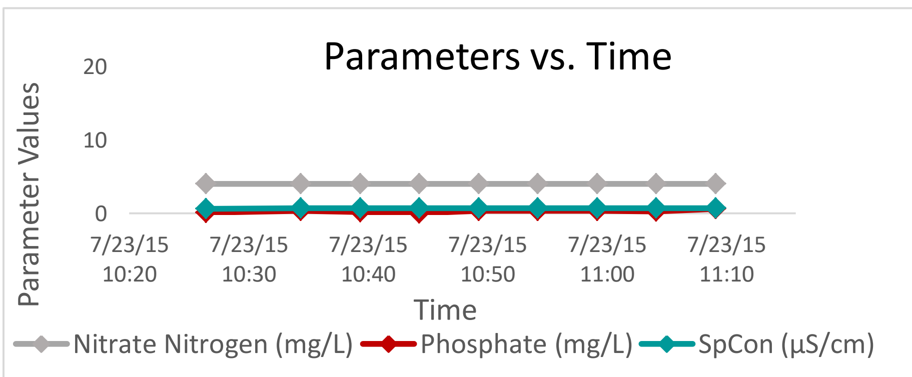

Figure 16. Shows trends of parameters during water main break

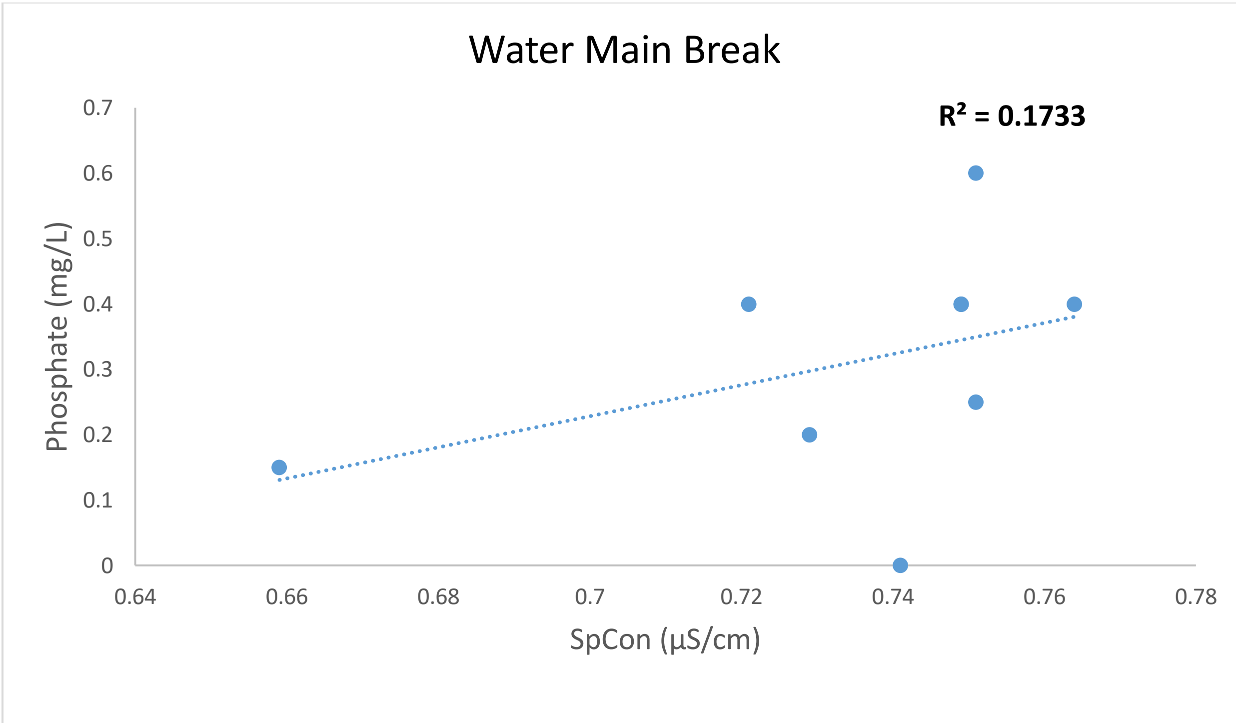

Figure 17. Water Main break on Jul 23 2015- comparison of phosphate and specific conductance

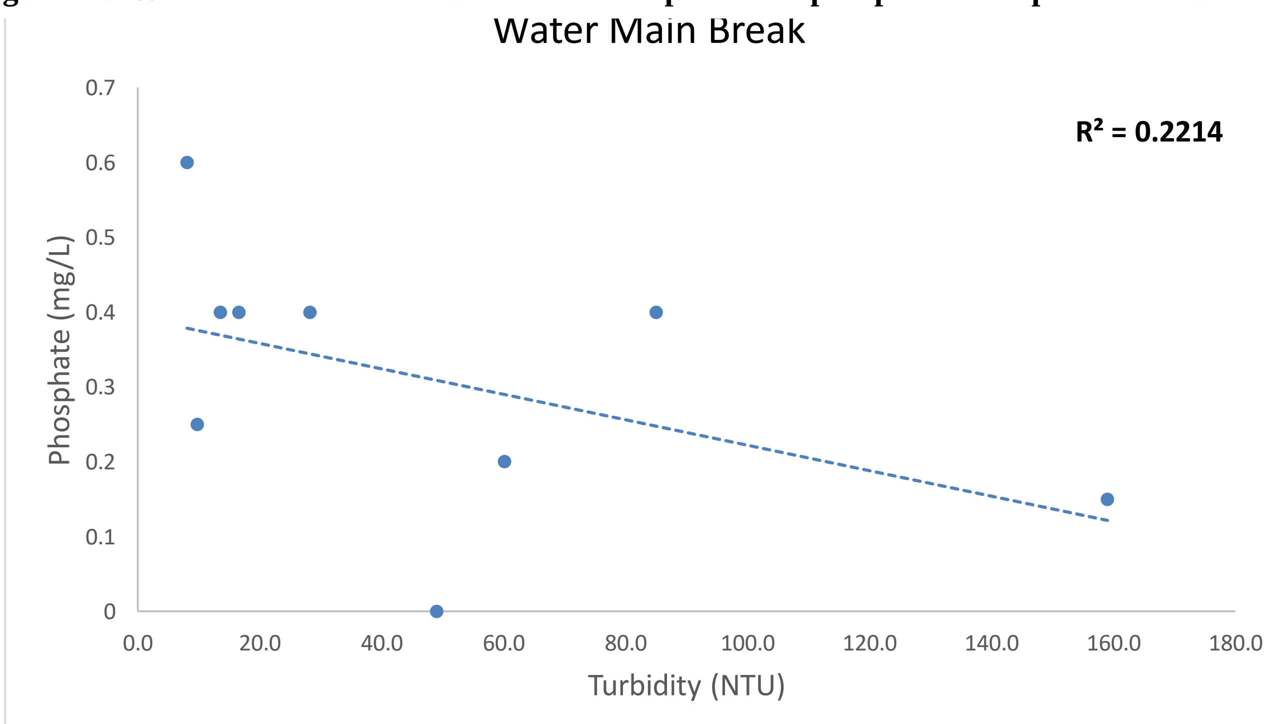

Figure 18. Water Main break on Jul 23 2015- comparison of phosphate and turbidity

phosphate and phosphate and specific conductance. However the R^2 values are too low to be able to develop an empirical relationship. Also a water break, is a case study, and is not a situation in the stream that regularly occurs such as storm flow.

4. Conclusions

Over all, this study found that empirical relationships are difficult to establish at base flow conditions due to minimal variation in the parameters measure. With no variation, a relationship cannot be formed. In addition, this study indicates that there may be a potential spatial relationship with specific conductance at base flow conditions. Further measurements need to be taken, and longer sampling periods are necessary to come to a solid conclusion on what this relationship may be. Additional data collection is needed during storm events in order to formulate proper surrogate relationships between the different parameters. Storm flow is key, due to the first flush effect, and the variation that is expected due to the introduction of runoff water. Therefore storm flow events must be analyzed in the future. Finally this study needs to be carried out over the course of at least one year. Each season is different in Blacksburg, VA. The seasonal differences relate to the weather, rainfall, temperature, and sunlight which is why a yearlong study is highly suggested in the future.

5. Acknowledgements
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Marcus Aguilar- assistance with R coding
NSF/REU Interdisciplinary Water Sciences and Engineering Cohort

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Implementation of the LEWAS Lab at Virginia Tech User Interfaces in a Professional Environment

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Abstract

The Learning Enhanced Watershed Assessment System (LEWAS) is a unique water quality monitoring system created at Virginia Tech. Although this system was originally intended for educational use, it is also used by professionals as well. Most of the LEWAS data collection tools have been designed with the idea of being used for research and education. Through this REU project, the design of a data collection tool that is geared toward professional use in the LEWAS lab is explored. A procedure was also developed to find locations contributing to pollution in our watershed. This procedure was ultimately created to serve as a new tool for the LEWAS lab to be used to assist both academics and professionals in collecting data from the LEWAS field site. A survey was created to gain qualitative and quantitative data from facilities services and the town of Blacksburg on how to create a data collection tool with their input in mind. Unfortunately the data was not collected over the finite amount of time this research program allows. However, the conception of the procedure created an opening for a user interface to be created that allows for pictures from the procedure to be uploaded into the LEWAS data base. The procedure and user interface are designed to be used by students, researches, and professionals and will be expanded upon by the LEWAS team in the future

Keywords: user interface, watersheds, data analysis, real-time data, hydrology, data monitoring, water data, database

1. Introduction

Virginia Tech is home to a water quality project known as the Learning Enhanced Water Assessment System (LEWAS). This project started its life out as a Ph.D. dissertation in 2009 (Brogan, Lohani, & Dymond, 2014), and has now been formed into a real time water quality lab that has the ultimate goal of being used as an education tool throughout engineering and environmental science curriculums (Basu, Purviance, Maczka, Mr. Brogan, & Lohani, Work-In-Progress: High-Frequency Environmental Monitoring Using a Raspberry Pi-Based System, 2014). The LEWAS lab is currently composed of around 15 scholars and researches, ranging from full professors to undergraduates. Different areas of expertise that each of these people possess help to keep the LEWAS lab interdisciplinary is nature, which is a core value to the LEWAS team. Engineering Education, Civil and Environmental Engineering, Electrical and Computer Engineering, Computer Science, Environmental Sciences, and Geology are all majors represented by people working in the LEWAS lab (The LEWAS Team, 2015). This team is in charge of controlling and expanding the application of the current system. Regular maintenance is also needed to –keep the entire system running at the highest accuracy and efficiency possible. By keeping the team of the LEWAS lab interdisciplinary, input from a large number of science realms can be accounted for in advancing this system to be used for more ambitious applications in the future.

The LEWAS field site is implemented in Stroubles Creek, a small water network that runs through the western part of the campus at Virginia Tech. The field site is in the Webb Branch Watershed that is about 95% urban is located at the bottom of the watershed (Clark, et al., 2013). The field site is composed of a series of instruments that are used to collect for data analysis as well (Basu, Purviance, Maczka, Brogan, & Lohani, Work-In-Progress: High-Frequency Environmental Monitoring Using a Raspberry Pi-Based System, 2014). This allows for patterns to be observed from relationships between the water and the weather conditions, which could be an extremely useful tool when looking at the water during a drastic change of conditions. All of this data is sent through a system that has been created by the LEWAS lab team to present all this data on different user interfaces. The most commonly used interface is seen on the LEWAS lab website and is known as the Online Watershed Learning System (OWLS). All data obtained from the LEWAS field site can be shown on the OWLS on a three axis graph, allowing the user to compare three parameters over a set amount of time. By having all of this observable data available for the LEWAS lab team, doors are opened to find relationships between different sets of data that could be presented as educational experiences for students, researchers, and other interested parties.water quantity, water quality, and weather related data. Water quantity data consist of stage, smoothed velocity, and flow to all be calculated in real time. Water quality data consist of pH, dissolved oxygen, turbidity, specific conductivity, water temperature, and oxidation-reduction potential. Finally, weather data consist of air temperature, humidity, air pressure, rain rate, and inverted rain rate to be collected

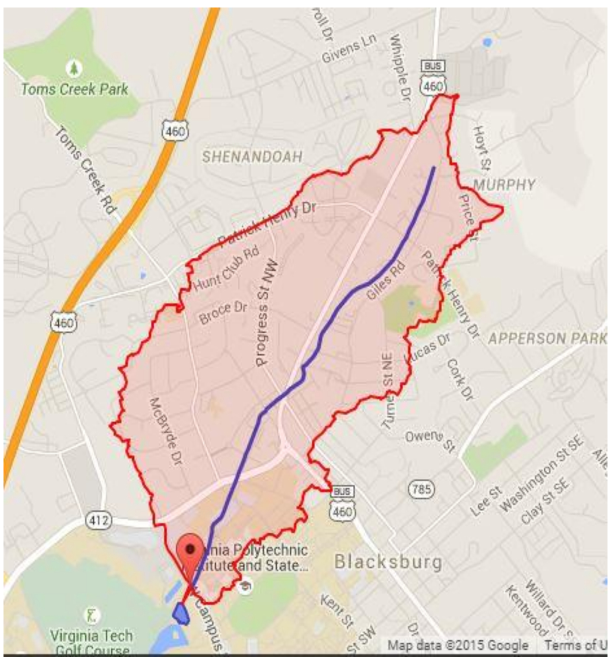

Figure 21: Webb Branch Watershed, LEWAS Field Site Marked
(Webb Branch Watershed, Overhead View, 2015)

Figure 20: The LEWAS Lab Field Site (Fry, 2015)

As previously stated, the LEWAS field site is made up of a series of instruments all working together to retrieve the status of the water and weather at the site in real time. The field site includes a water quality Sonde (Hydrolab Sonde MS5), which is installed at the site in Webb Branch and fixed into the stream to analyze the quality data of the stream such as pH, dissolved oxygen, temperature, and oxidation-reduction potential (Equipment, 2015). The Sonde works by using several probes all with jobs in measuring the quality data, but since this instrument is fixed in the water it can take constant real time measurements of each parameter (OTT, 2006). A Doppler current profiler (DCP) (Sontek Argonaut SW) is also fixed at the bottom of the creek to take velocity measurements for several cross sections of the stream (SonTek, 2007). This allows for a smoothed velocity value to be calculated as well as a flow parameter to be calculated, due to the fact that the cross-sectional area of the stream is known at the point where the DCP is installed (Equipment, 2015). A weather transmitter (Vaisala Oyj, 2012) allows for data to be collected outside of the water and gives us parameters like air temperature, humidity, wind, pressure, and other weather related data (Equipment, 2015). More instruments are on the field site but are currently not connected for real-time data collection (McDonald, Personal Communication). The field site also includes a camera that sends real time video footage of the LEWAS field site, giving a visual image to the data that is being presented on the user interface. The purpose of the camera is to make sense of the incoming data during large events. These instruments are planned for future expansion of the LEWAS system, and were a possible task to be completed during the summer of 2015. During event such as rain storms, the changes in data can often be seen visually through the camera and connect visual experiences with the incoming data. Each of the LEWAS field site instruments update anywhere from every 1-3 minutes, and are graphed over a certain time frame on the user interface (McDonald, Dymond, Lohani, & Brogan, 2014).

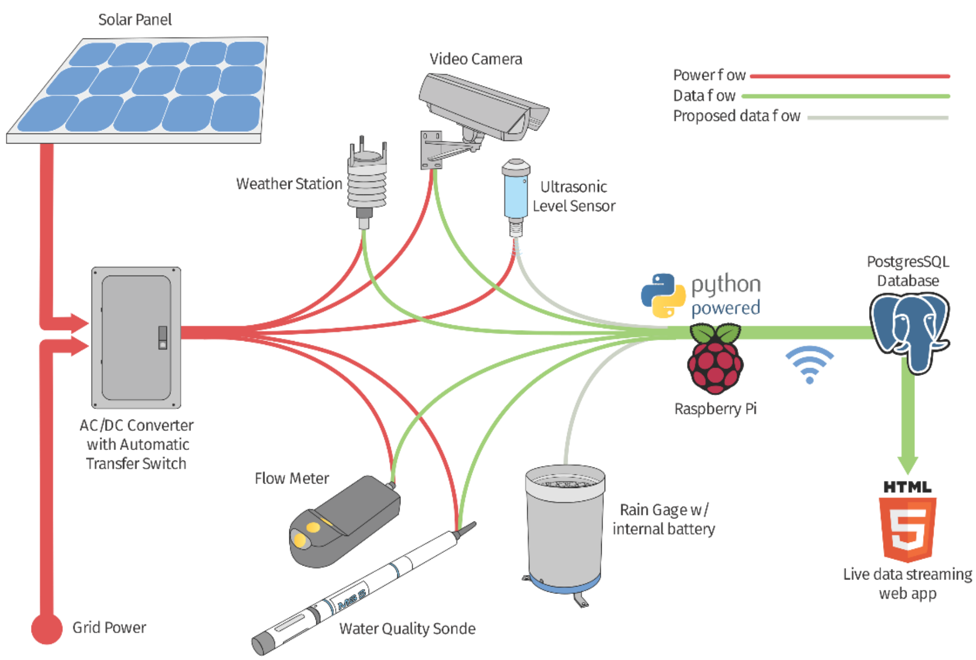

Figure *22*: A diagram of the LEWAS system *(Welcome, 2015)*

Figure 24: Sonde deployed at LEWAS field site (Fry, 2015)

Figure 23: The LEWAS field site (McDonald, 2015) with permission from authors.

The LEWAS lab system and project was originally designed to be an educational tool used by students and researchers in academia to better understand urban watersheds, but the LEWAS is not only a passive system. The results from the LEWAS can be used to help interested personal take action, provided a suitable interface to the data collected by the system. The original user interface to present the data from the field instruments was the OWLS, but it is not the only method of user interaction with the data from the LEWAS (figure 6). The user interfaces that have been applied to the system to present the data through different manners were designed toward the audience of engineering students and professors. Over time, this system has expanded to be used by facilities services at Virginia Tech to help manage the stream and watershed system running through the campus. There has been some effort in designing a user interface to serve the needs of facilities services, such as developing an alert system that sends an email when one of the water parameters is outside of an acceptable range own engineers from Blacksburg, Virginia, the location of Virginia Tech, are also know to use the LEWAS lab when investigating the condition of the local watersheds. In order to improve the user interface experience, more information is needed to provide direction from the users of the services that the LEWAS lab provides. The purpose of this study is ultimately to fill the need for finding this information and give direction to improving the LEWAS. This will allow for the LEWAS lab to not only serve an educational purpose, but a professional one as well. This will ultimately allow for the LEWAS lab to grow and be used by an increasing number of parties into the future.

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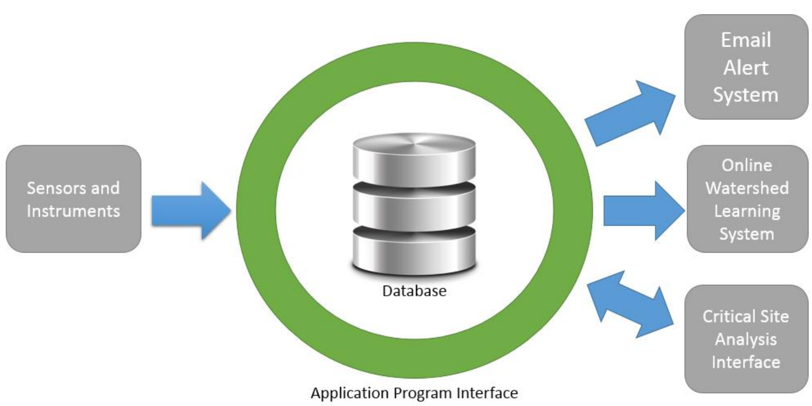

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Figure 25: LEWAS User Interfaces and Interaction with Database (Fry, 2015)

2. Research Methods

To be able to find out what type of features and functions are desired from a professional standpoint of Virginia Tech facilities services and the town of Blacksburg, a measurable form of qualitative or quantitative data must be obtained. Due to the amount of time that this study allows over the 10 week Research Experience for Undergraduates (REU) summer period, getting qualitative data from engineering students who are familiar with the LEWAS lab have proved to be extremely difficult. With this in mind, we know that it would not be beneficial to include engineering students in the survey. By gaining qualitative data from the professionals in this situation, we can explore the issue through a different lens than through the one that we define ourselves (Baxter & Jack, 2008). Qualitative studies can allow connections to emerge that might otherwise be overlooked by the researcher in a quantitative design. We also know that the experts in this realm of study, being the engineering professionals is this case, perceive data differently than novices in this realm of studying, being the students using LEWAS for educational purposes (Jarodzka, Scheiter, Gerjets, & van Gog, 2010). This allows us to expect differences in what professionals what from the LEWAS compared to the desires of engineering students.

Although the LEWAS lab was originally intended to be used as an educational tool, facilities services is already using the system to help with their professional work. To perform this implementation into the LEWAS lab, direction is needed from data obtained from the parties on interest in this situation. LEWAS has already developed a system that is directed at being professionally used by facilities services at Virginia Tech. This system works by automatically emailing facilities services (or any other subscribers) when a parameter of the water quality at the LEWAS test site has moved out of a predetermined acceptable range. In short, if the field site instruments obtain unusual data, subscribers receive an email containing the parameter and value that triggered the alert as well as a current photo taken by the field site camera. This system was turned off at the beginning of the summer 2015 REU program due to some technical difficulties with the Sonde, but was turned back on once the technical problems were resolved two weeks later to complement this study. Gaining data and information about how well the email alert system works for facilities services at Virginia Tech will inform future interface design to make the LEWAS more useful for professional users.

Virginia Tech is located within the town of Blacksburg, Virginia. Even though the town has a relatively small population that is approximately 50,000 (Town of Blacksburg, 2015), and over the summer included a large amount of construction in the area. These construction sites could be causing water pollution to be moving into the creek and into the water systems upstream from the LEWAS lab field site. Due to the location of the LEWAS field site at the bottom of the Webb Branch Watershed, it is known that any type of erosion and sediment runoff in those constructions site located upstream in the Webb Branch Watershed will ultimately move into the stream and pass through the LEWAS field site. Because of this, the LEWAS lab can be used as a tool to see if construction in the area could be leading to an increasing amount of sediment and pollution entering the Webb Branch Watershed. This brings the town of Blacksburg as a party of interest as it could the LEWAS lab to investigate the erosion and sediment control methods of the construction sites and compare them to the policies set up by the government in the area. This could lead to more enforcement of these erosions and sediment control policies if more information on the watershed quality is given to the town of Blacksburg. Creating features in the LEWAS could allow for this type of system to be better used by the town of Blacksburg in a professional standpoint to help enforces these policies and better trace the source of large spikes in water parameters that are recorded at the LEWAS field site. This could include features such as a map of the watershed with current construction projects listed on it, as well as a simple list of construction sites and locations. With this in mind, it is critical to collect input from the town of Blacksburg as well as facilities services at Virginia Tech.

Part of the time the LEWAS lab spent during the summer 2015 REU program was used to develop a procedure to propose to the town of Blacksburg to to collect data from critical sites from critical sites in the Webb Branch Watershed. The LEWAS team was successful in creating this procedure. With communication from the town of Blacksburg, all construction sites within the watershed were identified during the month of June 2015. These sites included everything from road repair to building full infrastructure from the ground up. These construction sites were considered "critical sites" from water quality impacts perspective to the Webb Branch Watershed and a measurement site on the creek was implemented as well. We define a critical site to be a location that has a significant risk of creating an abnormal increase in parameter values of water quality through a release of erosion, sediment, and pollution (Fry, 2015). Finding these critical sites will allow for a procedure to be developed to investigate the impact that these critical sites impose on the watershed. This system was already of interest to the LEWAS lab, but it could also be considered a new procedure to directly benefit the town of Blacksburg and the rest of the surrounding region.

Compared to a quantitative study, a qualitative study often involves defining fewer terms when designing a survey and allowing for more open ended questions to be present. By doing this, the main forms of information obtained are themes and patterns (Creswell, 2009). By allowing for more opened ended questions to the parties of interest, common themes will begin to appear that may inform where to take action. The common themes give us an idea of what professional users of the LEWAS want from the data collection tools provided. Using open ended questions also can be thought of as an informational "gold mine," as you are revealing the thought process participants on using these LEWAS user interfaces. (Singleton Jr. & Straits, 2009). This is all in comparison to performing a quantitative study, which would allow for more deductive modeling to be used but give up the in depth analysis as a tradeoff (Creswell, 2009). Quantitative studies often have more closed ended questions, which can seem appealing at first due to the fact that they are typically easier to answer by participants (Singleton Jr. & Straits, 2009). Although the advantage of using the numerical modeling that a quantitative study would allow seems very attractive, it is not possible to perform due to the lower number of people available for this study. For a solid quantitative study to be used that would allow for numerical statistic to be applied to the results found, the general rule calls for 30 people to take part in the study. Since both Virginia Tech facilities services and the town of Blacksburg would both allow for less than 30 people to take place, it is more appropriate to bring a qualitative study forward over the quantitative study. It is possible to expand upon the study to neighboring Virginia towns, such as Christiansburg, Radford, and Roanoke. This would allow for a higher number of people to be included in the survey which could bring the idea of a quantitative study and the numerical modeling attached to it in the realm of possibility. Since the end goal of this project is to design a new interface or make changes to an existing one, qualitative data is more valuable in designing a system to cater to a small number of people. Qualitative data will allow for us to directly discover what is wanted from the professional parties of interest, rather than just making an assumption from a quantitative set of data. A quantitative study can be performed to later assess the success of the new interface on a larger population to gain even more information on how the user interface can be improved.

This qualitative study came in the form of surveys and interviews. Two surveys were written for this project; one being created for current users of the LEWAS system and the other created for new users. The surveys asks how useful the OWLS and the email alert system has been in their profession and how it can be improved from there standpoint. These questions toward the end of the survey ask how these systems can be better focused to be more useful for their professional work. These questions are mostly open ended, allowing for the information to be qualitative and focused on a more personal level with these parties of interest. These surveys were designed in a similar format that was used on a previous survey given to hydrology students at Virginia Tech, (McDonald, Brogan, Dymond, & Lohani, 2015). Including the data from hydrology and urban hydrology courses at Virginia Tech will allow for a comparison to take place between the educational and professional use of the LEWAS. The results of the previous study are presented in the results section of this paper so a comparison may be able to take place.

On top of the overall research objective that comes with this study, many different side projects were performed in order to become more familiar with the LEWAS lab as well as its function at Virginia Tech. These projects would range anywhere from creating videos explaining the watershed to new users of the LEWAS to maintaining social media. Routine maintenance on the Sonde was also performed, as it helped gain hands on knowledge of how the system works and how data is retrieved at the field site. This maintenance also prevented damage to the system and made sure all instruments were functioning properly. The Sonde also needed to be calibrated about once per month. This would ensure that the Sonde was reading parameters accurately. Performing this job allowed for a deep understanding of the instruments of the LEWAS field sights and the amount of delicacy these object possess. This side projects allow for the researcher performing them to become familiar with the LEWAS and fully understand its potential when moving forward in research with LEWAS as a tool. The LEWAS is not an automated system, and requires human effort to keep the system running. Calibration and maintenance are all key parts of allowing the system to work to its greatest ability.

Overall, the research methods of this project have been broken down into three different task. The first of which is to design a procedure to collect data from critical sites located along the Webb Branch Watershed. The second part is obtaining qualitative data from facilities services and the town of Blacksburg at Virginia Tech through surveys and interviews to find out what is needed from these parties in respect to the LEWAS lab user interface. These data will all be compared against the previously obtained data that contains information on the OWLS interface and LEWAS lab in the eyes of hydrology students at Virginia Tech. All of this information will be taken into account to improve and update the LEWAS through a new interface with the remaining time of the REU program. If possible within the 10 week allowed for this study, the surveys will be expanded to include town engineers from neighboring cities, such as Christiansburg, Radford, and Roanoke.

3. Results and Discussion

3.1 Upstream Investigation Procedure

To be able to develop a procedure to investigate the upstream water conditions and what critical sites affect the stream turbidity, the term critical sites would have to have a solid definition. This can be seen through areas like waste sites or any other location that has the possibility of releasing harmful matter into the watershed. For this project, areas under construction in the Webb Branch Watershed are the main focus. If construction sites do not meet the standards set for erosion and sediment control, it is possible for soil erosion, water pollution, flooding, or damage to downstream properties to take place (Erosion and Sediment Control, 2015). At the time of the 2015 REU program, there were four ongoing construction projects that were located within the Webb Branch Watershed (Town of Blacksburg, June 2015). A list is provided in table 1 below.

Table 5: Active Construction in Blacksburg, VA in June 2015 (Fry, 2015)

Project Name	**Location**	**Description**
University Building	Price Fork & West Campus	Construction to create a new building just across the road from the LEWAS field site
Turner Streetscape	Price Fork & Turner	Repaving of Turner St just off of the Virginia Tech campus
Campus Auto II	North Main & Northview	Construction of an auto shop with a location right along Webb Branch
North Main Mixed Use	North Main	Construction a new building next to a dentist office. Located across the street from Campus Auto II

All of these construction sites can represent the definition of a critical site that was stated earlier. To find a measurement site for these critical sites, the nearest and most accessible location to Webb Branch was traced and then pinpointed. Due to Campus Auto II and North Main Mixed Use being so close to each other, there is only one measuring site along the creek that can be used to measure the parameters of interest. Therefore, in this situation we cannot easily separate those two construction sites in respect to how much sediment/pollution they contribute into Webb Branch. The following map (figure 9) shows construction sites (marked in yellow) and measurement sites (marked in red).

Figure *27*: Campus Auto II Construction (Fry, 2015)

Figure 26: University Building Construction (Fry, 2015)

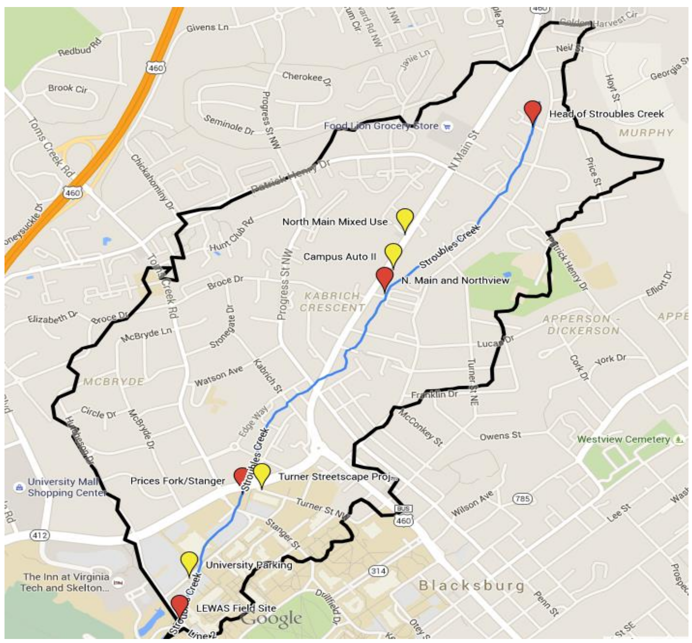

Figure *28*: Critical (yellow) and Measuring Sites (red) in the Webb Branch Watershed (Fry, 2015)

The measuring sites displayed in figure 9 , excluding the measuring site and the headwaters of the creek, were determined by finding the nearest reachable point downstream on Webb Branch from the constructions sites. The headwater site (figure 11) was put into place to act as a control to the rest of the measuring sites, as the water is hypothesized to have the lowest amount of erosion and pollution at this point. Also, since the LEWAS lab field site is near a construction site and at the bottom of the watershed (figure 13), it is logical to use the field site as a measuring site as well. As stated earlier, Campus Auto II and North Main Mixed Use are too close in location to separate them into two different measuring sites, thus they will both be included in the measuring site at North Main and Northview (figure 10).

There are currently very few things that can be measured at these sites with the current set up of the LEWAS system. There are no Sondes deployed at the measuring sites like the one installed at the LEWAS lab (the LEWAS lab only has two Sondes available as of 2015). The Sonde is how the LEWAS obtains most of its data, so another method is required obtain data. The Sonde at the LEWAS field site uses a nephelometer to measure turbidity. Since we do not have this type of equipment located at the other measuring sites, the turbidity can be documented and roughly estimated through photographs of the sites. Using a team of people during large scale events to go to these sites and take pictures, volunteers would get data needed to analysis the construction sites' impact on the turbidity of the stream. This data would then be shared through the LEWAS user interfaces for use by the town engineers or any other interested party. It would also help to geotag these pictures if the equipment is capable, as it would record the time and location of the picture and allow for comparison with data recorded at the same time at the LEWAS site (Maczka).

Figure 30: N. Main and Northview Measuring Site (Fry, 2015)

Figure 29: Headwater Measuring Site (Fry, 2015)

Figure 32: LEWAS Lab Measuring Site (Fry, 2015)

Figure 31: Price Fork & Turner Measuring Site (Fry, 2015)

This procedure will produce data that will aid in estimating to see what critical sites around Blacksburg in the Webb Branch Watershed are contributing to erosion and sediment entering Webb Branch, detected at the LEWAS field site as large spikes in turbidity during storm events. Upon future expansion of the LEWAS lab, Sondes could be deployed, permanently or temporarily, in these locations to obtain more accurate and quantitative data on the water in the stream. These Sondes would have to be installed into the streams in a more temporary setup than the current LEWAS site, as these critical site are dynamic due to changing construction in the area. This could be a semi-permanent set up or deployed during a storm event. A change to the LEWAS database would also need to be set in motion as more Sondes would be added to the LEWAS lab system. This type of expansion could be extremely beneficial to this system. Pictures are an acceptable way to be able to visualize the turbidity of the stream at each point, but numerical data would provide a much stronger cause when comparing these sites and how they contribute to Webb Branch's pollution.

There have been attempts to practice this procedure during the large scale rain events that occurred in Blacksburg over the summer of 2015. The first attempt at completing this procedure comprised of two people out in the field collecting data. Due to the small number of people working to gather data it was extremely difficult to obtain pictures at the same time. This procedure was also performed during the night. The camera used during this procedure, a GoPro Hero 4 (GoPro, 2015), did not have a flash function to capture photographs in low-light conditions. The result of this procedure were pictures that did not capture useful data. Even though the first attempt was not successful, it shows that the procedure is able to be performed in large scale events.

3.2 Facilities Services/Town of Blacksburg Survey

A survey was given to facilities services and the town of Blacksburg in order to receive qualitative data on their needs from the LEWAS and how the LEWAS lab can satisfy those needs (located in appendix). The survey was originally designed to reflect the questions of a previously designed survey for hydrology and urban hydrology students at Virginia Tech. Through this survey, the idea of open ended questions were very important, as we are trying to get the direct experiences of professional users of the LEWAS lab. Due to the fact that we were creating a system for a professional group, it is critical to allow them to give answers that are personal and direct to their needs. This accounts for the major difference between the surveys directed toward engineering students and those given to professional engineers. The survey includes both multiple choice questions to obtain quantitative data and open ended questions to qualitative data. The survey created is located in the appendix of this paper.

The survey was created and amended multiple times throughout the summer 2015 REU program, requiring submission to the Institutional Review Board (IRB) with each change. The final draft was composed of two surveys: one for current users of the LEWAS system and one for new users. The current user version was released to facilities services and the town of Blacksburg engineers on the eighth week of the summer research period. Data has not been obtained and the LEWAS team is still waiting on this data to come in. Even though the data is missing in this situation, plans to create a new interface based on the upstream investigation procedure were set in motion to be completed before the end of the program. Once the results come in from the parties of interest, the data will be put into consideration in improving the user interface created during this project.

There were many challenges that were faced in the creation of this survey. It was extremely important to create a survey that did not hint the one taking the survey to a certain answer, so questions were carefully written. This took a long amount of time, although necessary to ensure the smallest value of bias possible. When creating a survey with multiple people, many different input were taken account for and for each change an amendment to the IRB was required. These changes ranged from changing names in the invitation email to adding more question into the survey. A few days were required for the IRB to review these changes, so a large amount of changes created a late release data for the survey. The survey was also released in the form of an email, which could easily be mistaken for spam or junk mail. To ensure for the survey to have a higher rate of returning results, a more effective form should be used. Although no data was received in creating the survey, working through its creation allowed for us to looks at our user interfaces through the position of someone using it professionally. Using that information, we were able to use some of our hypothesis in creating the new user interface for professional use. The main purpose of this study to create a new data collection tool, and this was still completed regardless of the challenges face.

3.3 Creating the New User Interfac

Once the procedure was create to take pictures and measure the impact of the critical sites, a way to gather data from the procedure was needed. One way would be through a web-based interface to allow a user to upload the pictures taken from the procedure with their smartphone or other web-enabled device. This interface would allow for the both the time and location of the picture taken to be added to the LEWAS database, as well as displayed on a map so the user can see the spatial representation of this information. The idea behind this user interface is that the information found by performing the upstream investigation procedure will be available for analysis in the LEWAS database. Overall, the user interface allows for upstream behavior in the watershed to be linked to downstream behavior. There was not a previous system that was capable of preforming such a task at the LEWAS lab, so this interface serves a useful purpose in expanding the LEWAS as well. In particular, existing interfaces to the LEWAS data were one-way in that they let viewers interact with recorded data but provided no mechanism for a user to submit data they recorded or observed.

The prototype interface been written using HTML, CSS, and JavaScript. The website at which the user interface is located has been hosted through LEWASpedia, which is the server the LEWAS lab runs online internet services through. This user interface also uses a JavaScript library called React, also used by applications such as Facebook and Instagram. React allows for multiple users to use the interface and keep the system smoothly updating in real time. The theory behind this idea is that the critical site user interface can be used by multiple people during a large scale event, and the constant updating of the system will let people work together and see each other's progress in real time. So in practice, one person may upload a picture in the field and its information (time and location) will appear on the map. React makes it relatively easy to allow the interface to respond to new data recorded asynchronously so that it will also appear on the map of anyone who has the user interface open on their device. The user interface is formatted with mobile devices being the target system. This will allow for a team to go out in the field during a storm and collaborate to gather desired information with only their smartphone or other web-enabled mobile device. While the critical site user interface can be used in a professional environment to track down the sources pollution in Webb Branch and allow for enforcement of local and federal policies in terms of erosion and sediment control, its design does not limit its use to a particular geographical location. It may be used in any watershed to view and compare data recorded within the watershed.

This user interface works by allowing the user to upload photographs to the LEWAS database. When the application is opened, a map of the Blacksburg area is presented, as well as some information of some of the parameters at the LEWAS field site such as turbidity. Knowing the information at the field site will allow for an instant comparison between where the user is and the conditions of the field site. Pictures can be uploaded on the site from a phone, tablet, or similar device. Since the photograph is taken from a device that is capable of geotagging, code has been written to read the timestamp and geolocation of the photograph recorded by the device. The user interface will upload the picture into the LEWAS database for farther analysis, but it will also present the information from the photograph on the map (figure 16). Multiple users can upload pictures to the database fluidly and all information will show up on the map.

Since the data collected will be available to the public, professional engineers for the town of Blacksburg can use the data to track down sources of large scale pollution into the Webb Branch Watershed. The data that could be found in the future from the surveys and focus groups will also be used to expand upon how this critical site analysis user interface can be improved upon even farther, including how professionals can use this system as a tool in their line of work. There has also been a proposal to include this interface in some hydrology and engineering exploration coursework in the upcoming semesters. This could be used as a method for students to investigate how water quality and quantity parameters change as the water moves down a watershed. Not only has a useful professional tool been created but a strong educational one as well.

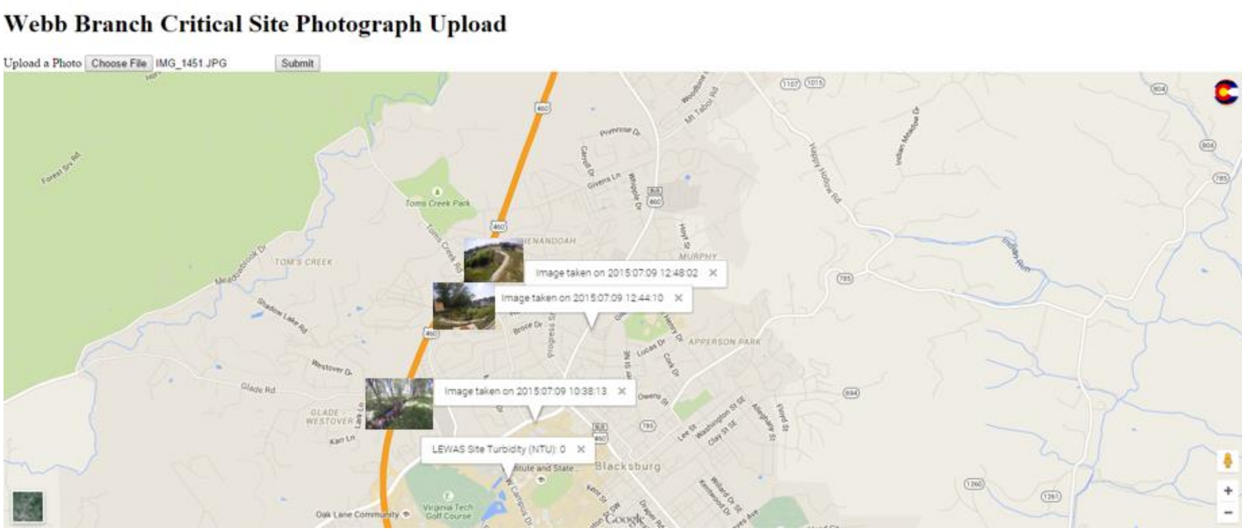

Figure *33*: A Prototype of the Upstream Investigation User Interface after Images have been uploaded (Fry, 2015)

4. Summary and Recommended Future Work

Since the survey portion of this project was unable to be completed in the time available in the 10 week REU period, there is more work that must be completed on the critical site user interface. The system has been completed to the point where pictures can be uploaded into the LEWAS database, as well as display information on the photograph and manual information entered by the person uploading the photograph. This interface, when paired with the upstream investigation procedure, is a potentially effective tool that the LEWAS lab now supports, but improvements and tests are needed for future use of the user interface. This improvements could including using a hashtag system similar to Twitter for organizing certain images with each other. Another improvement could be including “watershed awareness”, where only pictures inside the watershed will be displayed. These improvements would allow for this tool to be more powerful and more relevant to users in both education and professional environments.

As stated earlier, the user interface allows for photographs around the Webb Branch Watershed to be upload into the LEWAS database, as well as display geographic and timestamp information about the photograph. The use of specific JavaScript libraries such as React allow for multiple people to be using the critical site user interface with fluid and constant updating. This also allows for a note taking application to be integrated into the user interface, which gives the user the ability to add manual information about the photo they took. Although these features have great potential for investigation of the watershed, there are a few more features that have been proposed to the user interface. Adding a scrolling widget of the latest pictures that have been upload would allow for data to be more easily presented and accessed by any person using the system, and can easily be compared to photographs at the LEWAS site. This scrolling widget would also display the information manually entered by the uploader through the note taking feature, allowing for critical information of the site to be displayed. To ensure the use of the interface as an educational and professional tool stays intact, the user interface needs to be password protected. This user authentication will work by requiring a password upon entering this application. Once the correct password (which is given by the LEWAS team) in entered, the user interface will work normally with no restrictions. Further improvements may provide a mechanism for users to register themselves and create their own accounts on the system.

To better improve the user interface and the upstream investigation procedure, the ability to provide more information at the critical sites is a great way to expand upon the work done over the summer of 2015. Deploying more Sondes at the identified critical sites would allow for more data to be collected, in addition to just photographic evidence of turbidity. This is an expensive endeavor, as Sondes are several of thousands of dollar each, but it is a possible route to expand upon the LEWAS lab for multiple field sites. Temporary setup of Sondes is also recommended, as this would lead to the ability to move sampling locations when critical sites are removed or added. Temporary set up of Sondes has been used by a concurrent study that was performed in the summer of 2015 REU program using a chain to keep the Sonde on the bank of the creek. This system would make the critical site interface more powerful and usable by students, researchers, as well as professionals.

The original intent of this project was to obtain data from professional parties and use the qualitative data obtained to improve the current systems of the LEWAS to better suit the needs of the professional community. We unfortunately ran out of time during this REU period in creating this survey and did not collect the data that was intended for improving the user interface. The survey is still available online and the LEWAS team plans to analysis the data as intended when it is available. The qualitative data that will be received from Virginia Tech facilities services and the town of Blacksburg will then be used to add features/improvements to the critical site user interface that has been created over this REU period. Since a new user interface has already been put in motion, it would be beneficial for facilities services and the town of Blacksburg to test the system and give their input of the functionally of the system. This would allow the LEWAS to obtain qualitative and quantitative data on how well this new user interface can be used in a professional environment, as well as state what improvements can be made to directly benefit professional users. This will allow for the original intent of the project to be completed regardless of the finite amount of time allowed for the program competition.

Though there has been a test of the upstream investigation procedure using a GoPro Hero 4, the procedure has not been tested with the user interface. To examine how smoothly the user interface works during a large scale storm event, the procedure needs to be tested and the photographs from the procedure must be uploaded through the user interface to the LEWAS database. This test was planned to be completed on the ninth or tenth week of the REU program, but a lack of storms in the later part of the summer in Blacksburg prohibited this test. This test is still planned to be completed by the LEWAS team even after the end of the REU program once a large storm forms in the area. A trial run on this procedure will allow for the LEWAS team to analyze the strengths and weaknesses of the current setup of both the procedure and the user interface. Data that can be received from this test include how easy the user interface is to use on a mobile device in bad weather, as well as how well the system is connected when multiple people are out performing the procedure. Once this data is gathered, it can be used as another source of information on how the system can ultimately be improved as a tool created by the LEWAS lab.

All of these works in progress will allow for the work completed during the summer of 2015 REU program to be improved upon and a beneficial tool to be added to the many different components of the LEWAS lab. The upstream investigation procedure and the corresponding user interfaces are both valuable additions to the system, and can act as a base platform for more advanced tools and uses of the LEWAS. The LEWAS lab has been constantly expanding its presence in the educational realm. During this REU period, members of the LEWAS team travel to India in assisting with setting up a similar system as well as promoting using the LEWAS as a virtual educational tool. Similar movements in assisting a similar system have been taking place in Australia as well. Professional applications may currently only be relevant to Virginia Tech facilities services and the town of Blacksburg, but the creation of both educational and professional tools could let to an increases interest in using real-time water monitoring for similar tasks elsewhere. As the LEWAS team continues its goal to expand its educational use through an anywhere/anytime access setting this project has given the LEWAS a route to expand into a professional direction as well, ultimately transforming the LEWAS lab intto an environment in which professional users and educational users can interact with one another while exploring real-time hydrology data.

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6. Appendix

LEWAS Lab Professional Use Survey

Q25 The purpose of this questionnaire is to gather data about professional use of the Learning Enhanced Watershed Assessment System (LEWAS) which provides access to real-time high-frequency data collected from the Webb branch watershed as well as tools* that make use of these data. If your professional work includes components both related and not related to this data, please answer the following questions only with regards to the component of your professional work that relates to the data collected by the LEWAS.*currently available tools include the Online Watershed Learning System (OWLS) and the email alert system, both described later in this questionnaire

Q1 The Learning Enhanced Watershed Assessment System (LEWAS) autonomously collects high-frequency water quantity (velocity and estimated flow), water quality (pH, temperature, dissolved oxygen, oxidation reduction potential, turbidity, specific conductance), and weather (rain intensity, air pressure, relative humidity) data from a location in Webb Branch where it emerges from under West Campus Drive on the Virginia Tech campus. These data are stored in a database and made publicly accessible.

Q5 Besides the data collected continuously by the LEWAS, are there any other data parameters that you are monitoring? If so which parameters, where are they measured, at what frequency are they measured and are they collected continuously or with grab-samples?

Q6 To date we have been using the LEWAS to do base-line continuous water quality and quantity monitoring do normal precipitation event monitoring send email-alerts when parameters values are observed outside a nominal range What other types of uses or applications in stormwater management can you envision using this system for?

Q3 The online watershed learning system (OWLS) is a web-based data visualization application that makes use of the LEWAS data to present information about the watershed to a user. It currently allows a user to view time-series plots of any three user-selected parameters.

Q7 How often have you used the OWLS in your professional work?
- ❍ Never (1)
- ❍ Less than once a month (2)
- ❍ Once a month (3)
- ❍ 2-3 times a month (4)
- ❍ Once a week (5)
- ❍ 2-3 times a week (6)
- ❍ Daily (7)

If Never Is Selected, Then Skip To End of Block

Q8 The OWLS has been a helpful tool in visualizing high frequency watershed monitoring data from the Webb Branch watershed that includes a part of VT campus/town of Blacksburg.
- ❍ Strongly disagree (1)
- ❍ Somewhat disagree (2)
- ❍ Neither agree nor disagree (3)
- ❍ Somewhat agree (4)
- ❍ Strongly agree (5)

Q9 The following features of the OWLS were valuable to me in my professional work:

	Strongly disagree (1)	Somewhat disagree (2)	Neither Agree nor Disagree (3)	Somewhat agree (4)	Strongly Agree (5)
Interactive graphs (1)	❍	❍	❍	❍	❍
Real-time site view (camera) (2)	❍	❍	❍	❍	❍
Case studies (3)	❍	❍	❍	❍	❍
Background information (4)	❍	❍	❍	❍	❍
Real-time data (5)	❍	❍	❍	❍	❍
Anytime/anywhere access (6)	❍	❍	❍	❍	❍
Weather radar (7)	❍	❍	❍	❍	❍

Q17 Have you found the OWLS user interface to be confusing in any manner? Please explain.

Q21 What modifications would you want to see that would improve the OWLS for your professional work?

Q4 The email alert system monitors the LEWAS data and upon configurable trigger conditions (e.g., turbidity exceeds a given threshold) sends an email to a list of subscribers with the value of the monitored parameter, a link to the OWLS data viewer and an attached image of the current site conditions. Example email: From: LEWatcher <lewatcher@lewaspedia.enge.vt.edu> Date: June 4, 2015 at 6:25:33 PM EDT To: <recipients> Subject: LEWAS turbidity Event: Samples outside of range (0.0, 40.0) Recent samples outside of threshold range: 2015-06-04T22:25:28+00:00: 3000.0 2015-06-04T22:25:23+00:00: 3000.0 To see the conditions leading up to this event, and to watch it happen live, visit: http://www.lewas.centers.vt.edu/dataviewer/single_graph.html <camera-2015-06-04T18:25:40.692097.jpg>

Q18 As a subscriber of the email alert system, how many of the emails you received from the alert system were helpful to you in making decisions related to stormwater management?

- ❍ Every email I received was helpful (1)
- ❍ Most of the emails I received were helpful (2)
- ❍ A few of the emails I receive were helpful (3)
- ❍ None of the emails I received were helpful (4)

Q19 Emails sent from the email alert system contains the name of the water quality parameter associated with the alert, the current measured value for that parameter and the threshold value that triggers an alert as well as an attached image taken from the LEWAS camera at the time the alert was triggered and a link to the OWLS. Is there other information that could be provided in the email alert that you would consider to be helpful in your professional work?

Q20 Currently the link to the OWLS data-viewer included in email alerts takes the user to the default OWLS interface which displays a time-series graph of three default parameters. What would you like to see on the OWLS interface during an alert condition that might be helpful in making professional decisions?

Q22 What category best describes the employer for which you have done professional work related to stormwater monitoring?

- Town or municipality (1)
- State institution/university (2)
- Private company/institution (3)
- Self-employed (4)

NSF/REU Site Assessment Report

NSF REU Interdisciplinary Watershed Sciences and Engineering

Virginia Tech, Summer, 2015

Assessment Report

John Muffo

The following is an independent assessment of the level of success of the program conducted during the summer of 2015. As in 2007 through 2009 and in 2011-2015, my role was mainly to develop the entry and exit survey, to conduct the surveys, and then to conduct the focus group at the end of the summer. I had no contact with the faculty and students during the rest of the time when the students were at Virginia Tech.

Abstract

Overall the experience was a positive one for the students involved. My impression is that the students took this opportunity to explore whether or not they wanted to go to graduate school and generally speaking it confirmed their prior biases, i.e., those who were leaning towards graduate school confirmed those leanings even more and those leaning against graduate school likewise confirmed those leanings. It is not clear whether it is possible to generalize about level of intended study among those planning on going to graduate school.

The students in the program on average reported the greatest gains in understanding how to conduct scientific research independently, followed by being aware of the many ways in which scientists from different fields interact with each other in conducting research and knowing how to communicate research findings orally and documenting those findings in a research paper. Other areas of reported growth include knowing enough to conduct research in the library, having a good understanding of the role of ethics in scientific investigations, planning on joining industry after graduation, and having an appreciation for the role of graduate students in research work.

In addition, the students seemed to genuinely enjoy each other’s company, though there was some minor friction also. The suggestions for improving the program were modest and generally reflected logistical matters, with several mentioning concern over the meal arrangements. On the positive side, they found a number of the seminar presentations interesting, especially the ethics one and the faculty presentation of their research interests. The water treatment plant field trip was mentioned positively as well.

Entering Survey

There were nine students who completed the pre-test during the summer of 2015. Their responses are below, in order of the highest to lowest average responses. (The questions were developed in cooperation with the faculty who are the Principle Investigators for the project. They were revised in 2015 by deleting some of the questions used during 2011-2014 that were not yielding useful results and adding two others. This allowed for some comparability to the earlier surveys.)

Using the following scale:

1=Strongly Disagree; 2=Disagree; 3=Neutral/No Opinion; 4=Agree; 5=Strongly Agree

The entering students provided the following responses upon entry:

- I have an appreciation for the role of faculty in advising students in research work. – 4.67
- Water research can be challenging. – 4.67
- I have an appreciation for the role of faculty in research work. – 4.67
- I have an appreciation for the role of graduate students in research. – 4.44
- I am aware of many ways in which scientists serve their communities. – 4.22
- I need help from a peer/faculty member/mentor to conduct scientific research. – 4.22
- I am considering attending graduate school as one of my career options after I graduate. – 4.11
- I am aware of many opportunities for employment in the water field. – 4.00
- I have a good understanding of the role of ethics in scientific investigations. – 3.89
- I can communicate scientific concepts effectively to a scientific audience. – 3.56
- I plan on attending graduate school soon after I graduate. – 3.56
- I am aware of the many ways in which scientists from different fields interact with each other in conducting research in water sciences. – 3.44
- I know how to communicate my research findings orally and by documenting it in a research paper. – 3.33
- I know everything that I need to know to conduct research in the library. – 2.89
- I plan on joining industry soon after I graduate. – 2.89
- I am confident that I understand how to conduct scientific research independently. – 2.78

The students also answered the following open-ended questions; these were shared with the faculty. Their responses are contained in Appendix I.

- What suggestions do you have for improving the application process for this NSF/REU program?

- Do you think that we should advertise our program on social networking sites like Facebook, MySpace, etc.? Pl. explain your answer.

- Do you have any concerns about the program that you are beginning now? If so, what are they?

- List the top three things that you would like to learn/experience (academically and professionally) during this 10-week long NSF/REU program.

Exiting Survey

At the completion of the program the same nine students completed a follow-up survey containing the same 16 questions plus two additional ones. Their responses are below, again in order from the highest to lowest. The two questions not asked in the initial survey are listed last.

- I have an appreciation for the role of graduate students in research work. – 4.89

- I have an appreciation for the role of faculty in research work. – 4.89

- I have an appreciation for the role of faculty in advising students in research work. – 4.78

- Water research can be challenging. – 4.67

- I am aware of many ways in which scientists serve their communities. – 4.44

- I have a good understanding of the role of ethics in scientific investigations. – 4.33

- I need help from a peer/faculty member/mentor to conduct scientific research. – 4.33

- I am aware of the many ways in which scientists from different fields interact with each other in conducting research in water sciences. – 4.11

- I know how to communicate my research findings orally and by documenting it in a research paper. – 4.00

- I am confident that I understand how to conduct scientific research independently. – 3.89

- I can communicate scientific concepts effectively to a scientific audience. – 3.89

- I am aware of many opportunities for employment in the water field. – 3.89

- I am considering attending graduate school as one of my career options after I graduate. – 3.89
- I know everything that I need to know to conduct research in the library. – 3.33
- I plan on joining industry soon after I graduate. – 3.33
- I plan on attending graduate school soon after I graduate. – 3.33

- I was able to integrate different disciplinary perspectives into my research work. – 4.00
- I was engaged with a disciplinary research. – 3.89

The students also answered the following open-ended questions. Their responses are contained in Appendix II.

- Please comment on social activities during the 10-week program. Your suggestions for next year are most welcome.
- Please comment on the weekly seminars you attended during the past 10 weeks. Feel free to list the topics you liked and didn't like. Suggestions for next year are most welcome.
- Please comment on the merit and frequency of presentations you made during the last 10 weeks.
- List the things you learned/experienced (academically and professionally) during this 10-week long NSF/REU program.
- Please comment on any other concern/suggestion/fact you might have related to the 10-week experience that you might want to share.

Change Over the Summer

One of the more interesting aspects of the survey data is to look at the change over the summer or the difference between the exit responses versus the entrance ones. Of course there are some complicating factors such as ceiling effects, i.e., there is no way to increase a score that is a 5.00 on a 5.00 scale upon entrance and little room to improve a score that is 4.70 upon entrance. Below are listed the questions in order the magnitude of the change in their responses between the time that they began and exited the program. (Note that the numbers in parentheses are negatives.)

- I am confident that I understand how to conduct scientific research independently. – 1.11

- I am aware of the many ways in which scientists from different fields interact with each other in conducting research in watershed sciences. – 0.67

- I know how to communicate my research findings orally and by documenting it in a research paper. – 0.67

- I have an appreciation for the role of graduate students in research. – 0.45

- I know everything that I need to know to conduct research in the library. – 0.44

- I have a good understanding of the role of ethics in scientific investigations. – 0.44

- I plan on joining industry soon after I graduate. – 0.44

- I can communicate scientific concepts effectively to a scientific audience. – 0.33

- I am aware of many ways in which scientists serve their communities. – 0.22

- I have an appreciation for the role of faculty in research. – 0.22

- I have an appreciation for the role of faculty in advising students in research work. – 0.11

- I need help from a peer/faculty member/mentor to conduct scientific research. – 0.11

- Water research can be challenging. – 0.00

- I am aware of many opportunities for employment in the water field. – (0.11)

- I am considering attending graduate school as one of my career options after I graduate. – (0.22)

- I plan on attending graduate school soon after I graduate. – (0.23)

To summarize, the students reported the greatest gains in understanding how to conduct scientific research independently, followed by being aware of the many ways in which scientists from different fields interact with each other in conducting research and knowing how to communicate research findings orally and documenting those findings in a research paper. Other areas of reported growth include knowing enough to conduct research in the library, having a good understanding of the role of ethics in scientific investigations, planning on joining industry after graduation, and having an appreciation for the role of graduate students in research work. Once again, the gains were affected to some degree by how high the students rated themselves on each of these items upon entry into the program.

Focus Group Results

At the end of the program, at the end of the summer, a focus group was conducted of the ten students, nine who completed both the pre-test and post-test and one who was not present for the pre-test and whose responses were included only in the open-ended portion of the post-test. They were asked a series of open-ended questions by the evaluator. No faculty or other staff was present. Below is a summary of their responses.

1. What did you like about the program that you just completed?

- Working with other students and mentors from different disciplines and from around the country who were working together to accomplish the same goals in water sciences and engineering.
- The level of independence in the research project and the positive relationship with the mentor/advisor.
- Working with the graduate student mentors, who were enthusiastic and encouraging and thus motivating me to do good work.
- Being part of the research; not having done it before, getting that experience.
- Working with people at different academic levels who were working together, providing different insights.
- Getting experience with graduate school.
- The panel with all of the graduate students was helpful; those from different disciplines allowed the students to see what it's like in a range of disciplines and not in just one field.
- Faculty presentations allowed a broader view, seeing the passion of others.

2. Why do you think the program is useful/not useful?

- Getting an idea of research going on at your own university and elsewhere and how much variation there is; being able to try something new that is not being offered at your own school.
- Knowing that there are only ten weeks to learn and produce something, the time pressure forces a person to produce. At the same time, the ten-week limit assures that the commitment is not long-term.
- Useful for networking for future work.
- For one of the Virginia Tech students in the group, it was a good longer-term opportunity to become more familiar and better established with a research group.
- One negative aspect – the group did not feel that they got much of an industry perspective from the program.

3a. *What were the most important things that you learned academically (within and outside of your discipline) during this program?*

- How to go about conducting and presenting research. Learning about the difficulties faced in doing research.
- The importance of the other disciplines, e.g., engineering in doing research.
- All projects today require multi-disciplinary work; everybody crosses over to some extent.

- The expectations of master's and Ph.D. students and their relationships with their advisors. Better scientific communication skills and more in-depth about the publication process.

3b. What were the most important things that you learned/developed professionally during this program?

- Communication skills.
- Maintaining working relationships with professionals in the field.
- Taking charge of your own research and career path. Knowing how to interact professionally, e.g., being able to state your position constructively, even if you disagree with somebody.
- Understanding the clientele of a project; directing the project, keeping the perspective of the customers/clients in mind. As an example, closing of a plant for two weeks as part of a shutdown meant that two people were out of a job for two weeks.

4.a. How many of you are motivated to go to graduate school now? – did the NSF REU influence your motivation?

- Of 10 students present, a total of 8 expressed an interest in going to graduate school at the end of the summer.
- One of those who intends to go to graduate school stated that the program had more of a negative side effect in that the student is not as excited as before as a result of going through the program. The environment in which the student worked was one in which the work done was criticized a lot. Previously the goal was to get a Ph.D.; now the goal is to get a master's degree and begin work in an industry setting. Research can consume one's life; there is more of a balance working in industry.
- Another reported that the program motivated that student to get a Ph.D. Having the experience over the summer suggested enjoyment of the experience.
- Yet another student reported enjoying the experience as well, especially the independence aspects of doing research.
- An additional comment had to do with seeing graduate students being stuck for so long, not being able to get on with their lives. One student stated that situation as being undesirable and not wanting to be put in that position, including through the post-doc. experience.

4.b. How many of you intended to go to graduate school at the beginning of the summer?

- Of 10 students present, a total of 7 expressed an interest in going to graduate school at the beginning of the summer.
- Some feel that they would like to work for a few years first.
- One student has been delayed for two years as an undergraduate due to a change of major, leading for a desire to limit further education immediately after undergraduate school.

5. How do you think that your communication skills improved as a result of this program? [Probing questions – Verbal? Written? Facebook? YouTube? Other?]

- How important it is to stand up for yourself, explain why you are doing what you are doing. Every time you write a research paper, you learn to write better.

- Considering the background of the audience in terms of what they are likely to understand in what is being presented.
- Getting feedback from other students and mentors is helpful.
- Different modes of communication (oral, written, and presentation) taught students their strengths and weaknesses. Having all three due at the same time is very stressful, however.

6. In what ways, if any, did you find the field trips informative?

- The ethics one was beneficial; it made people think. What do you do in those situations where there are no easy answers? What do you do when you run into those hard situations working as scientists and engineers? There is a need to develop strong ethics before running into those situations.
- Faculty research presentations: would like to see more of these. They liked the wide range of them. It was interesting to see their educational backgrounds and how their research evolved.
- Liked the drinking water field trip. The weather service one was rushed; more could have been seen there.

7. How satisfied were you with your living environment at Virginia Tech? Your social/cultural environment?

- It would be nice to have better living accommodations. There was a summer camp feeling to it all. It was hot most of the time in Newman Hall, while the showers were cold. Such small things make for a more difficult time when one comes home at the end of a long day of work.
- The dining situation (20 meals/summer) was different from what was advertised. They were told beforehand that meals would be taken care of, but instead were covered for 20 meals for ten weeks for $400, only $200 of which was paid in advance with $200 more to be paid at the end of the summer. They were charged full cost for meals in the dining halls, making them overly expensive. They cooked for themselves mostly in the communal kitchens not really designed for regular meal preparation. They should either get all meals paid for or get the full $400 up front on the student dining plan. The program also should be more clear in its advertising about what is provided in the way of meals so that students better understand what to expect.
- There are some other logistical social issues, e.g., one student lived off-campus and did not have a key to the residence hall, making it more difficult to interact with the other students in the program.
- They liked being located together.

8. What concerns do you have about the program that just ended?

- None expressed

9. Other comments?

- [After the focus group interview, one of the participants took me aside and reported that one of the students had behaved in a socially and professionally immature manner this summer, which had caused some tension within the group. This was as the group was dispersing.]

Concluding Comments

The group in 2015 seemed to be committed to graduate study on average upon entry to the program and, after getting the chance to sample the life of a graduate student over the summer, seemed to solidify and strengthen the earlier leanings. In one or two cases, however, there is some concern about going on for a Ph.D. due to the length of time involved and related considerations. The most popular aspects of the program, in addition to the day-to-day work of simulating the graduate student experience seem to be those where the students can observe the lives of faculty and graduate students up close; the seminars describing ethical challenges and faculty research interests are good examples. The opportunities to improve professional communication skills rank high as well.

The strongest area of concern has to do with the dining situation. The housing, while somewhat basic, raised less concern than the dining. Socially the students appear to have liked living together and formed a generally cohesive group.

Overall the NSF REU Interdisciplinary Watershed Sciences and Engineering program in 2015 seemed to provide a sound educational experience for the ten undergraduate students involved. They got to test out being graduate students for ten weeks and improved their knowledge of that experience while also improving their disciplinary knowledge, research skills, and scientific communication skills while forming social bonds with a group of other students from around the country. While this does not guarantee that all will be going on to graduate school in STEM disciplines in the future, it does suggest that those who do should have a better idea of what to expect and therefore be better prepared for the experience.

Appendix I

Open Ended Questions – Beginning of the Summer

What suggestions do you have for improving the application process for this NSF/REU program?

- [Left blank]
- Allowing the students to have more time to decide on attendance. I think 1 week would be better instead of 3 days.
- Overall, out of the ones that I applied for, this one at VT was straightforward & pretty easy to navigate. I have no major improvements regarding the application process.
- I thought that the application process was pretty straightforward and inclusive, but one thing I thought it could include was a resume submission.
- Each faculty could have a specific question they want answered for students applying to their specific project, so that students answer three questions that are related more specifically to the project they are seeking.
- Explaining what each project works on in addition to the title would be helpful so that students know the details of the project they are applying for.
- The application process was extreme (sic) easy and efficient, but the training bit and COI was a little confusing to set up. I think explaining that situation more effectively would help.
- The application process is very typical – no complaints. If an extended period were given to decide on acceptance of an offer, that would be very helpful and less stressful.
- I was pleased with how simple the application process for this program was. I had no difficulties in completing the requirements.

Do you think that we should advertise our program on social networking sites like Facebook, Myspace, etc.? Pl. explain your answer.

- Advertising this program on such sites could potentially reach more students who may not have even considered a summer research program. Therefore, I think this could be a beneficial option to making the program known.
- Yes, many students use them & would be a great way for communication.
- No, the program would lose its prestige by ads on social media like Facebook. The only social media site I would possibly suggest would be LinkedIn to make sure it is still professional.
- I don't think that advertising on social networking sites is necessary because most students don't turn to Facebook for career building. Also, many of the programs featured on social networking sites are not as intensive – they are study abroad trips, easy jobs, etc.
- Yes, as it would make the REU program easier to find when students are searching for them on the internet.
- I think advertising the program on Facebook or LinkedIn would be beneficial because most college students have an account on either site. It would allow the program to be more well-known and may draw in more applicants.

- I think advertising on a site like Twitter would be more effective due to the more professional nature it has. I am willing to bet that it would be more successful through Twitter than Faceboook/MySpace.
- Yes, but I doubt that it would be very effective. A more effective method is to advertise to schools who then pass the information to students.
- Yes – but only on university pages (eg. CoE Facebook page). The best way to attract talented applicants is to contact relevant colleges/departments at universities around the country to disseminate applications to a wide pool of potential fellows.

Do you have any concerns about the program that you are beginning now? If so, what are they?

- I lack experience in conducting independent research and reporting it professionally. I hope this program will allow me to gain this experience and knowledge of new technologies.
- My specific project is still very vague to me. I have not been told my exact project. Also so far this experience has been very vague; check in etc.
- Only main concern is where I'll be conducting research for the project. I am sure I will hear today, but may have been nice to know a little earlier.
- I do not have many concerns as I feel I have been explained the expectations very well. I'm not exactly sure what my project entails, so maybe more information regarding specific work would be nice.
- No, I am very much looking forward to it.
- I do not have any major concerns. My only concerns are how many hours we are working per week (I am unsure) and what we will be doing on Fridays with Dr. Lohani. I'll learn soon!
- I am not aware of the schedule of how research is to be conducted at this moment in time. I think that I arrived in Blacksburg with little information, which could be my fault as well.
- The schedule has been very unclear thus far. E-mail communications are either conflicting or continuously changing. I really like to be informed from the start about activities, expectations, and schedules. That said, what I'm learning about the opportunities we'll be provided is really exciting/motivating.
- My only concern is that I do not know enough about my project's subject to best contribute to my research group's body of work – but that is why I am here to learn!

List the top three things that you would like to learn/experience (academically and professionally) during the 10-week long NSF/REU program.

#1
1. How to conduct scientific research independently
2. How to present research orally
3. How to write a professional research paper

#2
1. Advance in thinking like a researcher
2. Gain professional development towards presenting research
3. Strengthen my scientific writing skills

#3
1. Learn the roles and lifestyle graduate students have
2. Learn how to write & be involved in a research paper

3. Experience life at a large college around professional individuals

#4 1. Academic research – how to conduct it
2. Presenting said research
3. Networking

#5 1. Confidence in conducting research independently
2. Learning how to get into the water studies industry
3. How to clearly communicate findings in writing/make effective presentations

#6 1. What I can do for graduate school
2. What I could do for my future career
3. How I can change and help the water quality of our world

#7 1. Real world application of water engineering
2. Research methods [Independent]
3. Professional networking at Virginia Tech

#8 1. How to conduct research more independently and develop ideas for research projects
2. The benefits of a Ph.D. vs. Masters in Env. Engr. and career options that they hold
3. Research presentations from the VT faculty as well as grad. school/GRE/career advice

#9 1. Prepare a research paper and presentation for a conference in my field
2. Learn about my options after I graduate in graduate school and industry
3. Make lasting connections with other students, graduate students, and faculty to further my professional development as a water scientist

Appendix II

Open Ended Questions – End of the Summer

Please comment on social activities during the 10-week program. Your suggestions for next year are most welcome.

- During the 10-week program our REU group visited Washington, D.C., went to Myrtle Beach for the 4th of July, and explored Blacksburg. There is much to offer in this area of Virginia, including some great hikes that I would recommend to future years' students.
- We mostly planned our own social activities. I am a Virginia Tech student so I have many friends in the area and spent a lot of the time with them this summer, but still was able to get to know the other fellows.
- Social activities were very enjoyable. We had trips every weekend to explore the area. Overall, the group got along great. Soccer at the end of the REU picnic was very fun!
- Enjoyed group dinners and weekend trips.
- Went to D.C., picnics, South Carolina, dinners, etc. Doing social activities was important in creating a bond with my fellows, and made the program more fun.
- I really enjoyed the Memorial Day and concluding picnic organized by the graduate students. However, I feel that there could have been more social events organized in the middle of the summer to help us interact with and get to know the graduate students better.
- The cohort this year did a lot together, lots of random trips to see things. Helpful w/multiple people having cars, more flexibility. Other suggestions: lots of ice breakers, doing things together in 1st week, taking care of interpersonal situations before they become a problem.
- I enjoyed the hiking/exploring the group did together. Make sure to do a soccer game next year to keep the tradition going. If possible upon arrival, give a brief list of popular things Tech students do.
- I enjoyed the social aspects of the program. We all got along very well and went to many destinations. We went to South Carolina and DC! The ones put on by the REU mentors were OK, but they only had one event, snores (?). I would add more events or different ones at least.
- We all got along very well, and did lots of things on the weekends, to see as much of Virginia as possible. Without people having cars, this would have seem very challenging. It was a lot of fun.

Please comment on the weekly seminars you attended during the past 10 weeks. Feel free to list the topics you liked and didn't like. Suggestions for next year are most welcome.

- The seminars held every week really helped to engage us in discussion on our research and to teach us some important topics. The ethics presentation and hearing about when to act (follow your judgment) were well done. These seminars provide practice in group, professional-type meetings/discussions.
- The seminars with guest speakers were the best and most enjoyable; more speakers and related events would enhance Friday seminars.
- I didn't enjoy the modeling presentation: the software is complex but the ideas presented were too basic. The Ecohydrology (?) presentation was the best, in my opinion. I would have loved to hear more about more professors research during there (sic) seminars.

- Didn't enjoy most of them b/c they were so heavy in engineering that couldn't comprehend. Really enjoyed Dr Daniel McLaughlin as his talk pertained to nutrient analysis & hydrology.
- I liked all the speakers and field trips. I am not an engineer, so the first talk about modeling was confusing, but I was still interested. I liked that there was a range in speaker topics, highlighting engineering and life sciences.
- I enjoyed the ecological engineering seminar that we had at the final seminar the most. I also liked Dr. Edwards presentation, the water treatment plan (sic) field trip, and the graduate student panel. I found the NWS trip to be rather rushed, and the ethics presentation could have been approached better without the video.
- Really liked the hydrology pres. x drinking water treatment facility. Generally liked them all.
    - ➔ Didn't really care for the ethics video – felt it dragged on and not sure I actually learned anything.
    - ➔ Seminar on modeling didn't make sense to me – not sure why we were looking into it as these are many diff. programs.
    - ➔ I would like to see more that related to scientific industry in a research capacity (i.e. not just research in grad school).
- The only one I went to was the early/first one. It was too long and boring. If the seminars were more useful or had better speakers I would have went. Also, they started at ~ 4 pm and is difficult to be out of work and ready to go by this time.
- I did like the seminars. My favorite was when different faculty came in and presented their research. In the future, I would love to have some people come in and talk about some career options in water sciences and engineering.
- I enjoyed the presentations by the different faculty members. The NOAA trip was interesting but should be moved to a different Friday. I didn't think the graduate panel was all that helpful, especially since it was our mentors that we see & talk to every day. Thank you for not making us attend the all undergrad research presentations on Wednesdays.

Please comment on the merit and frequency of presentations you made during the last 10 weeks.

- I felt that the three presentations we each made was a very good idea. It really helped us to prepare and get some feedback from our peers to improve in the future. Building on both time and depth of the presentations made it easier to complete them.
- I believe my presentations have been well-presented; however, I wish I had the chance to practice more by presenting more frequent research updates.
- The presentations were very helpful to improve my communication skills. Timing and frequency were appropriate.
- It was a lot of work. I do not necessarily think it was needed to give 3 presentations.
- We made 2 oral presentations to the group, which was beneficial in receiving comments/advice. I had more help from my lab however because I presented them ~ 3 times. Maybe do more practices?
- I really appreciated the fact that we were asked to present our projects a few times during the 10 weeks. It made the last week much less stressful, because we already had a working powerpoint and an idea of what to present.
- 3 presentations: 5 min, 10 min, 12 min. felt I had uneven amounts of information to give during the 1st two, but that's unavoidable. They were helpful with students' feedback, as everyone is from different disciplines.

- In 10 weeks, I have made 6 presentations in including ‘practice’ presentations for faculty mentors. I believe I gained valuable experience in presenting as well as allowing my audience to learn something new.
- Overall we had three presentations. I believe that they improved drastically as time went by, and my communication/presentation skills improved as well.
- It was nice to be able to build up to the 15 min. presentation, and a way to become more familiar with how to communicate our work.

List the things you learned/experienced (academically and professionally) during this 10-week long NSF/REU program.

#1 - Ask questions – branch out, most people are willing to help & are great sources for different kinds of knowledge

- How to give successful, professional oral, poster, and written presentations of research
- How to collaborate as a team/the general research process

#2 - Experiments, more often than not, do not work out at all the first time! - Making small mistakes will happen – a lot

- If one is passionate about something, one will be successful after a significant amount of work and resource coordination

#3 - Expectations for PhD or Masters students

- Improved scientific presentations
- Independent lab work/data analysis/problem solving
- So much more about possible research areas in env. engr.
- Networking! Learning about and contacting other professors on and off the VT campus

#4 - Need to work on standing up for myself. Faculty mentors were never very supportive.

#5 - How to collaborate with others

- How to write a research paper about my own research project
- How to ask for help when confused
- How to network

#6 - The difficulties of organizing a project, considering feasibility, economics, technical skill, etc.

- How to write a research paper
- How to present scientific research
- About drought forecasting, and the measures we have in place to avoid extreme drought

#7 - Lab skills: dilutions, using instruments (vortex, centrifuge, VaprdVap (?), etc.), pipetting, importance/causes of contamination, sampling practices, accounting for variables of experimental set-ups.

- Writing lab reports – excel

- Making presentations – graphs of results, etc.

#8 - VT has a BSE program
- Every one is more than willing to help
- I have a greater appreciation for grad students & faculty
- Graduate school (at least master's) is worth the time
- Many problems occur during research which set back results/take longer

#9 - Communication/presentation skills
- Programming
- Careers in academia and industry
- Interdisciplinary learning
- How to write a research paper
- Time management

#10 - I learned a lot of technical skills, for example, Matlab, modeling, taeiminal (?); stuff that I can take away from this program and use in the future.

Please comment on any other concern/suggestion/fact you might have related to the 10 week experience that you might want to share.

- The field trips that we took as an REU group including the water plant and NWS were positive, interesting trips & more should be included in future programs.
- Despite the fact that another fellow decided she was not going to talk to me for the last two weeks of the program because I found out she had been saying false things about me, I enjoyed the program and am very happy to be continuing in my research lab.
- - A little more organization and communication would be appreciated. - I thought that accepting 20% of the REU cohort from VT was excessive. I found it unusual that 2 students would go to an REU at their school. – Advertise the program better. I really expected it to be more competitive. Though I appreciate my peers, I think that our VT freshman did not have the maturity to interact appropriately with her peers and occasionally with some supervisors. Though intelligence and drive were there, lack of maturity and appropriate communication skills were detrimental to the group. All others were fantastic overall.
- My faculty mentors often gave me harsh critism (sic) that was not helpful. They also were gone for about 2-3 weeks. Very stressful when it should not have been – I have a serious medical condition that is undiagnosis (sic) & this interferes w/my work occasionally & I was asked to do more upon returning from being sick than necessary – Also having a 15 min pres & poster, & research paper & Journal Entry all due w/in 48 hours of each other is too much, no matter how well you try to get things done early. I think there needs to be a cut off time for doing lab work/data collection in order to have enough time to edit paper poster & presentation thoroully (sic) & be able to do best job possible. Mentors often had unhelpful comments that came off harsh "What were you thinking putting this here?" "Why would you do that" – rude tone. Grad students were awesome & super helpful but over all did not enjoy the program. Very poor organization & communication: meals, parking, travel & mail.
- Maybe require students to attend the weekly seminars that undergrad research held? They seemed so interesting even though I was not able to go to any because of work.

- I think my project, especially, was unorganized. For the majority of the summer, I didn’t really know what I was doing, or why, and it was difficult to see the end goal of my research. It would have helped if my project was given a specific objective, and I was provided more instruction along the way. This made it difficult to have specific results or conclusions with such an open ended project.
- The REU general orientation in the first week was a waste of time. – Length requirement of journals caused me to focus more on filling space than actually saying anything. – Food money not distributed evenly; meal plans not worth it (esp. w/ dining hours). – Projects more clearly defined beforehand or right at beginning (mine was changed with random other aspects thrown on & didn’t plan for it).
- The main concern is the food/meal plan. Either have $400 given via check or work something out as more of a dining plan instead of dining dollars. – Possibly have a list of activities like certain hiking spots. Also, restaurants, however a basic online search accomplishes these things. – Organization overall. Arriving, I wasn’t sure how I’d get my key, but wasn’t a problem. Wi-fi access should be set up much sooner. I had to use my graduate student’s login for awhile.
- I think that the dining situation was a little tough, even though housing was pretty good. $200 is not enough to pay for the really expensive food at Virginia Tech. I guess if the situation is to continue, I would not include in the position description that meals will be provided, maybe instead saying that some meals will be included so that it doesn’t sound like food cost (sic) are completely covered.
- I think that the poster, and 15 min presentation, and paper was a little excessive. I prefer poster presentations because they make you have a thorough understanding of your work, but also have to be able to summarize it into a few minutes. They also let you get to interact and meet with people on a more personal level & answer a wider range of questions. I don’t think the 15 min presentation added as much to the experience. – My mentors were all wonderful, and extremely helpful. Had basically no background knowledge coming into the program about ocean engineering or modeling but they were always willing to answer questions. Sometimes they did assume that I knew something or how to do it, which was frustrating, but I was able to learn.

NSF/REU Site Announcements

Short Announcement

Summer 2015 (May 24 – August 1, 2015)
Undergraduate Research Fellowships Announcement
National Science Foundation Research Experiences for Undergraduates (REU) Site
INTERDISCIPLINARY WATER SCIENCES AND ENGINEERING
Virginia Tech, Blacksburg, Virginia
Application Deadline February 27, 2015 (5:00 PM, EST)

Applications are invited from qualified and motivated undergraduate students (rising sophomores, juniors and seniors) from all U.S. colleges/universities to participate in a 10-week (May 24-August 1, 2015) summer research in interdisciplinary water sciences and engineering at Virginia Tech. U.S. Citizens or Permanent Residents are eligible to apply. The research program is funded through the National Science Foundation – Research Experiences for Undergraduates (NSF REU) program. The 10-week internship will begin on May 24, 2015 (arrival day) at Virginia Tech and end on August 1, 2015 (departure day). The research internship includes a stipend of $450/week, housing (two persons per room), $400 for meal, and travel expenses (limited to a maximum of $500 per person). We have already graduated 66 excellent undergraduate researchers representing 45+ institutions in the United States during 2007-09 and 2011-14. Application materials, details of Research Mentors along with summer 2015 research projects and other program activities are posted on the following website:

http://www.lewas.centers.vt.edu/index.php?option=com_wrapper&view=wrapper&Itemid=528

Applicants are requested to upload their applications along with other required documents by the deadline (February 27, 2015, 5:00 pm, EST). Successful applicants will be informed by March 9, 2015. Please contact Dr. Vinod K Lohani (phone: (540)231-9545; FAX: (540) 231-6903; E-mail: vlohani@vt.edu) for questions.

Titles of Summer 2015 Projects

Project ID#1. Evaluating the factors driving the vertical distribution of cyanobacteria in drinking water reservoirs; (Carey and Schreiber)
Project ID#2: Drinking Water Quality; (Dietrich)
Project ID#3: Hydrology and Hydraulics Impacts on Ecological Health and Water Quality of Streams and Rivers; (Hester)
Project ID#4: Quantification of distinguishing features of tsunami versus hurricane sediment overwash events; (Irish and Weiss)
Project ID#5: Recovery of Nutrients and Water from Wastewater Using an Integrated Osmotic Bio-electrochemical System; (He)
Project ID#6(A&B): Implementation of a Raspberry Pi-based System for Processing and Remote Access of High Frequency Environmental Data and Hydrologic Analysis; (Lohani and Dymond)
Project ID#7: Investigation of the occurrence and fate of 4-nonylphenol, an endocrine disruptor, in urban-impacted watersheds; (Xia)
Project ID#8: Water Conservation and Waterborne Disease Nexus of Faucets; (Pruden and Edwards)

Long Announcement

Summer 2015 (May 24 – August 1, 2015)
Undergraduate Research Fellowships Announcement
National Science Foundation Research Experiences for Undergraduates (REU) Site
INTERDISCIPLINARY WATER SCIENCES AND ENGINEERING
Virginia Tech, Blacksburg, Virginia
Application Deadline March 13, 2015 (5:00 PM, EST)

Program Description: Applications are invited from qualified and motivated undergraduate students (rising sophomores, juniors and seniors) from all U.S. colleges/universities to participate in a 10-week summer research in interdisciplinary water sciences and engineering at Virginia Tech. U.S. Citizens or Permanent Residents are eligible to apply. The research program is funded through the National Science Foundation – Research Experiences for Undergraduates (NSF REU) program. The 10-week internship will begin on May 24, 2015 (arrival day) at Virginia Tech and end on August 1, 2015 (departure day). We have already graduated 66 excellent undergraduate researchers representing 45+ institutions in the United States during 2007-09 and 2011-14.
Successful applicants (hereafter referred to as REU fellows) will join one of the ongoing research projects in interdisciplinary water sciences and engineering and conduct research under the supervision of Virginia Tech faculty and graduate students. Research projects address interdisciplinary issues related to water science and engineering involving field work, laboratory simulations, literature review, and analysis of data. See Appendices 1 and 2 for list of faculty advisors and typical 2015 summer research projects, respectively. The summer research program is complemented by other professional activities. For example, REU fellows will attend weekly forums and participate in a few field trips. Speakers at these forums will include VT faculty members, graduate students and experts from water industry and government. These weekly forums provide an excellent opportunity to REU fellows to learn about commonalities between their various research projects, interact with each other and with other research mentors. REU fellows will make frequent presentations to their peers about their research progress and ultimately prepare a research report in collaboration with their research mentors suitable for conference presentation and/or publishing in a refereed journal or other appropriate publications.

Social interaction and networking is a major goal of the program. Several social activities are organized to encourage informal personal interaction between REU Fellows and the research team and the larger university community. See Appendix 3 for possible recreational activities.

Financial Support: The research internship includes a stipend of $450/week, housing (two persons per room), $400 for meal, and travel expenses (limited to a maximum of $500 per person).

Application: The deadline to receive all application materials is **March 13, 2015 (5pm, EST)**. Applications should be submitted online via the website: **http://www.lewas.centers.vt.edu/.** The application should include:
1. A 300-word essay about your interest in water/environment research and professional goals, and indicate top two choices of summer research project including a brief justification (see

Appendix 2). The justification should be part of your essay. This should be uploaded as a PDF document in the online application form.

2. Unofficial College transcripts, to be uploaded as a PDF document in the online application form.

3. Two letters of reference to be sent by your referees (Referees are requested to upload a pdf document using a URL that will be emailed to them for our application system. Potential candidates are requested to remind their referees about this requirement. *Letters should address candidate's motivation to pursue research, enthusiasm, reliability, team-work skills and personality*.

Applicants are requested to upload their applications along with other required documents by the deadline (**March 13, 2015**, **5:00 pm, EST**). We have started reviewing the applications and will begin contacting the successful applicants beginning in the **middle of March, 2015**. For questions, please contact: **Dr. Vinod K Lohani**, NSF REU Program Director, e-mail: vlohani@vt.edu; Phone: (540) 231-9545; FAX: (540) 231-6903

Appendix 1

Program Management Team and Research Mentors

Name	Organization	Responsibility	Academic Discipline and Field of Study
Dr. Carey	Virginia Tech	Research Mentor; Participant Selection	Biological Sciences; Freshwater Ecology
Dr. Hester	Virginia Tech	Research Mentor; Participant Selection	Civil & Environ Eng.; Ecohydraulics
Dr. Edwards	Virginia Tech	Research Mentor; Participant Selection	Civil & Environ Eng.; Water Infrastructure
Dr. Dietrich	Virginia Tech	Research Mentor; Participant Selection	Civil & Environ Eng.; Analytical Chemistry
Dr. Xia	Virginia Tech	Research Mentor; Participant Selection	Crop & Soil Environ Sciences – Soil Chemistry
Dr. Weiss	Virginia Tech	Research Mentor; Participant Selection	Geoscience; Coastal Engineering
Dr. Lohani*	Virginia Tech	Project Director (PI); Program Coordinator; Recruitment & Selection; Assessment; Cohort Experiences/ Professional Development; Dissemination; Research Mentor	Civil and Agricultural Engineering; Watershed Instrumentation, Hydrology, and Engineering Education
Dr. Irish	Virginia Tech	Research Mentor; Participant Selection	Civil & Environ Eng.; Coastal Engineering
Dr. Pruden	Virginia Tech	Research Mentor; Participant Selection	Civil & Environ Eng.; Environmental Contaminants
Dr. Schreiber	Virginia Tech	Research Mentor; Participant Selection	Hydrogeosciences; Chemical Hydrogeology
Dr. Dymond	Virginia Tech	Research Mentor; Participant Selection	Civil & Env. Engineering; Hydrology
Dr. He	Virginia Tech	Research Mentor; Participant Selection	Civil & Env. Engineering; Environmental biotechnology
Dr. Muffo	Independent Assessment Consultant	Evaluation/Assessment	Academic Assessment

* Project Management

Appendix 2

Virginia Tech NSF/REU Site: Interdisciplinary Water Sciences and Engineering
NSF REU Summer 2015 Research Projects
REU Site Duration: May 24 – August 1, 2015

Project ID# 1: Evaluating the factors driving the vertical distribution of cyanobacteria in drinking water reservoirs; Mentors: Drs. Carey and Schreiber
Cyanobacterial (blue-green algal) blooms are increasing in many freshwater lakes and reservoirs worldwide, and pose substantial risks to drinking water quality because of their scums, odors, and toxins. Because most drinking water reservoirs are able to control the depth of their source water withdrawal, determining the vertical distribution of cyanobacteria and other phytoplankton populations in the water column is critically important for protecting drinking water quality. The REU participant will be involved in a project in collaboration with the Western Virginia Water Authority (WVWA) to study the vertical distribution of different phytoplankton taxa in drinking water reservoirs, using both high-frequency sensors and manual sampling methods. The REU student will work with a graduate student mentor to conduct intensive field sampling to monitor water chemistry and the vertical distribution of phytoplankton in several different reservoirs, and analyze the factors (e.g., nutrients, light, reservoir management) that influence phytoplankton community structure. We seek an REU student that has experience and interest in field sampling and data analysis, and can work independently while participating in a fun, collaborative team in the field.

Project ID#2. Drinking Water Quality; Mentor: Dr. Dietrich
Worldwide, the increasing population/agriculture/industry causes increased natural and anthropogenic contamination of water supplies that has led to the need to use lower quality water sources for drinking water. Research projects will focus on the effects of source water quality on the resulting drinking water and human health. These projects include: 1) modeling human exposure at the air-water interface to contaminants that are volatilized from drinking water and inhaled by humans; 2) evaluating consumer perception of drinking water through analysis of utility consumer complaints pertaining to the quality of the drinking water; 3) assessing reactivity of zero-valent iron in aqueous solutions; 4) investigating communication strategies for informing the public about water quality.

Project ID#3: Hydrology and Hydraulics Impacts on Ecological Health and Water Quality of Streams and Rivers; Mentor: Dr. Hester
This research aims to understand the mechanisms connecting human activities in stream corridors and watersheds with degradation of stream and river ecosystems and water quality, to allow better informed ecological stream and river restoration design, pollutant attenuation by natural processes, and watershed planning. Current projects entail field work and associated data analysis to evaluate the effect of human activities such as stream restoration on surface water-groundwater exchange, floodplain hydraulics, and water quality in streams and rivers. The REU participant's role will vary but typically entail installing piezometers or stream gauges; installing, monitoring, or downloading hydraulic and water quality sensors; assisting with tracer tests in streams; surveying streambed and floodplain topography; collecting water quality samples; analyzing sensor or survey data; and presenting results in a written report or oral presentation.

Project ID#4: Quantification of distinguishing features of tsunami versus hurricane sediment overwash events; Mentors: Drs. Irish and Weiss

Coastal hazards like tsunamis and hurricanes can move large volumes of sediment at the coast, drastically changing the coastal landscape. Since these coastal hazards are relatively rare, it is difficult to accurately quantify the risk posed by these hazards strictly from contemporary history of such events. Thus, there is a need to better understand these processes in a way that enables meaningful interpretation of information in the geological record. In this study, distinguishing characteristics between tsunami and hurricane sediment overwash events will be investigated. The purpose of this investigation is to identify (a) which hurricane surge and wave conditions lead to sediment overwash volumes of specified magnitudes and (b) which tsunami runup heights lead to sediment overwash volumes of specified magnitudes. The REU student will be responsible for carrying out a series of idealized computational simulations with the open-source code XBeach and evaluating model results to identify patterns between the input forcing (waves and water levels) and overwash characteristics. The student will be expected to write a document and present results of the XBeach model setup, its application, and results.

Project ID#5: Recovery of Nutrients and Water from Wastewater Using an Integrated Osmotic Bio-electrochemical System; Mentor: Dr. He

Sustainable wastewater treatment should significantly clean polluted water while minimize energy consumption of the treatment process and decrease the carbon footprint. Wastewater contains more energy contents than what is required for treatment process, and extracting such contents from contaminants will help accomplish sustainable wastewater treatment. In addition, water and nutrients are valuable resource that can be recovered from wastewater. An innovative system based on synergistic cooperation between microbial electrolysis cells (MECs) and forward osmosis (FO) has been developed at Virginia Tech. MECs oxidize organic matters in wastewater for electricity generation, which drives the recovery of ammonia. Ammonia is then used as a draw solute in FO for recovering high-quality water from the treated wastewater from MECs. In this project, the developed system will be examined for treating the effluent from anaerobic digesters. The REU participant will work with a graduate student and obtain hands-on experiences in reactor setup and operation, and chemical analysis. The participant will be a part of multidisciplinary team and learn the knowledge in engineering, electrochemistry, materials, and biotechnology. The results will be presented in major conferences, and a research paper will be highly desired."

Project ID#6 (A&B): Implementation of a Raspberry Pi-based System for Processing and Remote Access of High Frequency Environmental Data and Hydrologic Analysis; Mentors: Drs. Lohani and Dymond

A Learning Enhanced Watershed Assessment System (LEWAS) (old name: LabVIEW Enabled Watershed Assessment System) lab was established on Virginia Tech campus for remotely assessing high frequency water quality and quantity data from a creek that flows through the campus. A water quality sonde provides the capability to sense temperature, conductivity, dissolved oxygen, turbidity, and pH of water. A flow meter and an ultrasonic sensor measure the flow in a real time. In addition, a weather station has also been integrated into LEWAS to allow real-time monitoring of weather parameters like precipitation, temperature, humidity, etc. The data is shared with remote clients via Wireless LAN through a user interface. Seven NSF/REU participants have worked in this lab since 2008. In 2014, a Raspberry Pi, a single board computer with LINUX environment, based system was conceived and partly implemented to collect data from the LEWAS sensors and store these in a database. Ultimately, a user will be able to access the high frequency data from this database through an interactive user interface. This project will engage two REU participants who will work in the LEWAS lab. Participant one will learn to calibrate the LEWAS sensors and collect data, conduct hydrologic analysis of high frequency (every 3-5 min) water data and develop case studies to demonstrate use of high frequency data in environmental monitoring. Please pick project ID: 6A if you are interested in the hydrologic analysis work. Participant two will participate in integrating the hardware and software components of the Raspberry Pi system using programming languages such as Python, PHP and SQL. Please pick project ID: 6B if you are interested in the Raspberry Pi system work. The REU participants will be mentored by 2 PhD student/s along with Drs. Lohani and Dymond. Each participant will write a research paper to document her/his research experiences.

Project ID#7: Investigation of the occurrence and fate of 4-nonylphenol, an endocrine disruptor, in urban-impacted watersheds; Mentor: Dr. Xia

Due to rapid urbanization in the State of Virginia and nationwide, many watersheds are increasingly affected by urban activities. Nutrient loading and biological indicators have been the focus for water quality monitoring in the affected watersheds. Limited effort has been devoted to assessing the occurrence of organic contaminants associated with urban activities. The objective of this REU project is to assess urban impact on the water quality of Stroubles Creek Watershed and the New River Watershed by monitoring the levels of 4-nonylphenol, an anthropogenic organic compound, often used as an indicator for urban impact. The REU student will participate in a team effort to assess how leaky sewer systems affect stormwater water quality and Stroubles Creek water quality by investigating the occurrence and levels of anthropogenic chemical indicator such as 4-nonyphenol as well as human pathogens in the stormwater and receiving surface stream. The REU student will learn latest techniques for analysis of organic contaminants in environmental samples and gain hands on experience with the state-of-the art analytical instrument such as gas chromatography-tandem mass spectrometry (GC/MS/MS). The REU student will be working with graduate students under Dr. Xia's guidance and is expected to write up the results and present the work at a research conference.

Project ID#8: Water Conservation and Waterborne Disease Nexus of Faucets; Mentors: Drs. Pruden and Edwards

Legionella pneumophila is an opportunistic pathogen found in building plumbing. *L. pneumophila* can cause Legionnaire's Disease (severe pneumonia) in immuno- compromised individuals, hospitalizing 8,000 to 18,000 people each year and is responsible for a majority of the waterborne disease deaths in the U.S. At the same time, society is striving to become more energy and water sustainable, prompting installation of low (and lower) flow faucets in hospitals, schools, and homes around the country. Limited sampling to date has raised concern about these new "green" faucets, because they seem to have much higher levels of *L.pneumophila* than normal faucets. This research would be the first to systematically study this issue. In addition to operating a plumbing rig to generate samples and explore the relationship between *L. pneumophila*, flow rates, and flow volumes, the REU student would monitor *L. pneumophila* levels via qPCR and agar plating. Temperature, TOC, ICP and 16S rRNA genes (total bacteria) will also be quantified. The overall goal is to determine if the prior sampling results correctly indicated a systemic problem with low flow faucets causing higher L. *pneumophila*, and to consider what can be done about it. The plumbing rig will be constructed and ready for the REU to lead experiments summer 2015 in collaboration with a graduate student and under the direction of Drs. Edwards/Pruden. The REU student will write up the results and be encouraged to present work at conferences.

Appendix 3

Recreational Activities around Blacksburg, Virginia

Virginia Tech is located in Blacksburg, Virginia and surrounded by the Blue Ridge Mountains. The Appalachian Trail runs through the area and affords many hiking trails. Other hiking trails off the Appalachian Trail include a 2-mile hike to the Cascades Waterfall and Wind Rock, which affords panoramic views of nearby mountain ridges. The New River is located nearby providing kayaking, canoeing, inner tube floating, and fishing during the summer. Other outdoor activities include mountain biking at Pandapas Pond, road biking the Blue Ridge Parkway, and walking, running or biking the Huckleberry trail. The Salem Avalanche, a Class A Affiliate of the Houston Astros, play in nearby Salem, VA.

Live music in both indoor and outdoor venues is available. Friday Night Jamboree in Floyd, VA has been listed as one of the two best places to hear bluegrass music in the United States. Friday nights on Henderson Lawn (located on campus and next to downtown) is an opportunity to hear live music free during the summer. Several restaurants provide live music throughout the week such as Jazz and Bluegrass. Unique eating experiences include local eateries such as Mike’s Grill (burgers and fries), More than Coffee (Mediterranean cuisine), Cabo Fish Taco, Boudreaux’s (Cajun style food), The Cellar (Greek cuisine), Gillie’s (vegetarian fare), Excellent Table (Ethiopian fare) as well as numerous coffee shops located next to campus. Next to campus is The Lyric, a non-profit venue that shows weekly movies and with occasional live performances and a large stadium style movie theatre is located 5 miles away in Christiansburg adjacent to the New River Mall. This is just a sample of the wide varieties of things to do and see in and around Blacksburg.

Pictures from the summer 2015 REU Site