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# Table of Contents

Acknowledgements ........................................................................................................................................... 3  
Summary .......................................................................................................................................................... 4  
Research Papers .............................................................................................................................................. 7  
  William Scally*, Walter M. McDonald**, Dr. Randel Dymond**, Dr. Vinod K. Lohani*** ......................... 8  
  Mariah Haberman*, Dr. Cayelan Carey**, M.S. Candidates: Alexandra Gerling**, Kate Hamre** .......... 23  
  Lauren Wind*, Katherine Phetxumphou**, and Andrea Dietrich** .......................................................... 35  
  Melissa Wilson*, Sheldon Masters**, Dr. Marc Edwards** ................................................................. 48  
  Steven T. Keith *, Dr. Jenifer Irish **, Dr. Robert Weiss; ***, Stephanie Smallegan **, Wei Cheng*** ........... 57  
  Savannah Cranford*, Professor Brook Kennedy** .................................................................................. 70  
  John Purviance*, Debarati Basu**, Daniel Brogan**, Dr. Vinod K. Lohani** ............................................. 83  
  Mariah Redmond*, Dr. Madeline Schreiber**, Zackary Munger **, Dr. Cayelan Carey*** ....................... 94  
  Jamie Keyes*, Asso. Prof. Akshay Sharma** ....................................................................................... 113  
  James von Dollen*, Theresa Sosienski**, Dr. Kang Xia** ...................................................................... 125  
  Kara Harrison*, Rebekah Hupp**, Caitlin Proctor**, Dr. Marc Edwards**, Dr. Amy Pruden**, Dr. Vinod Lohani*** ......................................................................................................................... 139  
NSF/REU Site Assessment Report ............................................................................................................. 147  
  Appendix I .................................................................................................................................................. 155  
  Appendix II ............................................................................................................................................... 158  
NSF/REU Site Announcements .................................................................................................................... 161  
  Short Announcement ............................................................................................................................... 162  
  Long Announcement ............................................................................................................................... 163  
Pictures from the summer 2014 REU Site ................................................................................................. 170
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Summary

This Research Proceedings includes papers of undergraduate research that was conducted at Virginia Tech during summer 2014 as part of an NSF/REU Site on Interdisciplinary Water Sciences and Engineering. This was the first year of the 3\textsuperscript{rd} cycle of the NSF/REU Site that will be implemented during 2014, 2015, and 2016. This 3\textsuperscript{rd} 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 2014, 66 REU Fellows (39 women and 27 men) have graduated from REU Sites. Exposing qualified undergraduates to interdisciplinary research issues in water sciences and engineering is the key goal of this REU Site. Faculty members from five departments (Engineering Education, Civil and Environmental Engineering, Biological Sciences, Geosciences, Industrial Design, and Crop and Soil Environmental Sciences) at Virginia Tech mentored 10 excellent undergraduates who were recruited out of a nation-wide competition. This is the first year our faculty mentorship team included two colleagues from College of Architecture and Urban Studies. 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 – 2014 Research Work

Mr. Scally, an REU fellow sponsored by his university (Florida International University), and his co-investigators analyzed flow computation methods in an urban storm water network and collected flow data from an urban stream (Stroubles Creek) flowing through Virginia Tech campus. The index velocity method which relates the index velocity given by an acoustic Doppler current meter to the mean velocity of the channel was employed to computer flow. The investigators sought to improve upon the index velocity method by relating the cell velocities of
a Sontek Argonaut-SW-Acoustic Doppler current meter to the mean velocity recorded by a handheld Sontek FlowTracker as well as the discharge computed through a stage-discharge weir rating curve. Ms. Haberman, an REU fellow from Stanford, and her co-investigators investigated the water quality of Beaverdam Reservoir (Blue Ridge, VA), a reservoir that flows into a drinking-water source managed by the Western Virginia Water Authority. Beaverdam Reservoir provides a critical water resource for the residents of Roanoke, VA. The researchers monitored depth-profiles of temperature and dissolved oxygen for 3 months (April to July, 2014) and found that the thermal stratification intensified resulting in anoxic conditions within the bottom 4 meters of the reservoir with the progression of summer. Additionally, a substantial increase in phosphate and ammonium concentrations one-meter above the sediments was seen later in the summer corresponding to the anoxic period. The investigators also constructed the bathymetric map of the reservoir and calculated the potential nutrient loads of total phosphorus and nitrate-nitrite that could flow into Falling Creek Reservoir. Ms. Wind, an REU scholar from Allegheny College and her co-authors investigated the reactivity of nanoiron materials. The goal of Ms. Wind’s research was to assess reactivity of nZVI by measuring how much Fe$^{2+}$ is produced when reacted with human saliva, and its implications on water quality and human health aesthetics. Ms. Wilson, an REU scholar from East Carolina University and her co-authors examined the effect of particulate iron and temperature on the rate of dissolution from three lead solids (lead oxide, lead carbonate, and lead phosphate) that typically form the plumbing materials. It was found that higher lead observed at higher temperature cannot be due to faster dissolution or higher equilibrium values of soluble lead. An REU scholar from Washington State Univ. (Mr. Keith) and his co-investigators quantified the distinguishing features of Tsunami vs. Hurricane sediment overwash events. Xbeach model was calibrated to investigate sediment transport from an idealized barrier island. It was found that in general higher surge levels produce a larger amount of erosion. The respective tsunamis show similar behavior but transport sediment farther than storms. Ms. Cranford from Penn State and her faculty mentor investigated the potential of fog capture for meeting people’s potable water needs. A design of a fog capture system was presented that is adaptable on site to wind conditions and expandable as needed. Mr. Purviance, an REU scholar from Virginia Tech, and his co-authors documented use of a Raspberry Pi for accessing real-time high frequency data from water and weather sensors in a Learning Enhanced Watershed Assessment System (LEWAS) lab on Virginia Tech campus. A local database on the Pi used a mirroring process to replicate the local database to a remote database established for storing and sharing the LEWAS data with users for education and research. An REU scholar from Florida International University, Ms. Redmond, investigated the release potential and mobility of sediment phosphorus in a drinking water reservoir (Falling Creek Reservoir) in Roanoke, Virginia. The study examined mobility of Phosphorus in sediments under different controlled oxygen conditions and results are useful for preventing cyanobacterial blooms in reservoirs. A study to investigate the benefits of Greywater system with special focus on India was conducted by an REU scholar, Mr. Keyes, from University of Kentucky and his faculty mentor. Possible costs and benefits of these systems were analyzed using examples from Africana and Asia. Mr. Dollen, an REU scholar from University of Tennessee at Martin, and his co-authors analyzed the environmental impacts of animal manure which is used to fertilize the soil. The study site is located in Stroubles Creek watershed and eleven hormones were suspected in the soils due to the fertilizer and it was found that these do travel due to runoff. However, additional samples are needed to provide statistical evidence. Lastly, Ms. Harrison, an REU scholar from Virginia Tech, and her co-authors conducted a study to examine an opportunistic
pathogen (Legionella pneumophila) in pipes and fixtures of the water distribution systems. An experiment was conducted to investigate whether the total organic carbon affects the L. pneumophila growth.

Disclaimer

The opinions, findings, and conclusions or recommendations expressed in this proceedings are those of the authors and do not necessarily reflect the views of the National Science Foundation or Virginia Tech.
Research Papers
Comparison of Flow Computation Methods in an Urban Storm Water Network
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Abstract

Computing flow in urban stormwater networks is important because it is necessary to understand pollutant loads, record urban water flow, and monitor the efficiency of our urban stormwater infrastructure. One specific method to compute flow is the index velocity method which relates the index velocity given by an acoustic Doppler current meter to the mean velocity of the channel. This method however does not take into account the vertical cell velocity profiles recorded by the current meter. This paper seeks to improve upon the index velocity method by relating the cell velocities of a Sontek Argonaut-SW-SW Acoustic Doppler current meter to the mean velocity recorded by a handheld Sontek FlowTracker as well as the discharge computed through a stage-discharge weir rating curve. Stage behind the weir is recorded by a Global Water WL705 ultrasonic level transducer. Data was collected over the span of 10 weeks at a location on Stroubles Creek south of West Campus Drive on Virginia Tech campus in Blacksburg, VA. Results from this study are expected to improve the index velocity method by relating individual velocity cells from the index velocity profile to the mean velocity given by the ADV and flow given by the weir.

Keywords: Doppler, flow measurement, current meter, index velocity.

I. Introduction

Hydrometry is the study of volumetric flow rate. Volumetric flow rate (cfs) in open channels can be determined a variety of ways. The velocity-area method is product of velocity (ft/s) of the fluid, multiplied by the area (ft²) of the stream. The area of a stream is calculated by determining the height (ft) of a stream, multiplied by the width (ft). At normal conditions it has been observed that the smaller the stream’s total area, the higher the velocity of the stream. Conversely, a larger cross section area of the stream results in a lower velocity, given the same volumetric flow rate. Measuring the overall fluctuations of a stream’s area and velocity at different portions of the stream allows for the calculation of volumetric flow.

Surveying equipment, like the Total Station Instrument, aids hydrologists in determining the exact width and depth of a natural stream cross-section. The area of a natural stream’s volumetric flow is generally constant at a given stream when the stream height (stage) remains steady. Sensors like the Sontek Acoustic Doppler Velocity Meter (ADCP) and Sontek Acoustic Doppler Velocimeter (ADV) use sound waves to detect particles within the stream to determine the velocity of the current.

Hydraulic structures find volumetric flow from the velocity-area ratings of two key areas within the stream. These structures (weirs and flumes) are physical controls installed within the cross section of
the stream that restricts the area of the stream. Using the knowledge of stage of a stream before the water enters, the weir or flume, in comparison with the flow to the area and stage of the stream when leaving the hydraulic structure gives a unique ratio. This ratio can be used to algebraically find initial and final velocities and using velocity-area method equation to ultimately find volumetric flow (Akers 1978).

Another method that finds volumetric flow is the dilution technique. This method uses a measured amount of solution tracer, known as a slug, like salt (NaOH) or a radioactive isotope. This solution tracer is injected into the stream at a specific point and time. A sensor located farther downstream is used to detect the spike in the normal water conditions due to the slug injection. The time of the start of the slug peak, to the time that the concentration of the solution tracer sensor stops reading a peak is directly correlated to the velocity of the stream.

This paper seeks to improve upon the index velocity method by relating the cell velocities of a Sontek Argonaut_SW Acoustic Doppler current meter to the mean velocity recorded by a handheld Sontek FlowTracker Acoustic Doppler Velocimeter as well as the volumetric flow computed through a “stage-discharge weir rating curve.” Several limitations were faced throughout the duration of this research. The trapezoidal weir found within the culvert has a specified stage limit when it functions as a weir or flume, when the stream height (stage) exceeds the height of the sloped concrete sides of the weir the control structure cannot no longer calculate velocity. The ADCP is able to calculate velocity during higher stage; conversely there is only one cell available to calculate velocity during low flow or base flow. Control structures like the trapezoidal weir, stone rip rap and cement hill located farther downstream dissipate the potential energy of the stream flow resulting in reverse flow or backflow. The trapezoidal weir has large amounts of sediment behind the weir causing the cement floor of the approach channel to experience scouring. The scouring of the cement floor creates in accurate reading of the stage height of the approach channel. The ADV has complications calculating velocity during turbulent flow. The stage is constantly fluctuating during high flow causing inaccurate readings of the area of the cross stream in calculating volumetric flow for ADV method. The stage-area rating curve assembled over a span of several years has a high degree of range.

II. Research Methods and Experiment Setup

LEWAS Site Description

The Learning Enhanced Watershed Assessment System (LEWAS) has been developed by the Engineering Education Department at Stroubles Creek on the campus of Virginia Tech. The two main advantages of having a high-frequency real-time watershed monitoring system is that the overall health of the creek can be observed as a way to determine the impacts of a controlled urban system. Stroubles Creek has a unique characteristic, natural springs supplying the creek provide an isolated watershed. The benefit of this situation is that any damage to the quality to the stream can be traced to activity occurring in the local community.

The LEWAS site can also be used to give a qualitative real-time analysis of the creek to be used for educational purposes. There are a multitude of systems that the LEWAS site utilizes to analyze the creek. Data collected by: Acoustic Doppler Velocimeter (ADV), Acoustic Doppler Current Profiler (ADCP), Water Sonde, weather station and Ultrasonic Level Transducer, are processed and stored on a local database by the LEWAS lab computer science team. Solar panels that are used to supply electricity for the LEWAS site are handled by an electrical engineering team. The trapezoidal weir, ADV, ADCP
and Water Sonde, are used to analyze and compare data relationships for overall quality and quantity by civil and environmental engineering students. These three fields and their respective curriculum requirements are enriched by the unique interactive modules the real-time data provided by the LEWAS Lab.

Prevention of stream bank failure has been resolved in this section of Stroubles Creek by creating a compound storm drainage project covered by stone rip rap along with a windrow revetment. A compound storm system is created by benching which reduces the slope of the stream banks to reduce the risk of stream erosion. A small step is created where the primary river bank or revetment exists. This is followed by a windrow revetment, a larger secondary step that is behind the first revetment. The stone rip rap is a high density number large stones along the channel that makes up the revetment, increasing the roughness or turbulence of the stream flow. Another structure within the LEWAS site is a soil-cement hill on the right side of the stream, causing a bend in the stream flow. These control structures with the addition of the weir creates a high dissipation of potential energy. The result of having high energy dissipation is the generation of reverse stream flow or back flow (Julien 2002).

Many thriving neighborhoods like Blacksburg, Virginia, are experiencing a surge in urban development projects. The increases in land use change from urban expansion commonly result in: an influx in affluent storm water and excess sediment runoff (pollutant loads). Alterations in infiltration versus runoff ratio are a result of the conversion of large sections of undisturbed land into sidewalks and parking lots. High precipitation events that normally seep (infiltrate) into the land, ends up becoming runoff because of the impervious concrete surfaces. This characteristic of urbanization gradually causes watersheds to become unfit for handle the massive volumes of storm flow. Construction sites with poorly managed silt fences allow large amounts of sedimentation, during storms, into the watershed. The foreign sediment may cause disruptions the natural water chemistry of the creek thus affecting the local aquatic ecosystem. Thoroughly understanding the volumetric flow of an urban stormwater system allows for an accurate assessment of the pollutant loads experienced.

The runoff from impervious structures also contributes to thermal pollution within the watershed, resulting in severe disruptions to the sensitive ecological system surrounding the watershed. Thermal pollution is caused by the heating of the water runoff by low albedo surfaces like parking lots. Albedo is the ability of a surface to reflect solar radiation. When the heated runoff enters watershed like Stroubles creek, it causes a spike in temperature of the creek, causing organisms like crayfish within the environment to perish.

2.2 Flow Measurement Devices

\[
Q = \sum_{n=1}^{N} \frac{1}{2} \left( h_n + h_{n-1} \right) \left( w_n - w_{n-1} \right) \left( v_n + v_{n-1} \right)
\]

EQ. 1

\(Q\) is Volumetric Flow (ft\(^3\)/s). \(H\) is height of stage (ft). \(W\) is width of creek cross section (ft). \(V\) is velocity of the creek (ft).

**Handheld ADV**

Sontek Acoustic Doppler Velocimeter (ADV) is a manually operated sensing device. It is comprised of three separate acoustic transducers. This instrument is comprised of bistatic radar, meaning
transducers are specifically either a transmitter or receiver. The 2-dimensional Sontek ADV has two arms positioned on the left and right sides of the probe. Located at the end of the arms are receiver transducers which are focused on a definite position located approximately 3.93 inches in front of the central probe. From the Doppler Shift Equation:

\[ F_r = -F_s \left( V/C \right) \quad \text{EQ. 2} \]

\( F_r \) is the Doppler shift recorded by the receiver transducer, \( F_s \) is the sound pulse generated by the transmitter transducer. \( V \) is the velocity of source from the receiver. \( C \) is the speed of sound. To account for a change in the sound frequency due to fluctuation in water temperature the ADV has a thermistor installed within the probe head (Sontek/YSI 2003).

The operator can manually choose how many seconds they want stay at each point within the stream. The higher the amount of time spent at each point in the cross section increases the overall confidence of the accuracy of the ADV device in calculating the exact velocity of the point. At each second the transmitter transducer is submerged under the water surface, it emits ten sound pulses. These sound pulses (pings) are averaged together to give a mean velocity. Quality control (QC) checks for inaccurate velocity readings. A Doppler shift reading that is out of the standard deviation range of the other pings (called a boundary adjustment) is omitted from the overall velocity the ADV determines to be accepted (Sontek/YSI 2003).

Sontek Argonaut SW (ADCP)

The ADCP is installed on the bottom of the creek in the up-ward looking position, within the stream midsection. For optimal quality of vertical velocity data, the ADCP is suggested to be installed at the creek’s midsection. Normally, creeks have the highest velocity within the midsection. Once ADCP is installed, continuous velocity data can be recorded by this remote device. The advantage of having continuous velocity recordings is being able to use this data in a real-time monitoring system (Sontek 2009).

The ADCP has a similar operation as the ADV. The ADCP has three transducers, and a built in temperature sensor. The temperature sensor has a similar function as the thermistor inside the ADV. The two 45 degree angled transducers are used emit a ping but unlike the ADV, the transducers are not separated. The two angled transducers functions a transmitter and receiver. The Doppler shift:

\[ F_r = -2F_s \left( V/C \right) \quad \text{EQ. 3} \]

\( F_r \) is the Doppler shift recorded by the receiver transducer, \( F_s \) is the sound pulse generated by the transmitter transducer. \( V \) is the velocity of source from the receiver. \( C \) is the speed of sound (Sontek 2009).

ADCP has a special feature called Dynamic Boundary Adjustment. This allows velocity data to be interpreted in two ways. The velocity points recorded by the transducers can be taken as a whole set and average together, giving a total average velocity of the river. The second way of computing the data is by dividing the entire range of velocity data into vertically integrated velocity cells. The ability of the instrument to record vertically integrated cells, allows hydrologists to understand the exact velocity of every layer within the stream (Sontek 2009).

The third transducer, located in the center of the devise, is used for determining the stage height of the creek. The central transducer sends a pulse but instead of detecting suspended particles, this transducer is calibrated to detect the surface of water above the instrument. The ADCP has a designated distance (.23 ft) above of the transducers where no Doppler shift is recorded (blanking distance).
Blanking distance is required by the ADCP to allow ample time for the transducer to convert from transmitter to receiving function. When stage height is recorded by the device, 0.23ft is automatically added the initial stage data to provide an accurate stage height. This continuous stage height provides the ADCP with the ability to process a continuous volumetric flow (EQ.1) of the midpoint of the creek (Sontek 2009).

**Ultrasonic Level Transducer**

Ultrasonic Level Transducer (ULT) is a cylindrical metal sensor that contains a transducer positioned on the end of the instrument. ULT functions as both a transmitter and receiver like the central transducer ADCP sensor, but emits ultrasonic waves instead of sound waves. ULT is not submerged underwater like the other sensors used at the LEWAS site, the ULT will be installed hanging at a 90 degree angle on the top portion of the weir ceiling. To properly read the stage of the creek before it enters the weir structure, the ULT is required to be installed six feet upstream from the weir. Once the stream is within a distance of 6 feet or less from the weir structure it begins to decrease in stage height. ULT will provide the LEWAS Lab with continuous information on initial stage height. This piece of data is essential for attaining the volumetric flow at the weir site.

**Trapezoidal Weir**

Types of control structures used to measure hyrometry are Weirs and Flumes. Both structures function by having a pressure distribution that is hydrostatic at a critical flow point. By measuring the stage height, specific energy head of the flow upstream of the weir, hydrostatic pressure can be determined (Bos 1985). Figure 1. and Equation 4. shows the relationship of stage and hydrostatic pressure from a one dimensional view. “An equation for accurately describing the head-discharge relationship over a weir under free-flow conditions cannot be derived purely from theoretical considerations… (Merkley 2004).”

![Figure 1. Diagram Of Determining Mean Flow Velocity Using Bernolli Equation In Terms Of One Dimensional Flow.](image)

\[ h_t = h + \frac{v_u^2}{2g} = Ch_t + h_L \frac{v_m^2}{2g} \]  

EQ.4

\( h_t \) is the difference between the weir height and \( h \), \( \frac{v_u^2}{2g} \) is atmospheric pressure, \( Ch_t + h_L \frac{v_m^2}{2g} \) is hydrostatic pressure.

**HACH Hydrometer MS5 water quality Sonde**

To measure water quality in the stream a Hydrolab MS5 Water Quality Sonde is installed in a permanent housing within the middle of the stream. The Sonde is a multi-parameter probe that measures
pH, temperature, specific conductance, oxidation reduction potential (ORP), turbidity and dissolved oxygen (DO). These parameters were chosen because taken together they give a good representation of the health of the stream and are robust enough to endure continuous high-frequency collection over an extended period of time. Although phosphorous and nitrogen are important stormwater pollutants of interest in the state of Virginia (VDEQ 1999), there exist no environmental sensors for such nutrients that can withstand the rigor of a long-term deployment. To protect the multiple probes within the Sonde a perforated stainless steel cover sleeve surrounds the device which blocks debris while allowing contact with stream flow. It is vertically mounted on a steel frame in the center of the stream and submerged 13 cm from the bed. The Sonde takes measurements in the stream in 3 minutes intervals.

**Vaisala Weather Transmitter WXT520**

Figure A 2 illustrates a cut away view of the Vaisala Weather Transmitter WXT520 (WXT520). This device is equipped with three transducers to measure wind speed changes labeled 1 and a precipitation sensor labeled 2. The pressure sensor, label 3, and the humidity and temperature sensors, 4, are housed within the WXT520 device. The main goal of the WXT520 is to collect precipitation data for a complete hydrograph of the LEWAS site during storm events increasing the stage of the creek. Pressure sensors located on the top portion of the WXT520 housing device, determines the rainfall intensity at continuous ten second intervals (Viasala 2010).

**Index Velocity Method**

The need for a graphical correlation of comparing different measuring devices is resolved by the Index Velocity Method (IVM). \( V_i \) is an average of velocities given by the ADCP. \( V_m \) is the averaged velocities given by the trapezoidal weir or the averaged velocities by the ADV. Graphical representation using linear regression \( R^2 = 0 \rightarrow 1 \) of Acoustic Doppler Velocimeter \( V_i \), (x-axis) and Index Mean Velocity (\( V_m \)) from ADCP averages. The Velocity Index is interpreted by an average of the Cell heights taken by the Argonaut_SW. The current parameters only have the bottom three cells (out of a total nine) calculating velocity data during base height.

During storm events, when the weir isn’t capable of proper function (no nappe) yet still can operate using flume like calculations, the 4 other cells in the ADCP are able to calculate viable velocity data:

\[
Q_2 = V_1A_1 + V_2A_2 \ldots \quad \text{(EQ.5)}
\]

\( Q_2 \) is the Volumetric Flow, \( V \) is Velocity, \( A \) is Area

\[
V_m = \frac{V_1A_1 + V_2A_2}{A_1 + A_2} \ldots \quad \text{(EQ.6)}
\]

\( V_m \) is Mean Velocity, \( V \) is Velocity, \( A \) is Area

**Data Collection Methods**

**Handheld ADV**

A major drawback of this device is that it becomes very difficult to calculate velocity when stage has exceeded the primary revetment in the compound stream. I observed this type of phenomena on July 13th. As the stage exceeds the primary revetment, the total area of the creek increases as well.
Unfortunately, the vegetation on top of the revetment creates too much noise for the use of the sonar. The ADV ability to function is compromised without the use of the sonar. During occasional situations where the stage height exceeds normal boundaries, both the ADV and weir become compromised, thus ADCP is the only suitable way of calculating stream flow.

After conducting handheld ADV measurements at the downstream cross section, it is shown that velocity near the hill obstruction is much faster than the stream velocity on the far side of the stream. One possible explanation is that the hill is slowly eroding into the stream causing the stream bed to increase in height. An increase in stream bed height causes the water to flow faster through a smaller area than a deeper stream bed.

![Velocity Profile Of ADV Cross Section On July 14th, 2014 During Baseflow (top) And Stormflow (Bottom).](image)

One challenge when using the ADV are the errors that occur while trying to measure velocities in the stream during storm flows. Possible errors include a large standard error of velocity. Highly turbulent environment or highly aerated water causes the pings to be incorrectly recorded by the receiver transducers. The standard error threshold (0.01 m/s / 0.033 ft/s) for each ping measurement is determined by “dividing the standard deviation of one-second samples by the square root of the number of samples (Sontek 2009).”

Argonaut-SW

Weir

Upstream of the LEWAS site is a constructed weir inside at 4m x 4m box culvert. The weir was constructed in 2003 and was modified in 2014 to create free flow conditions. In addition, in 2014 a stage measurement stick was installed behind the weir to provide stage measurements. A model of the weir was constructed and installed in a hydraulic flume in the Celso Baker Lab on Virginia Tech campus. From this study an equation was developed to relate the stage behind the weir to the discharge of the channel. This equation can be applied to stage measurements taken from the measurement stick behind the weir to estimate flow at the site. When the ultrasonic level transducer is installed at the site, it will provide continuous stage measurements behind the weir to estimate real-time flow at the LEWAS site.
Surveying

A Total Station Instrument (TSI) was used to collect elevation data across the ADV and Argonaut-SW-SW cross sections. Figure 1 shows LEWAS Lab members William Scally and Walter McDonald taking elevation profiles of the ADV cross section. This elevation information is used to create the stage-area rating that is critical to computing the flow rate. To conduct a survey, a long line with plotted measurements like a measuring tape, must be laid at the cross section of the stream. Originally, the length of the measuring tape used was about twenty feet in length. Surveying for the bank of the creek we took prism measurements at every foot, once we reached the streambed measurements were taken every half foot. The prism was leveled using a spirit level so that the shaft directly perpendicular to the ground. The actual (TSI) recording apparatus was positioned about twenty-five feet away and has an eye piece with cross hairs inside of it. Using two knobs one that controls the X-direction (Easting position) and one on the side of the device that controlled the eye piece in the Y-Direction (Northing Position) I was able to locate the cross-hairs within the prism and find out the exact position of it. When the data was brought back to the lab, the spreadsheet data was extracted from the (TSI) which only had Northing and Easting plots for each location. Using the theorem of Pythagoras, the distances of the points in respect to one another were determined. To calculate the height from the northing data, first the lowest depth must be found on the data points and that will be determined as the base value. Then, the other northing values are subtracted using that minimum base value. Once the distances and height are determined a Stage-height rating can be constructed. The stage graph, produced from the survey, can determine the area of the stream using the Riemann sums:

\[
\text{Area} = \lim_{n \to \infty} \sum_{k=1}^{n} f(X_k^*) \Delta x
\]

EQ. 7

Where \( f(X_k^*) \) a specific height of a trapezoid at a given number and \( n \) is the number of rectangles up to the 16\(^{th}\) station, and \( \Delta x \) represents the base of the rectangle. Once the area of the stream is known the multiplication of the area of the stream at a given height can be multiplied by the velocity to give the volumetric flow.

![Figure 3. Surveying At The ADV Cross Section](June 17th, 2014)

Multiple cross section profiles were taken at the location of the ADCP over the period from spring 2012 to summer 2014. Similarly to the Surveying process, the first step in taking the cross section
using the Sontek Handheld ADV is putting a measuring tape across the stream, then taking measurements with the ADV device at half a foot sections in the stream.

One problem encountered with taking the ADV measurements at the ADCP cross-section was that unlike the designated ADV cross-section downstream as shown in Figure 3, the cross-section at the Argonaut-SW site was not exactly demarcated with stakes to show the actual surveying path. To resolve this issue, the surveying heights were cross referenced with the placement of the mounted ADCP to accurately match the data. The demarcations on the ADV pole were used to determine the stage height at every half foot. This data was entered manually into the reading monitor. Then the device had to be correctly positioned perpendicular to the stream and the pole had to be correctly balanced using the leveling circle before pressing the measure button.

III. Results and Discussion

Stage Area Rating

Stage-area ratings for the ADCP and ADV cross sections were applied to the velocities and stage measured at the site to compute flow. The stage-area ratings developed for both cross sections were essential for computing accurate flow measurements. To understand what the uncertainties associated with surveying the cross sections and developing stage area ratings at the site were, two different studies were undertaken.

The first is a longitudinal study that focused on the change in the cross section at the ADCP over time. The same cross section was surveyed four times over the course of over two years to understand what the change in the cross section is over time. Figure 5. illustrates the stage-area rating of the four surveys and includes the upper and lower 95% Gaussian distribution confidence intervals. As can be seen, at lower stages the confidence intervals are close; however, as the stage increases, the confidence intervals split apart and begin to deviate more. This indicates that the channel has changed at the banks over time and especially at stages over 2-3 feet. However, this error could also be due to other uncertainty factors besides physical cross section changes such as instrument uncertainty or human induced errors.

![Figure 4. Stage-Area Rating Comparisons 2012-2014 Before Data Shift (left), Stage-Area Comparison From yrs.2012-2014 After Data Shift (right)](image-url)

To investigate other uncertainty factors besides physical cross section changes that could contribute to the deviation in upper and lower confidence intervals in the longitudinal study, a second
study was conducted. In this study, six different cross sections were surveyed on the same day by two different users. This study sought to determine what the uncertainty in stage-area ratings were due to the methodology in taking the survey and due to different users. Figure 4 illustrates the stage-area ratings for the six different surveys. Three surveys were taken by one user and three by another. As can be seen in the figure there is deviation between the surveys taken during this period of time. User 1 has some deviation between surveys 1-3, whereas User 2 does not have substantial deviation between surveys 4-6. However, the stage-area ratings between User 1 and User 2 are preforming, deviate at all stages. This indicates that there is uncertainty in the methodology, shown between the different stage-area ratings by User 1, and uncertainty due to different users, shown by the difference between User 1 and User 2. It should be noted that this was only the second experience in surveying for User 1 but User 2 had significant training and experience in the equipment.

Sources of human error when taking surveying measurements with the Total Station Instrument can be a result of:
1. Inaccurate leveling of the prism
2. Prism bottom not accurately positioned on the designated spot assigned on the measuring tape.
3. Device incorrectly calibrated
4. The “F1” button pressed too hard causing the station to shift, causing the reading to be distorted right of the prism location.

Index Velocity Rating

The ADV was deployed during a summer thunderstorm on July 14th, 2014 and July 15th, 2014. During this time the ADCP was continuously recording stage and velocity measurements at 1 min intervals and the stage behind the weir was recorded at the beginning and end of each ADV deployment. The flow captured by the ADV, ADCP, and weir are shown in Figure 6. over the July 14th, 2014 thunderstorm. To compare the flow of the ADV, ADCP, and weir together, the flow captured by the ADCP and weir had to be averaged over the time interval that it took to compute flow captured by the ADV. The average time interval to capture the full range of velocities across the ADV cross sections was
10 minutes. As can be seen in Figure 6, the team captured the tailing end of the hydrograph. The flows from all three measurement devices compare well across all flow ranges, with the ADCP and weir following the most closely.

Figure 6. Flow Measurements
(July 14, 2014.)

The primary goal of this study is to determine if a better relationship can be created for the index-velocity rating than the mean velocity to index velocity rating established using an ADV and ADCP. The first test is to see if the mean velocity, as captured by the flow from the weir, has a closer relationship to the index velocity than does the mean velocity captured by the ADV. The index velocity rating developed using flows estimated with velocities captured by the ADV is illustrated in Figure 7. The index velocity rating developed using the flows estimated by the weir is illustrated in Figure 8. Both of these plots had a linear trend line fitted to the data. The ADV index velocity rating has an $R^2$ value of 0.9353 compared to the $R^2$ of 0.9901 from the Weir index velocity rating. It is clear from this storm that the mean velocity developed using the weir has a closer relationship to the index velocity from the ADCP. This could be due to a variety of factors. One reason could be that the flows estimated using the ADV are more susceptible to uncertainties due to human-induced errors as it is up to the user to take velocities over time at precise locations across the cross section during high flows. It could also indicate that the weir produces more reliable flow estimates than does the ADV, as the weir flow in Figure 8 produces a more linear trend than the ADV does.
Multi-Cell Regression

Another method to improve upon the standard index-velocity rating was to try to develop a mean-velocity to cell velocity relationship using the cell velocities delivered by the ADCP. During this storm the maximum number of cells that could be used was the first cell, as the storm captured the first cell completely and only part of the second cell. Each cell is 0.3 m with a blanking distance between the ADCP and the cells of 0.07 m. Due to the limited number of cells that could be used in this experiment, further storms with cell data will have to be analyzed to determine if there are better relationships between certain cells. Figure 8 illustrates the relationship between the velocities as captured by cell 01 and the mean velocity from the ADV. The R-squared from this relationship was 0.9303, slightly less than the 0.9353 using the averaged cell velocity. One reason for this is that during the tail end of the storm,
when flows were closer to base flow, there was a negative velocity captured by Cell 01. This is due to eddies and backflow that occur at the ADCP cross section during low flows. Because of this, further studies need to investigate at what stages velocities from the ADCP are appropriate for use in estimating flow.

Figure 9. Index Velocity Rating Using Cell 01 velocities

IV. Conclusion

This paper has investigated methodologies to improve upon the index-velocity rating applied to a small urban stream using an ADCP at a natural cross section. Results from the stage-area case studies indicate that the cross section at the ADCP location does change over time due to sedimentation, but also that there are uncertainties due to methodologies and human-induced errors when creating the stage-area ratings. This has implications in determining what the overall uncertainties are in estimating flow at a natural stream cross section in a small urban watershed. Results from the index-velocity rating case study indicate that using mean velocities captured by flow estimated from a weir produces a more reliable index-velocity rating. This has implications for hydrologists that develop index-velocity ratings for locations in small urban watersheds. Results suggest that installing a structure, such as a temporary flume or weir, is a more reliable way to develop an index velocity rating. Results from the ADCP cell velocities case study are inconclusive and suggest that more data captured at higher stages will need to be analyzed to determine if more reliable relationships can be established.

Future work should include continued monitoring of the cross section to see how sedimentation and erosion affect the stage-area rating over time. More data that captures runoff over various storm events should be used to determine if the weir index velocity rating does in fact produce a more stable relationship with the ADCP than the ADV index velocity rating.

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Appendix A

Figure A 1. ADCP Cross Section Profiles

Figure A 2. Cut Away View Of WXT520
A Full Investigation and Water Quality Report of Beaverdam Reservoir, a Critical Drinking Water Resource for Roanoke, VA

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Abstract

To best manage our drinking water resources, it is imperative to define the physical characteristics of a reservoir, as well as monitor its chemistry and biology. For this project, we investigated the water quality of Beaverdam Reservoir (Blue Ridge, VA), a reservoir that flows into a drinking-water source managed by the Western Virginia Water Authority. Although Beaverdam Reservoir provides a critical water resource for the residents of Roanoke, VA, its detailed water quality remains unknown. From April 2014 through July 2014 we monitored depth-profiles of temperature and dissolved oxygen. It is clear that as summer progressed, thermal stratification intensified resulting in anoxic conditions within the bottom 4 meters of the reservoir. Additionally, we collected water samples to analyze phosphate, nitrate-nitrite, and ammonium concentrations. A substantial increase in phosphate and ammonium concentrations one-meter above the sediments was seen later in the summer corresponding to the anoxic period. In addition to water quality monitoring, we constructed the first-ever bathymetric map of the reservoir using Acoustic Doppler Current Profiling and GIS. From these data we determined the surface area and total volume of the reservoir and then calculated the potential nutrient loads of total phosphorus and nitrate-nitrite that could flow into Falling Creek Reservoir given a decrease in Beaverdam Reservoir Volume.

Keywords: Dissolved Oxygen (DO), Nutrients, Nutrient-Loading, Anoxia, Hypoxia, Watershed, Bathymetry, Thermal Stratification, Sediments, Phosphate, Total Phosphorus, Nitrate-Nitrite, and Ammonium.

I. Introduction

Beaverdam Reservoir (BVR) is located in Bedford County, Virginia and is owned and operated by the Western Virginia Water Authority (WVWA). It serves as the direct upstream inflow to its smaller counterpart Falling Creek Reservoir (FCR) also owned by the WVWA (“Water Sources”, 2014) (see figure 1). Although FCR serves as a primary drinking-water source for Roanoke County, VA, very little is known about its inflow source Beaverdam (WVWA personal communication). Neither the water-quality nor quantity of BVR has been completely investigated, raising concern for its long-term use. As the water of BVR influences the conditions of FCR and the resulting treatment and management practices that are implemented to preserve human health, it is imperative that the quality-climate of BVR be analyzed and regularly monitored. This served as the

Figure 1: Both Reservoirs

(google maps, modified by Haberman, 2014)
primary motivation for our research, with the objective to analyze not only the chemical and physical characteristics of BVR, but also to research its history and that of pre-reservoir land-use both in and near the watershed. We hope that our historical findings along with our scientific data will aid the WVWA in implementing best management practices as well as shed light on future research that will further aid in prolonging the health of the reservoirs.

Figure 2: Map of Beaverdam Reservoir With Respect to Virginia
(http://www.nationsonline.org/oneworld/map/google_map_usa.htm)

Key Research Questions

1. What is the history of Beaverdam Reservoir including pre-dam and early-dam land use in and near the watershed?
2. What are the physical characteristics of Beaverdam Reservoir and how can we use these to better understand nutrient-loading (specifically total phosphorous and nitrate-nitrite) into Falling Creek Reservoir?
3. What is the overall water-quality of Beaverdam Reservoir and how have quality-characteristics affected nutrient concentrations over time?

Background on BVR Physical Characteristics

Prior to our research no bathymetric map of BVR was in existence. According to the water authority, BVR has a maximum capacity of 435 million gallons and an area of 69 acres (“Water Sources, 2014). However, it is unknown exactly when and how these figures were last calculated. Due to normal fluctuations in precipitation and erosion, it would not be surprising if BVR’s surface area and volume have changed over time. However, such changes must be updated and regularly monitored so the WVWA may best estimate the appropriate amount of water to withdraw from the reservoir (based on nutrient concentrations per volume) to ensure that neither the BVR nor FCR ecosystems are adversely affected.

Background on Water Quality

Thermal stratification is a process of varying severity that that occurs within all bodies of water. Stratification is due to the differences in densities between water at various temperatures. Warmer water is less dense and thus floats atop cooler. Within inland bodies of water such as a reservoir, the epilimnion is classified as the surface layer that contains the reservoir’s warmest water. The bottom layer, the hypolimnion, contains the densest and coldest water (“Dissolved Oxygen in Lakes”).

Thermal stratification is known to intensify during summer months (“Dissolved Oxygen in Lakes”). Additionally, thermally stratified waters tend to deplete dissolved oxygen concentration within
the hypolimnion ("Water Properties: Dissolved oxygen"). Dissolved oxygen (DO) is essential to many forms of aquatic life within a reservoir ("Dissolved Oxygen in Lakes"). In addition to supporting life, DO is known to help limit Phosphorus releases from the sediments as DO contributes to a key chemical redox reaction that keeps phosphate (PO$_4$) bound in the sediments (Singleton 2006, pg. 1).

Thus, during hypoxic and anoxic conditions within the hypolimnion, phosphate is more likely to be released from the sediments and dissolved within the water column. Similarly, lake oxygenation of surface waters has been shown to limit the release of ammonium from sediments (Beutel 2006). Additionally, when operated continually, hypolimnetic aeration systems have also been shown to help limit the concentrations of other nutrients such as iron and manganese within the water column (Gantzer et. al. 2009). From this data it appears that DO is helpful in reducing soluble concentrations of certain nutrients within reservoirs. Reducing soluble nutrient concentrations within the water column is very important as certain forms of algae such as toxic-cyanobacteria (also known as blue-green algae) can thrive on said nutrients- particularly Phosphorus (Carey et. al, 2012). Thus an increase in such nutrients could even lead result in algal blooms ("Lake restoration and management for algae"). It is interesting to note that BVR’s downstream counterpart, FCR, has an unique oxygenation system installed along the reservoir bottom to help increase DO content within the hypolimnion and help prevent algal blooms ("Gantzer Water Resources"). To date, no system exists for BVR and we would like to investigate its potential need further.

II. Research Methods

Beaverdam Reservoir Historical Investigation

In order to get an accurate idea of the pre-dam and early-dam land use in/near the Beaverdam watershed it was necessary to travel to where the majority of private water-related documents are housed, the Western Virginia Water Authority in Roanoke, VA. Upon obtaining permission from the WVWA to browse its historical records, we met with Nora Piotrowski an Engineer/GIS Technician who scanned and uploaded most of the relevant historical documents to the WVWA internal server. The documents were collected from all past water-companies that once served the Roanoke area. We were able to download these documents and analyze them individually. Additionally, we were able to communicate with WVWA employees such as Sarah Baumgard the Environmental Communications Coordinator to get a sense of what they knew about the history of BVR. In addition to visiting the WVWA, our historical research methods included a rigorous web-based search of reputable sources including official federal and state websites/documents, historical books of the Roanoke County area, as well as other published works. Upon obtaining all the necessary documents, we set out to analyze them in order to create an approximate timeline of the reservoir as well as determine any substantial-facts that might have some indication of influence on BVR’s current water-quality.

Beaverdam Reservoir’s Physical Characteristics
As one of our goals is to best understand the potential nutrient loads flowing from BVR into FCR, it is important that we have a valid estimate of nutrient concentrations per volume. In order to approximate this, we first needed an accurate estimation of reservoir total volume, surface area, and bathymetry (i.e. depth contours). To obtain the data with which to calculate these values, we made use of a 1200 kHz RD-Instruments Workhorse-Rio-Grande Acoustic Doppler Current Profiler (see figure 4) in conjunction with the software program WINRIVERII, which manages ADCP commands and records all relevant data. To begin, we put the ADCP into a Trimaran riverboat designed to keep it steady while being pulled behind our small boat traveling at about 5 mph. Atop this device, we mounted a GPS system to record the coordinates (in decimal degrees) of our location per each depth reading. The ADCP sent out an acoustic ping about every 2 seconds. We connected these devices to the WINRIVERII software in order for it to record both depth and the GPS coordinates simultaneously. We began our cruise-track by outlining the perimeter of the reservoir as close to the shoreline as possible. After that, we pulled the ADCP in a zigzag pattern across the width of the main reservoir and its branches (see figure 5). We collected the data continuously.

Once the data-collection was complete we then used the WINRIVERII software to export just the latitude, longitude, and depth data out of each ADCP transect file into a text file. After doing so, we consolidated all the data into a singular text file so it could be imported easily into MATLAB and GIS. After consolidating the data we then sorted through the file to find all data-points that were invalid (usually not read because the boat may have been going too fast) and deleted them. After filtering out the invalid data points we imported the data file into MATLAB and used interpolation to approximate the depth values over all GPS coordinates within the reservoir. This was to ensure that the data looked accurate enough to work with prior to starting the GIS process. Fortunately, we could make-out the outline of the reservoir from the MATLAB figure, indicating that the data was good. It is important to note that upon data collection we recorded the surface of the reservoir to be about 2.6 feet below full pond. To create a figure that would be representative of total surface area and volume at full-pond, we added 2.6feet onto each depth data-point within our data file. This would give us the max-depth from the surface of the reservoir.

Subsequently, we imported the data file into GIS and began making a depth map of 2-meter contour intervals over the entire area of the reservoir. To do so, we pre-loaded a satellite image of BVR into GIS and overlaid it with our data. We were able to use GIS to calculate the surface area and volume at each of these intervals and therefore were able to calculate total surface area and volume at full pond. Finally, because we wanted to know the approximate volume per 1-meter depth layer in order to best calculate nutrient loading, we were able to use interpolation to calculate the surface area and volume per 1-meter depth intervals.

“The GIS Steps are as follows:

1. Import Lat/Long/Depth data (with 2.6 feet added)
2. Define the shoreline by adding points along the shoreline (based on the aerial image) and giving these points a depth of zero.
3. Use geoprocessing tool “XY to Raster” to convert from XYZ data to raster data
4. Use geoprocessing tool “Contour” to generate contour lines at 1-m intervals
5. Create map with 2-m contour intervals (for clarity in the final map)
6. For Volume/SA calculations:
   a. SA: Used the built-in field calculator to calculate the area enclosed by each contour
   b. Volume: Used geoprocessing tool “Surface Volume” to calculate volume in each 1-m thick layer” (Bierlein 2014).

**Nutrient Data Collection and Analysis**

In order to obtain nutrient concentration data within the reservoir we collected water samples from a singular location over approximately 4 months. Our goal was to sample a selection of depths ranging from the surface to the sediments. Therefore, we selected the sample-site estimated by the WVWA to be the location of most depth (around 13 meters). Our sample depths were as follows: 0, 4, 8, and 12 meters. We used a Van-Dorn to collect such samples. The Van Dorn was lowered to depth while open, allowing water to flood in. Once at the appropriate depth, we sent a messenger down its rope to trigger the closing mechanism in order to trap the water in the Van Dorn. Once back on the surface, the water was poured into a bucket where we then collected small volumes of it with syringes. We then used the water to rinse our collection syringes 3 times. Once rinsed, we collected small volumes of water within the syringes and filtered them into pre-acidified bottles (washed with 10% HCl solution and then rinsed with deionized water to ensure the only ions we measured were those collected from the reservoir). This was to ensure that upon analysis the water samples were already soluble in nature and did not require additional reagents to analyze. The samples were then frozen until ready to be mixed with reagents and run through a Lachat. The Lachat results gave us PO$_4$, NO$_2$-NO$_3$, and NH$_4$ nutrient concentrations in micrograms per liter for each dated sample. Based on these data we were able to plot time series of the nutrient concentrations at different depths.

We were then able to use the average of the highest concentrations recorded between each of the depth intervals (0-4, 4-8, 8-12) to do “back of the envelope” calculations incorporating the volume in the reservoir per 1-meter layer of depth to determine the potential nutrient loadings that can flow into Beaverdam Reservoir if the WVWA lowers the depth below full capacity.

**Water Quality Data Collection**

For this research, we were primarily interested in analyzing the reservoir’s temperature and dissolved oxygen variance with both depth and time. In order to collect this data, we implemented the use of a CTD device at the same location from which we took our water-samples for nutrient analysis. The CTD device used has 1cm depth resolution. We used a winch to slowly lower the CTD from the surface of BVR to its...
bottom-depth while it recorded temperature and dissolved oxygen concentrations. Upon data collection we imported the dataset values into a MATLAB code and used interpolation to fill in the data between the 1cm depth intervals. The results gave us color-contour time-series figures that we could then analyze and compare against the nutrient figures.

III. Results and Discussions

Historical Data

Our historical research yielded several interesting findings. First we learned that the initial Beaverdam Reservoir was built sometime between 1869 and 1898. Based on correspondence with the WVWA, Beaverdam Reservoir had to have been built prior to Falling Creek Reservoir. Apparently, the water authority initially had plans to use the location of Beaverdam to house a treatment facility but then discovered it was too difficult to do so given the elevation. Thus, Beaverdam Reservoir was built primarily as a source to fill Falling Creek Reservoir, the new location of the treatment plant (WVWA Personal Communication, 2014). The oldest document we found showing both FCR and BVR in existence is dated 1899. Similarly, we found a map dated 1869 showing neither FCR nor BVR in existence. Additionally, it appears that by at least 1899, plans for the first pipeline between BVR and FCR were in existence (WVWA Historical Docs, 2014). This 8inch pipeline seemed to be completed by 1907 according to another document displaying its presence. However this pipeline was not the one we use today, which flows from the west side of BVR to the east side of FCR, but rather a pipeline flowing from the base of the actual dam of BVR to slightly downstream of FCR. This pipeline went south of “Weaver’s Knob”, a notable highpoint in the topography within the FCR watershed (“My WATERS Mapper”). It is currently unclear what has become of this first pipeline (WVWA Historical Docs, 2014). Based on historical photographs retained by the Water Authority it is clear the Beaverdam Reservoir was completely rebuilt between the years of 1924-1926. Not only was the actual dam structure remodeled with a concrete base, but also it appears that much of the surrounding forest area was clear-cut to make the reservoir much larger than it was in prior years. Based on the photos, it is clear that at least some or the entire reservoir had to be drained to accomplish this (WVWA Historical Docs, 2014). Because of this, we believe that a topographic map of the area that we found (undated) was most likely made during the reconstruction period of the dam. Additionally, It is around this time in 1924 that we believe the path of the new 12-inch pipeline – the path still used today -was established (see figure 7). This path travels north of Weaver’s Knob from the west end of BVR, under the highpoint separating the FCR and BVR watersheds (i.e. the watershed divide) and to the eastern end of FCR (WVWA Historical Docs 2014). Its outlet is slightly upstream of the dam and the water flows from the pipe into a small stream that serves as the inflow to FCR. We know today the intake depths of the pipeline from BVR are at 1.5m, 4.5m, and 9m from the surface of the reservoir respectively (WVWA Personal Communication, 2014).
WVWA historical documents, it appears that most of the pre-dam and early dam land use was agricultural in nature. The early maps and charts show parcels of land complete with houses, fences, barns, stables, timber cribs, and a wide diversity of trees. The agricultural nature of land-use was confirmed as it appears that prior to 1909, the watersheds were almost completely farmed. But around the end of the first decade of the 20th century the local water authority of the time the “Vinton-Roanoke Water Company” began replanting the surrounding region (Jack, G. S., & Jacobs, E. B. 1912). This replanting corresponds to the approximate age of forest growth around the BVR area.

Additionally, we initially thought there might have been some mining in the area due to the extremely high concentrations of iron we found within our water samples (see figure 8). According to a document in 1954, there were several Hematite mines only a few miles away from the BVR watershed (Gooch, E. O. 1954). Unfortunately, we did not find evidence of mining within the actual BVR watershed (“My WATERS Mapper”). However, the fact that several Hematite mines were close-by could imply a similar sediment make-up (Watson, T. L. 1911).

Temperature and Dissolved Oxygen Results

Upon importing the CTD data into excel and interpolating between the points we were able to create color-contour plots detailing the environment within Beaverdam Reservoir. In figure 9 we can see that thermal stratification begins to intensify around May 15th as we see more temperature layers with depth. Thermal stratification continues to intensify as the summer progresses through the end of July until eventually we see a typical surface water temperature of between 25-30 degrees Celsius while the water within the hypolimnion remains cold. It can also be seen in figure 9 that dissolved oxygen concentrations begin to reach hypoxic conditions (DO<2 mg/L) around when thermal stratification intensifies (~May 15th). Similarly around June 1st we start to see anoxic conditions (DO < 0 mg/L) within approximately the bottom 4 meters of the reservoir. It is clear that an increase in thermal stratification in Beaverdam Reservoir is promoting anoxic conditions near the sediments.

![Figure 9: Color Contour Maps of Temperature (left) and Dissolved Oxygen Concentration (right).](Gerling&Haberman 2014)

Nutrient Results

Upon plotting the time series of PO4, NO3-NO2, and NH4 concentrations at each of the 4 depths, it was clear that the data within the first three layers did not show much of an upward or downward trend. However, upon plotting time series of each of the nutrients taken at approximately 12 meters depth, concentrations of both phosphate and ammonium were clearly much higher as the summer progressed when dissolved oxygen concentrations were lowest (see figures 10 and 11). Both nutrients showed much higher concentrations around June 1st and after. As stated above, this is only shortly after thermal
stratification intensified around May 15th. It is clear that temperature and dissolved oxygen play a role in nutrient releases from the sediments and ultimate concentrations within the water column.

Table 1. Average Nutrient Concentrations Per Depth.

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Average Concentration NH₄(∥g/L)</th>
<th>Average Concentration PO₄(∥g/L)</th>
<th>Average Concentration NO₃-No₂ (∥g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.1</td>
<td>4.4</td>
<td>2.7</td>
</tr>
<tr>
<td>4</td>
<td>7.7</td>
<td>3.8</td>
<td>2.9</td>
</tr>
<tr>
<td>8</td>
<td>7.7</td>
<td>4.3</td>
<td>3.1</td>
</tr>
<tr>
<td>12</td>
<td>618.2</td>
<td>14.5</td>
<td>4.2</td>
</tr>
</tbody>
</table>

(Haberman, 2014).

Figure 10: Phosphate and Nitrate-Nitrite Nutrient Concentration Time-Series at 12m Depth.

(Haberman, 2014).
Physical Data Results

Upon obtaining nutrient concentration data for each of the depths we then wanted to determine potential nutriment loads that could flow from Beaverdam and into Falling Creek Reservoir. Prior to doing so we first needed to get an accurate estimate of the volume of the reservoir. After exporting the latitude, longitude, and depth data collected from the CTD we were able to import said data into GIS and make the first-every bathymetric map of Beaverdam Reservoir as shown in figure 12.

We can see that our sample site was indeed within the deepest part of the reservoir as we expected. Similarly we can see the approximate depth on the west mid-section of the reservoir where the water authority has intake pipes at 3 different depths flowing from Beaverdam to Falling Creek. In addition to creating the bathymetric map we were also able to use GIS to calculate the total surface area and volume. We calculated the surface area to be about .39(km²) and the total volume to be about 1,400,000 (m³) as can be seen in the first row of table 2. These values match very closely to the estimates we found from the 1920 topographic map.

However, the estimates from the 1960s, which the Water Authority still uses today, were slightly different. We think this could be due to normal fluctuations in precipitation and erosion over time. However, the variations merely demonstrate how important it is for the
water authority to have an updated and accurate volume approximation.

Additionally we were able to determine the volumes per 1-meter layer of the reservoir and use these values in conjunction with our average-highest nutrient concentrations to do some “back-of-the-envelope” calculations to determine the potential mass of nutrients – specifically total phosphorus and nitrate-nitrate that could flow from Beaverdam into Falling Creek (see figure 13). From this figure it is clear that there is more of a potential for an increase in nutrient loading of total phosphorus within approximately the first 5 meters below full reservoir capacity (this corresponds to the higher slope of the phosphorus plot). Additionally, the slope of the nitrate-nitrite line is greatest within the first 8 meters below maximum capacity. Ultimately, if the WVWA were to lower the reservoir by about 2 meters below full capacity that would correspond to an approximate mass of about 1 kg of total phosphorus flowing into FCR and almost 2kg of nitrate-nitrite. Considering the small size of FCR these mass loads are quite substantial. If too many nutrients flow into Falling Creek then the current treatment methods of the WVWA could become ineffective and could jeopardize the health of the reservoir (Gantzer et. al, 2009 pg. 1286).

![Potential Nutrient Loads into Falling Creek](image)

**Figure 13: Potential Nutrient Loads into Falling Creek.**

(Haberman, 2014).

### IV. Conclusions

It is clear that there is intense thermal stratification within the summer months in Beaverdam Reservoir causing anoxic conditions within the bottom 4 meters of the reservoir. It is also clear that to some extent low dissolved oxygen concentrations correspond to an increase in concentrations of most notably ammonium and phosphate within the meter above the sediments.

We were able to make the first bathymetric map of Beaverdam Reservoir and were able to use it to calculate the total volume as well as the volume per 1-meter layer of the reservoir. Determining these physical characteristics enabled us to approximate potential nutrient loading from BVR into Falling Creek and will ultimately help inform the WVWA about when and how to drain water from BVR and into FCR so as to avoid any negative affects to either reservoir.
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Bierlein, Kevin. Graduate Student at VT that helped make figures including the bathymetric map.


Gerling, Alex. Graduate student at VT. Helped make figures.


Google maps.

Haberman, Mariah. Myself. Took photos and created figures/did calculations.


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Assessing Reactivity of Nanoiron through a Colorimetric Assay, SPME-GCMS, and Thiobarbitutric Acid Reactive Substances

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Abstract

More information is needed about the reactivity of nanoiron materials. The objectives of this research were: (1) measure ferrous ion concentrations produced from Fe(SO$_4$) and nZVI in solution using a phenanthroline colorimetric assay; (2) determine salivary lipid oxidation by malondialdehyde (MDA) production through TBARs; and (3) develop a procedure to measure the amount of n-hexanal produced by iron materials using SPME GM-MS. Results show that FeSO$_4$ produced 100% ferrous ions, aged nZVI produced 88% ferrous ions, and new nZVI produced 56% ferrous ions in solution. FeSO$_4$ produced more MDA than aged nZVI, and new nZVI induced the least MDA. n-hexanal, a salivary lipid oxidation byproduct, was produced when iron materials were exposed to lipids, but quantitatively cannot be analyzed at this time.

Keywords: Lipid Oxidation, Nanoiron, Saliva, Hexanal

I. Introduction

Zerovalent Iron Nanoparticles.

In today’s world, nanoengineering is becoming more prevalent due to its broad array of application and specific nanoparticle characterization, which increases efficiency in environmental, industry, medical, technology, and consumer usage fields (EPA, 2014 and Tsuji et al., 2009). Nanoparticles are characterized as being less than 100 nanometers in size and having significantly different physical and chemical properties than their larger counterparts (Wigginton et al., 2007). Iron, the most abundant metal in the world, is one element that’s reactivity differs between its nano and larger particle forms. Nanoiron materials are widely being used for groundwater remediation and in the future, could be used in food engineering. As nanoiron technology evolves, there becomes an increasing need to study its reactivity and exposure potentials to humans and the environment.

Physically, nanoiron differs from elemental iron is it has a reactive iron (Fe$^0$) core that is surrounded in nonreactive oxide and surfactant coatings (Kennan, 2009 and Ramos et al., 2009). The oxide and surfactant coatings surround the reactive Fe$^0$ core of the nanoparticle, which suppresses the reactive nanoiron to only reduce when it comes in contact with dissolved oxygen (Reaction 1) and water (Reaction 2) (Figure 1) (Ponder et al., 2000).

$$2\text{Fe}^0(s) + \text{O}_2(g) + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+}(_\text{aq}) + 4\text{OH}^(-(_\text{aq})$$  \hspace{1cm} (1)

$$\text{Fe}^0(s) + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+}(_\text{aq}) + \text{H}_2(g) + 2\text{OH}^(-(_\text{aq})$$  \hspace{1cm} (2)
Figure 1. A nanoiron Particle Depicting The Difference Between The Reactive Iron core, Fe\(^0\), And The Iron Oxide Coating (Phetxumphou, 2014).

Oxidation reactions occur causing the reactive iron core to lose electrons when reduced to a stable ferrous, Fe(II), iron form (Wigginton et al., 2007). A fairly efficient and economic method to measure ferrous ion concentration is the Phenanthroline Colorimetric Assay. The phenanthroline complex reacts with only the reactive iron in solution and after 5 minutes, the ferrous ion concentration can be calculated by absorbance spectroscopy (Standards Method 3500 Fe, 1997). Environmentally, ferrous concentration has been recorded as ranging from 0.5 mg/L to 10 mg/L in anaerobic ground water and 0.7 mg/L in surface water (WHO, 2011). The EPA regulates iron in water at 0.3 mg/L for safe human consumption (EPA).

Although, iron is naturally occurring in its nanoparticle and elemental form, there is a rise in concern to study its potential exposure to humans with the future increase of using nanoiron in groundwater remediation and food engineering. Elemental iron is not stable in aquatic environments because it is easily oxidized and presents concerns to human health and environmental issues (Kennan et al., 2009). Nanoiron is less mobile in its oxidized forms and will most likely not increase human exposure when used in ground water remediation (Hochella et al., 2008).

Current research involving groundwater remediation treatments with nanoiron have been quite successful (Waychunans et al., 2005; Hochella et al., 2008). Nanoiron particles are able to remove toxic contaminants by encapsulating the metal contaminant up to 30 years (EPA). The nanoiron particle absorbs the metal contaminant, reduces it, and forms the metal-iron alloy, which stabilizes the contaminant. The encapsulated contaminant is then able to be transported through drinking water systems, but will most likely increase the human toxicity potential (Hochella et al., 2005). Designer engineered nanoparticles are being manufactured to make ground water remediation more efficient with increasing the nanoiron mobility. In order to manufacture more efficient particles, stabilizing agents (surfactants and polymers), must be changed, which may lead to increased toxicity (Phetxumphou, 2014). As more research is completed on how to engineer the best nanoiron particle, there needs to be a distinguishable method to determine how much Fe\(^0\) and Fe-oxide is present in the nanoparticle to assess what is likely to occur in environmental situations involving nanoiron particles.

As nanoiron moves toward being used in ground water remediation, it will mostly likely also be used in food and agricultural engineering (Gray, 2010a; Derbyshire et al., 2010) in the future. Nanotechnology looks to improve the food industry from packaging to taste (Beltrami et al., 2011). Nanoiron will be able to fortify foods and provide the necessary iron to well over the 2 billion people who suffer from iron deficiency (Derbyshire et al., 2010; Hilty et al., 2011). There needs to be more research to assess the reactivity of nanoiron, and its overall toxicity when humans consume or are exposed to it. The best way to assess nanoiron reactivity across all of its fields of application is to measure the oxidized and reduced iron concentration and the Fe\(^0\) content in nanoiron particles (Faulkner et al., 1999).

Salivary Lipid Oxidation by Nanoiron.

Metals are known to oxidize lipids. Iron, as Fe\(^{2+}\), has been shown to oxidize cell membrane lipids through reduction (Reaction 1 and 2) (Ömür-Özbek et al., 2012; Phetxumphou, 2014) As ground water remediation and food fortification move toward using nanoiron to efficiently remove contaminants from
water and increase nutrients in food, there will most likely be an increase in human iron consumption. Lipid oxidation will occur when iron is consumed and comes in contact with the lipid filled cell membranes and saliva in the mouth (Ömür-Özbek et al., 2012). Research conducted by Ömür-Özbek et al. (2012) found that ferrous ions caused the greatest lipid oxidation and byproduct production in oral cavities when compared to cupric and cuprous ions.

Phospholipids are the main component of all cell membranes and naturally occur everywhere. Lipids are compounds composed of fatty acids with hydrophilic and hydrophobic tail ends to create permeable barriers. Lipids are organic compounds which dissolve in organic solvents, but are insoluble in water due to their hydrophobic tails (Defago et al., 2011). Aquatic organisms are covered in lipids, and humans and mammals have them in their oral cavities, saliva, skin, digestive systems, and lungs (Phetxumphou, 2014). Lipids are in constant contact with the environment through taste and touch, and these interactions cause lipids to undergo oxidation. Lipid oxidation is a form of oxidative stress, or an imbalance between free radical cells and antioxidants in the body, which ultimately causes cell damage (Gille & Joenje, 1991; Symons & Gutteridge, 1998).

During lipid oxidation, the starting unsaturated fatty acid, a lipid, goes through a chain reaction involving initiation, propagation, and termination (Phetxumphou, 2014). Lipid oxidation reduces, or removes an electron, from the compound that acts upon the unsaturated fatty acid. The initial unsaturated fatty acid has C=C bonds, which allows for the surrounding covalent H bonds to break and form radicals (Catala, 2009). The radicals, compounds with unpaired electrons, react with oxygen and form hydroperoxides. The hydroperoxides are then able to terminate the lipid oxidation reaction, and produce byproducts, like malondialdehyde and n-hexanal (Mallia et al., 2009; Meynier et al., 1998; Selke et al., 1977; Withycombe et al., 1971).

Lipid oxidation has been successfully quantified measuring malondialdehyde (MDA) production using the thiobarbituric acid reactive substances (TBARs) assay. TBARs is a method prominently used to determine lipid oxidation in tissues, fluids, drugs, and food even though it is time consuming and not always accurate due to its lack of reactive aldehyde characterization (Phetxumphou, 2014). MDA is an indicator of oxidative stress in oral cavities and can be colorimetrically analyzed on a UV-VIS spectrometer (Yagi, 1998) because when reacted with TBA, its complex forms a pink color. The lipid peroxidation reaction with TBARs and MDA is shown in Figure 2.

![Figure 2. Reaction Of TBARs With MDA (Phetxumphou, 2014).](image)

If nZVI in food fortification induces lipid oxidation, it will be very important to study the effects of nZVI on naturally occurring lipids in food and oral cavities (Phetxumphou, 2014). Human saliva consists of organic proteins and inorganic salts (Larsson et al., 1996; Defago et al., 2010). Human saliva also contains the lipids available for iron materials to undergo reduction. On average, it can be suggested that human saliva contains about 3 mg of lipids per 100 mL of saliva (Larsson et al., 1996; Mandel and Einstein, 1969). In oral cavities, the amount of lipids in saliva is not the only thing that can react with iron materials to produce salivary lipid oxidation; food humans consume also have natural and unnatural lipids that are able to react with iron.

Soybean oil, which contains unsaturated fatty acids, is used in 90% of food worldwide, and is the main lipid source in food (Gunstone, 2006). Protein oxidation provides food with texture, taste, and nutrients; whereas, lipid oxidation can spoil, disrupt cell membranes, and change the flavor and aesthetics.
of food (Kanner, 2007). n-Hexanal, a lipid oxidation byproduct, is also a food additive that enhances flavor and is FDA regulated (n-Hexanal). The flavor of n-hexanal can be described as a nice, grassy odor commonly found in drinking water (Ömür-Özbek & Dietrich, 2008). n-Hexanal is already being consumed by humans, and with the projected increase of nZVI consumption from fortified foods and ground water remediation, n-hexanal production in oral cavities may increase to levels above FDA regulation and may lead to possible health effects as a result.

The goal of this research was to assess reactivity of nZVI by measuring how much Fe\(^{2+}\) is produced when reacted with human saliva, and its implications on water quality and human health aesthetics. Three specific objectives focused on were: (1) measure ferrous ion concentrations produced from Fe(SO\(_4\))\(_2\) and nZVI in solution using a phenanthroline colorimetric assay; (2) determine salivary lipid oxidation through TBARs; and (3) develop a procedure to measure the amount of n-hexanal produced by iron materials using SPME-GCMS.

II. Research Methods

Testing Solutions

Preparation of iron solutions. Iron solutions included 10 mg/L total iron for ferrous sulfate (FeSO\(_4\)) and zerovalent nanoiron (nZVI), Nanofer 25S, throughout the experiments. The ferrous sulfate (Sigma-Aldrich, PA, CAS #13463-43-9) and nZVI (provided by from Nanoiron Ltd., Rajhrad, Czech Republic, EU) were the iron materials used in all reactions. Two different batches, 2010 (referred to as aged nZVI), and 2014 (referred to as new), of nZVI were analyzed and compared. The iron solutions were made by diluting 0.0124 g FeSO\(_4\), 20.7 uL of aged nZVI, and 41.5 uL of new nZVI in 250 mL, 500 mL, and 500 mL of nanopure water, respectively. All iron solutions were made fresh daily and run on the Atomic Absorbance Spectroscopy (AAS) (Perkin-Elmer, 5100PC AAS, Waltham, MA, USA) via acid digestion, 5% HNO\(_3\) by volume, to confirm total iron content.

Preparation of aqueous media. Aqueous media for all experiments included solutions of nanopure water (TDS=0 mg/L), tap water (TDS=75 mg/L), an inorganic salt mixture (TDS=3100 mg/L), and an artificial saliva, which is comparable to human saliva (Phetxumphou, 2014). The inorganic salt solution was concocted based on human saliva’s salt characteristics (Gal et al. 2001; Mirlohi, 2012; Tang, 2010). The inorganic stock solution included: NaCl, 0.126; KCl, 0.964; KSCN, 0.189; KH\(_2\)PO\(_4\), 0.655; Na\(_2\)SO\(_4\), 0.337; NH\(_4\)Cl, 0.178; CaCl\(_2\), 0.155; NaHCO\(_3\), 0.568 grams, which were dissolved in 1000 mL nanopure water (Phetxumphou, 2014, unpublished). The artificial saliva solution included: 30 mg of soybean oil, 0.54 g of mucin and 1.36 g α-amylase proteins which were added to 1000 mL of inorganic stock solution. The soybean oil adds lipids, and the mucin and α-amylase add proteins to mimic human saliva.

Measuring Reactive Fe\(^{2+}\)

Phenanthroline Colorimetric Assay. Adapted from Standard Methods 3500-Fe (1997), the ferrous ion content from iron materials was measured using the phenanthroline complex through a colorimetric assay. The ammonium acetate buffer, phenanthroline solutions, and standard curves were based off of Phetxumphou (2014). Aqueous media, prepared fresh daily, consisted of nanopure water, tap water, and inorganic solution. The 5 mg/L total iron solutions of FeSO\(_4\), aged nZVI, and new nZVI. In a 1.5 mL cuvet, 200 uL of ammonium acetate buffer, 400 uL of phenanthroline solution, 500 uL of aqueous media, and 500 uL of 10 mg/L iron material were mixed. The reaction was left in the dark, to negate from any light induced ferrous ion production for 5 minutes. Each sample’s absorbance was read at 510 nm on a UV-VIS spectrometer and converted to concentration using a standard curve from FeSO\(_4\). The phenanthroline colorimetric assay also tested ferrous ion production for each iron material in each aqueous media over time for up to an hour.
Measuring Salivary Lipid Oxidation

Thiobarbituric Acid Reactive Substances (TBARs) Assay. The Spanier TBARs method (1991) was used to measure lipid oxidation via MDA production in 10 mg/L and 25 mg/L iron solutions in nanopure water and artificial saliva aqueous media. The method was adjusted to account for low MDA production (Wang, 2009). MDA standards (0.0313, 0.0625, 0.125, 0.25, 0.5, 0.75, 1.00, 2.00, 4.00, and 10.0 uM) were used to produce a standard curve at 532 nm on a UV-VIS Spectrometer. Samples were prepared mixing 2 mL of iron solution with 2 mL of aqueous media in 50 mL propylene test tubes. Every control and iron treatment were tested in triplicate. The test tubes were placed in a 37°C water bath for 15 minutes to resemble the temperature and conditions in the oral cavity. After the incubation period, the samples were immediately analyzed for salivary lipid oxidation using the TBARs method, which measures iron-induced oxidative stress within the oral cavity. All samples were measured for absorbance on the UV-VIS Spectrometer and converted to MDA concentration per mg of total iron.

Preparation of hexanal standard solutions. n-Hexanal standard solutions were made using a 10,000 ug/L stock solution of high purity n-Hexanal (Sigma-Aldrich, PA, CAS #66-25-1). n-Hexanal standard solutions (100, 200, 400, 500, 800, 1000, and 1500 ug/L) were made fresh daily by adding the appropriate stock solution diluted with nanopure water in 50 mL volumetric flasks. For the standard curve, a 1:1 6 mL mixture of n-hexanal and inorganic stock solution with mucin and α-amylase because that was the aqueous media the iron would react with.

Lipid Oxidation Hexanal Production. Solid phase microextraction (SPME) and gas chromatography (GC) paired with mass spectroscopy was used to measure the salivary lipid oxidation byproduct, n-hexanal, headspace concentration. A 6 mL sample of a 1:1 mixture of 10 mg/L total iron solution and aqueous media was enclosed, via septum, in a 40 mL amber vial. After the samples incubated for 1 hour in a 45°C water bath, the conditioned sixty micrometer PDMS/DVB SPME fiber (Supelco, Bellefonte, PA) was injected and exposed to the headspace for 5 minutes. An Agilent 6890 series GC was used and it’s conditions and methods for n-hexanal detection were adapted from Ömür-Özbek and Dietrich (2008). The GC was adapted to increase oven temperature to 220°C and decrease elution time to 2.83 minutes. The Agilent 5973 series MS detected n-hexanal via sim m/z 44, 56, and 100 ions. n-hexanal peak areas and signals were measured using a n-hexanal standard curve made daily to calibrate the GCMS. The n-hexanal concentration (ug/L) calculated was then converted to the headspace n-hexanal concentration (ug/L-air) using the Henry’s Law constant, 0.0355, found by Ömür-Özbek and Dietrich (2008) at 45°C.

III. Results and Discussion

Phenanthroline Colorimetric Assay

Ferrous Ions by Phenanthroline Colorimetric Assay. The phenanthroline colorimetric assay, Standard Method 3500-Fe (1997) was adjusted to account for high concentrations of Fe²⁺ iron reacting with phenanthroline using methods from Phetxumphou (2014). Total iron was confirmed for each sample through AA, and results were normalized based on total iron and ferrous iron. Calculations of total and ferrous iron used the 10 minutes absorbance readings from the phenanthroline time-lapse experiment in nanopure water, seen in Figure 3, because the ferrous-phenanthroline complex ceases between 5 and 10 minutes.
When calculated based on total iron concentration, new nZVI produced 1.056 mg of Fe$^{2+}$/ 1 mg of total iron, which was the highest. Aged nZVI and new nZVI produced 0.92 and 0.56 mg of Fe$^{2+}$/ 1 mg of total iron, respectively (Figure 4). FeSO$_4$, aged nZVI, and new nZVI all produced 1.056 mg of Fe$^{2+}$/ 1 mg of ferrous iron on a ferrous iron basis. Assuming FeSO$_4$ produces 100% ferrous ions in solution because it is 100% reactive iron (Fe$^{2+}$), aged nZVI and new nZVI produced 88% and 56% ferrous ion in solution. nZVI materials contain Fe$^0$ and Fe-oxides, which confirms that the original reactive iron is not 100% of the nZVI particle and therefore, will not produce 100% ferrous ions in solution. Through AA and the phenanthroline assay, our results conclude that the aged nZVI is more reactive than the new nZVI. The less reactive nZVI could be accounted for by suggesting Nanoiron Ltd. reduced its nZVI content in Nanofer 25S or by the production of hydrogen gas through the reduction of water by iron over time to increase the aged nZVI’s Fe$^0$ content. (Reinsch et al., 2010).

Water Quality. Using the adapted phenanthroline method, iron materials were reacted for an hour in different aqueous media to analyze what occurs in different water types and the effects on the water quality. Following the same trends seen in ferrous ion concentration, nZVI produced the least Fe$^{2+}$ over time. The aged nZVI produced more ferrous ions over time, but still does not produce 100% ferrous ion as seen in FeSO$_4$ (Figure 5).
FeSO₄ produces Fe²⁺ in solution immediately, and the ferrous-phenanthroline complex remains relatively stable for the entire length of the reaction. However, nZVI does not become stable until about 10 minutes. FeSO₄ is stable because its reactive iron content is not encapsulated with Fe-oxides, and therefore reacts with the phenanthroline complex immediately. The nZVI materials’ reactive iron is encapsulated, and therefore it takes about 10 minutes for the phenanthroline complex to reach the reactive iron in the particles and react to form the orange hue. Phetxumphou (2014) found similar results where FeSO₄ is stable, and the nZVI takes time to stabilize. Photochemical reduction reactions have the ability to cause nonreactive ferric iron into ferrous iron over time, which could account for the increasing formation of ferrous ions over time for the nZVI materials (Phetxumphou, 2014). Results for the effects of water quality suggest that the formation of ferrous ions in solution are increased when iron reacts with tap water, then inorganic solutions, and finally the nanopure water produces the least. Further analysis is needed to determine why the tap water produced the most ferrous ions in solution when reacted with iron, when it was expected that the inorganic aqueous media will cause the most ferrous ion production.

Salivary Lipid Oxidation by TBARs

TBARs. Salivary lipid oxidation does occur when nZVI is in the presence of saliva. Using the TBARs assay, salivary lipid oxidation was analyzed by MDA production. All iron solutions used in the assay were based on 10 mg/L iron because when based on 5 mg/L iron, the pink MDA product was not concentrated enough to be read on the UV-VIS spectrometer. On a total iron basis, MDA production follows the ferrous ion concentration trends seen above. FeSO₄ produced the highest MDA concentration, 0.07 μM MDA/mg of total iron, aged nZVI produced 0.05 μM MDA/mg of total iron, which was more than the new nZVI, which produced 0.04 μM MDA/mg of total iron (Figure 6). Based on MDA production, lipid oxidation did occur and the new nZVI is still less reactive than the aged nZVI. These results support what Phetxumphou (2014) found comparing salivary lipid oxidation between FeSO₄ and nZVI.
When analyzed based on ferrous iron content, all iron solutions produced the same MDA concentration because MDA production was due to the production of ferrous ions in solution. Since all iron solutions were normalized to the same ferrous iron content, the MDA concentration produced will be the same across all iron materials tested. It is important to continue to study the effects of nanoparticles on lipids since aquatic organisms may be exposed to more nanoiron through groundwater remediation and humans may be exposed to it through food fortification in the future (Ömür-Özbek et al., 2012; Phetxumphou, 2014, unpub.).

Salivary Lipid Oxidation by SPME-GCMS

SPME-GCMS Conditions and Development
Salivary lipid oxidation was also confirmed by detecting n-hexanal production. Methods for determining n-hexanal on the GCMS were produced for this experiment. SPME techniques and GCMS conditions were originally based on Ömür-Özbek and Dietrich’s (2008) developed method for measuring n-hexanal in relation to odor. After 8 weeks of trial and error, the best experimental conditions for sample preparation to detect n-hexanal were found. In an acid washed, 40 mL amber vial, a 6 mL 1:1 (iron: artificial saliva) sample was injected and sealed using an unpunctured septum system. The sample reacted within a dark 45°C water bath for one hour to allow for equilibrium. While waiting on the reaction, SPME was conditioned on the GCMS. After one hour, SPME was injected into the septum and the fiber was exposed to the vial headspace, being very careful not to break or put the fiber into the liquid sample, for 5 minutes. SPME was then injected into the GC, ran according to Ömür-Özbek and Dietrich (2008) methods, and analyzed for n-hexanal using the GC-MS.

In developing the SPME-GCMS method for n-hexanal detection, multiple experimental conditions were tested. The size of the vial played a role in analyzing n-gexanal concentration in the headspace. When the reaction was tested in 4 mL and 15 mL amber vials, it was believed that the n-hexanal headspace concentration overloaded the SPME fiber capacity and no n-hexanal peaks were detected by the GCMS. Sample volume is also important. A 1 mL 1:1 (iron: artificial saliva) was used, but there was not enough reactive iron in the 500 uL of a 5 mg/L iron solution to produce detectable n-hexanal. A standard increase of 2, 4, 6, 8, 10 mL samples were analyzed, and the 6 mL volume was the best condition to produce detectable n-hexanal without overloading the SPME fiber capacity.

A n-hexanal standard curve (100, 200, 400, 500, 800, and 1000 ug/L) was made fresh daily before all samples were run on the GCMS in order to account for the different peak areas of replicable samples from day to day. The standard samples were made using a 6 mL 1:1 (hexanal: inorganic and protein solution) samples in order to decrease the background noise on the GCMS and mimic the conditions of the matrix. The samples were placed in a 45°C water bath to imitate the warm conditions.
that causes salivary lipid oxidation in the human mouth. Due to photochemical reactions that have been proven to occur when iron reduces in the present of light, the samples were kept in the dark to eliminate unwanted reactions (Phetxumphou, 2014). After trying 5, 10, 15, and 30 minute SPME exposures to samples, 5 minutes was used because hexanal was detected after 5 minutes on the GCMS and exposure time of 5 minutes is recommended by the Supelco SPME manufacturer. Overall, the methods developed for hexanal detection using SPME-GC in this experiment are preliminary and improvement is necessary to increase hexanal detection accuracy and precision.

Salivary Lipid Oxidation forming n-Hexanal. Qualitatively, n-hexanal was produced as a result of salivary lipid oxidation when iron reacts with artificial saliva with lipids present. A 5 mg/L total iron of FeSO₄ solution was tested for n-hexanal production against different aqueous media on the GCMS. When FeSO₄ reacted with nanopure water, tap water, and the inorganic solutions; no hexanal was detected by the GCMS. When FeSO₄ reacted with artificial saliva; n-hexanal was detected by the GCMS. This confirms that n-hexanal is a salivary lipid oxidation byproduct and will be produced when iron reduces with lipids present in the artificial saliva. Again, the importance of further research is needed to know more about lipid oxidation with nanoparticles and human saliva since ground water remediation and food fortification may lead to increase iron exposure and consumption by aquatic organisms and humans (Gray, 2010a; Derbyshire et al., 2010).

Quantitatively, n-hexanal concentration could be measured using SPME-GCMS. Based on a n-hexanal standard curve (y=34127x + 2E+06), n-hexanal concentration was calculated based on the peak area detected by the GCMS (Figure 7).

![Hexanal Standard Curve](image)

Figure 7. The Standard Curve Made For n-hexanal In An Inorganic and Proteins Aqueous Media On The GCMS (Wind, 2014).

FeSO₄ continues to follow the reactivity trends seen in ferrous ion concentration and TBARs by producing the most hexanal, 20.8 ug/mg of total iron, when induced by lipids in saliva. Aged nZVI produced 18.1 ug of hexanal/mg of total iron, followed by the new nZVI, which produced 10.6 ug of hexanal/mg of total iron (Figure 8). These results continue to suggest that the new nZVI is less reactive than the old nZVI, and nZVI produces less n-hexanal than FeSO₄ because it has less Fe⁰ content.
When n-hexanal was analyzed on a ferrous iron basis, all iron materials produced the same amount of n-hexanal because n-hexanal production is directly related to the amount of reactive iron available (Figure 7). Further investigation is needed to produce reproducible standard curves and decrease the high standard deviation and variability found while analyzing n-hexanal peaks on the GCMS. Other research measuring n-hexanal suggest using a High Performance Liquid Chromatograph instead of GCMS to increase detection precision and accuracy (n-hexanal).

IV. Conclusions

Not all nZVI are alike, even if samples come from same manufacturer, nZVI needs to be pre-measured and standardized before using. nZVI has been shown to have less Fe$^0$ than FeSO$_4$. The amount of total iron measured for FeSO$_4$, aged nZVI, and new nZVI are the same, but the amount of Fe$^0$, which reduces to reactive ferrous ions is different in each iron material. Based on AA and the phenanthroline colorimetric assay, all iron materials produced different amount of ferrous ions after reduction occurred. Approximately 100% of the FeSO$_4$ reduced to ferrous ions, whereas, the aged nZVI and the new nZVI reduced to 88% and 56% ferrous ions in solution, respectively. FeSO$_4$ reacts with phenanthroline immediately, but nZVI takes up to 10 minutes to form stabilized ferrous-phenanthroline complexes.

All iron materials induced salivary lipid oxidation when in the presence of artificial saliva, which contains lipids. On a total iron basis, TBARs showed that FeSO$_4$ produced the most MDA, followed by aged nZVI, and then new nZVI. The TBARs results share the same trend in analyzing the reactivity of iron materials. n-Hexanal, another salivary lipid oxidation byproduct, was qualitatively identified to have been produced when the iron material was in the presence of artificial saliva using the developed SPME-GCMS procedure. Quantitatively, further investigation is needed to improve SPME-GCMS techniques to obtain a reproducible n-hexanal standard curve and n-hexanal peak areas for all iron induced samples.

nZVI is less reactive than FeSO$_4$ because on a total iron basis, it has less Fe$^0$ due to its oxide, nonreactive ferric coatings, which produces less ferrous ions and lipid oxidation byproducts in solution.
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References


Effect of Particulate Iron and Temperature of Dissolution and Solubility of Lead Solids

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Abstract

Higher temperatures and the presence of iron in potable water are possible factors exacerbating release of lead from plumbing materials (lead pipes, brass fixtures, and lead based solder). This work examined the effects of higher temperature and iron on the rate of dissolution from three representative lead solids (lead oxide, lead carbonate, and lead phosphate) that commonly form on plumbing materials. Even though it was hypothesized that higher temperatures would result in more soluble lead and greater rates of dissolution, in the case of lead carbonate and lead oxide, a lower temperature actually resulted in > 26% soluble lead after 4 hours, and for lead phosphate lead levels did not change significantly with temperature. These results suggest that higher lead observed at higher temperatures cannot be due to faster dissolution or higher equilibrium values of soluble lead. The presence of particulate iron maintained lower levels of soluble lead in the water, which can maintain higher rates of lead dissolution from pipe and explain higher total lead levels in water after stagnation when iron particles are present.

Keywords: Lead Oxide, lead phosphate, lead carbonate, dissolution

I. Introduction

The corrosion of materials that contain lead such as pipe, faucets, and fittings can contaminate the water supply with lead (Britton and Richards, 1981; Schock, 1999; Triantafyllidou and Edwards, 2011). Exposure to lead from drinking water has been associated with higher incidence of spontaneous abortions in pregnant women (Edwards 2014) and increased incidence of lead poisoning for young children (Edwards, Triantafyllidou, and Best 2009; Brown et al. 2011; Deshommes and Prévost 2012). Water utilities attempt to control the release of lead from lead bearing pipe materials by maintaining water chemistry conditions (i.e. pH and alkalinity) that reduce the solubility of lead corrosion products that coat plumbing materials (Schock, Wagner, and Oliphant 1996; Sheiham, I. and Jackson 1981). Representative lead solids include lead phosphate, Pb(II) carbonates, and Pb(IV) oxides (Schock et al. 2005; Schock, Hyland, and Welch 2008; Kim et al. 2011).

In general Pb(IV) oxides form in distribution systems with a free chlorine residual and other factors, and they have extremely low solubility (Edwards and Dudi 2004 but add Arnold…??) (Edwards and Dudi 2004; Lytle and Schock 2005; Vasquez et al. 2006). Low solubility lead phosphate scales are also commonly found in distribution systems that employ orthophosphate as a corrosion inhibitor (McNeill and Edwards 2002; Davidson et al. 2004), and if adequate levels of phosphate or free chlorine are not present higher solubility lead carbonates such as cerussite (PbCO₃) and hydrocerussite (Pb₃(OH)₂(CO₃)₂) tend to form (Schock 1989; Kim et al. 2011; Xie and Giammar 2011).

Prior research has often associated measured higher levels of lead in plumbing systems with higher temperature, and the conventional wisdom is that this is due to higher solubility and/or dissolution rates for lead solids (Schaut n.d.; Moore 1973; Karalekas, Ryan, and Taylor 1983; Gregory and Jackson 1984; van den Hoven 1985; Schock 1990; Colling et al. 1992; Clement, Seux, and Rabarot 2000; Lintereur et al. 2010; Tang et al. 2006; Cartier et al. 2012; Deshommes et al. 2013). The dissolution rates of lead oxide
(Dryer and Korshin 2007; Lin, Washburn, and Valentine 2008; Lin and Valentine 2008, 2009; Shi and Stone 2009a, 2009b), lead carbonate (Xie and Giammar 2011; Noel, Wang, and Giammar 2014), and lead phosphate (Sauvé, McBride, and Hendershot 1998) have been studied under various water quality conditions, but the role of temperature on the rate of dissolution and equilibrium solubility of lead solids has never been studied (Schock et al. 1996). The dissolution of lead solids can also be further complicated by the presence of inorganic solids such as particulate iron, which has been hypothesized to increase overall release of lead to drinking water by sorption Masters et al. (2013).

This study aims to examine the impact of temperature and particulate iron on the dissolution of various lead solids (i.e. lead carbonate, lead phosphate, and lead oxide). The current study will further the current understanding of consumer exposure to lead as well as the development of practical corrosion control strategies.

II. Materials and Methods

Synthesis of Lead Solids: Lead Carbonate (cerrussite) was synthesized similar to the approach outlined by Noel at al. (2014). Cerrusite was precipitated from a supersaturated lead carbonate solution by simultaneously adding 0.1 M NaHCO₃ and 0.15 M Pb(NO₃)₂ to 3.5-L of deionized water in a well mixed batch reactor at 20˚C. The Pb:C stoichiometric ratio was maintained at 3:2. The solution pH was adjusted to 7.5 since cerrusite tends to form below pH 8 (Liu et al. 2008). Lead oxide was produced similar to the method of Triantafyllidou, Parks, and Edwards (2007) by completely oxidizing a 1000 mg/L as Pb solution of lead chloride by adding excess hypochlorous acid at pH 7.5. Lead Phosphate (Pb₃(PO₄)₂) was synthesized by thoroughly mixing 1.75-L of a 12 mM PbCl₂ solution with 1.75-L of 0.25 M phosphoric acid (H₃PO₄) resulting in a white precipitate. After synthesis, all suspensions were aged for 8 days.

Synthesis of Iron Hydroxide: Iron Hydroxide was produced following the method of Edwards and Benjamin (1992). Sodium hydroxide (NaOH) was added dropwise to a solution of 0.083 M FeCl₃ resulting in the formation of a red/brown precipitate. Iron hydroxide was added to each iron condition in a 1:0.7 ratio of lead: iron.

Collection of Lead Solids: After measuring the concentration of both filtered (0.45 µm filter) and unfiltered lead in each sample, the volume of solution that should be filtered to capture XX ug of lead on each filter was calculated.

Dissolution of Lead Solids: A dissolution experiment was started by adding a filter with lead solids (xx ug total Pb) into a 1 L jar containing 800 mL of synthesized tap water. Four conditions were tested for each type of solid including 1) 4˚C with iron, 2) 4˚C without iron, 3) 20˚C with iron, and 4) 20˚C without iron, leading to 12 batch reactors (3 lead solids × 4 conditions) overall (Table 1). The batch reactors were mixed at 100 rpm. Sample aliquots of 10 mL were first pre-filtered through a 0.2 µm filter before final filtration through a 0.1 µm filter at 2, 4, 9 and 29 hours. Metal concentrations were analyzed using inductively coupled plasma mass spectrometry (ICP-MS; Agilent Technologies, Santa Clara, CA) in an ISO 179025-certified laboratory based on Standard Method 3125B (APHA 1998).
Table 1: Summary Of Water Conditions

<table>
<thead>
<tr>
<th>Condition Number</th>
<th>Lead Solid</th>
<th>Temp (°C)</th>
<th>Chlorine (mg/L)</th>
<th>Orthophosphate (mg/L as P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Lead Oxide</td>
<td>4</td>
<td>2.7</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Lead Oxide with Iron</td>
<td>4</td>
<td>2.7</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Lead Oxide</td>
<td>20</td>
<td>2.7</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>Lead Oxide with Iron</td>
<td>20</td>
<td>2.7</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>Lead Carbonate</td>
<td>4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>Lead Carbonate with Iron</td>
<td>4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>Lead Carbonate</td>
<td>20</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>Lead Carbonate with Iron</td>
<td>20</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>Lead Phosphate</td>
<td>4</td>
<td>0</td>
<td>1.5</td>
</tr>
<tr>
<td>10</td>
<td>Lead Phosphate with Iron</td>
<td>4</td>
<td>0</td>
<td>1.5</td>
</tr>
<tr>
<td>11</td>
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</tr>
<tr>
<td>12</td>
<td>Lead Phosphate with Iron</td>
<td>20</td>
<td>0</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Despite a sample with anomalously high lead at t = 0 for a few samples which is possibly due to anomalous filtration results, dissolved lead concentrations increased with time. After 4 hours, the concentration of lead dissolved from lead carbonate was at least 26% higher at 4°C when compared to the 20°C condition, suggesting that in the case of lead carbonate, a decrease in temperature will tend to increase the equilibrium solubility. For lead carbonate at 20°C, the presence of iron decreased the soluble lead concentration as would be expected, due to sorption of lead to the iron surfaces. This resulted in a dissolved lead concentration that was consistently below 5 ug/L. At 4°C the lead carbonate condition with iron had a dissolved lead concentration less than 7 ug/L for the first 9 hours of the experiment. After 29 hours, the concentration of dissolved lead increased to ~160 ug/L. Thus, as was the case without iron, the condition with lower temperature had a higher final concentration of soluble lead.

For the lead oxide condition at 4°C the initial dissolved lead concentration was 4.4 ug/L and increased to 24 ug/L after 29 hours (Figure 1b). At 20°C, the dissolved lead from lead oxide was consistently below 3.3 ug/L. Lead oxide is very insoluble in the presence of a strong oxidant and the chlorine residual was at least 1.20 mg/L in all conditions throughout the experiment. Similarly, in all other lead oxide conditions the dissolved lead concentration remained relatively low. It should be noted that the 2 hour and 4 hour data points for Condition 2 and 3 respectively were deleted from the analysis due to suspected contamination.

III. Results and Discussion

Despite a sample with anomalously high lead at t = 0 for a few samples which is possibly due to anomalous filtration results, dissolved lead concentrations increased with time. After 4 hours, the concentration of lead dissolved from lead carbonate was at least 26% higher at 4°C when compared to the 20°C condition, suggesting that in the case of lead carbonate, a decrease in temperature will tend to increase the equilibrium solubility. For lead carbonate at 20°C, the presence of iron decreased the soluble lead concentration as would be expected, due to sorption of lead to the iron surfaces. This resulted in a dissolved lead concentration that was consistently below 5 ug/L. At 4°C the lead carbonate condition with iron had a dissolved lead concentration less than 7 ug/L for the first 9 hours of the experiment. After 29 hours, the concentration of dissolved lead increased to ~160 ug/L. Thus, as was the case without iron, the condition with lower temperature had a higher final concentration of soluble lead.
Figure 6: Dissolution Of (a) Lead Carbonate, (b) Lead Oxide, And (c) Lead Phosphate.
For the lead oxide condition at 4˚C the initial dissolved lead concentration was 4.4 ug/L and increased to 24 ug/L after 29 hours (Figure 1b). At 20˚C, the dissolved lead from lead oxide was consistently below 3.3 ug/L. Lead oxide is very insoluble in the presence of a strong oxidant and the chlorine residual was at least 1.20 mg/L in all conditions throughout the experiment. Similarly, in all other lead oxide conditions the dissolved lead concentration remained relatively low. It should be noted that the 2 hour and 4 hour data points for Condition 2 and 3 respectively were deleted from the analysis due to suspected contamination.

The dissolved lead released from lead phosphate at 4˚C and 20˚C followed the same pattern. The lead phosphate conditions with iron also had similar trends to each other. The lead phosphate conditions without particulate iron had at least twice as much dissolved lead as conditions with iron. Additionally, the phosphate residual decreased only slightly for conditions without iron, from ~1.5 mg/L to ~1.3 mg/L (Figure 2). However, for conditions containing particulate iron there was no soluble phosphate

![Figure 7: Change In Phosphate Concentration Over Time.](image)

**IV. Environmental Implications**

In general, lead carbonate had the highest dissolution rate followed by lead oxide and the lead phosphate. The slow dissolution of lead oxide and lead phosphate in particular suggests that the dissolution rate of these solids may be more important than the equilibrium solubility. As Xie et al. (2010) point out, in such cases, a long stagnation time in pipes in contact with these solids could result in high lead levels. The current Environmental Protection Agency warns consumers to avoid consuming hot water, because it is believed to have much higher concentrations of lead, but at present there is no data scientifically supporting this warning (EPA). This suggest that creating the water chemistry conditions that promote the formation of lead oxide or lead phosphate would reduce the likelihood of dissolved lead in drinking water. In general, the presence of particulate iron in reduced tended to decrease the soluble lead levels.
However, even though utilities tend to reduce consumer exposure to lead by creating conditions that reduce soluble lead, particulate iron has been shown to reduce soluble lead while significantly increasing total lead release (Masters et al. 2013).

V. Acknowledgements

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Sheldon Masters, Student Mentor

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References


Quantification of Distinguishing Features of Tsunami Versus Hurricane Sediment Overwash Events

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Abstract

Identifying the difference between hurricanes and tsunams is an important task in locations where the two events commonly occur. There are a wide variety of methods to distinguish the two types of events from the geologic record; however, these methods are not always sufficient. There is a very small sample size of events to determine the intensity of paleo-events for frequency models to protect and inform coastal regions due to the difficulty to collect data from either event and to differentiate the two. With a quantifiable difference between hurricane and tsunami deposits it will be possible to study paleo-events and use the data to build a better model to predict their return periods. This paper will investigate sediment transport from an idealized barrier island with XBeach, a model for extreme beach conditions, using a series of hurricanes of varying sizes and tsunamis of a comparable magnitude (1:100). Hurricane parameters will be varied while only the tsunami wave heights will vary to keep the energy ratio consistent. In general higher surge levels produce a larger amount of erosion and when coupled with large waves the island erodes away. The respective tsunamis exhibit similar behavior but transport sediment farther than storms.

Keywords: Hurricane, tsunami, XBeach, overwash, sedimen

I. Introduction

Tsunamis and hurricanes are common dangerous water hazards that effect coastal regions worldwide. Both tsunamis and storms are frequent, cause severe structural and economical damage and can result in loss of life. Very little data exists for studies to have an acceptable sample size, and research has and is being done to develop criteria to distinguish tsunamis from storm deposits. For rare and extreme cases differentiating the two events can be easy. Large sediment (boulders) are indicative of tsunamis, but both events, tsunamis and storms, result in deposition of sand, mud, and some gravel making distinguishing the two events from one another difficult (Morton et al., 2007). By studying the geologic record it is possible to reconstruct tsunami and storm inundation history in order to get a better understanding of coastal hazards however, current methods must be improved.

Background Information
A 2011 paper by Goff et al. defined the term palaeotsunami and palaeostorm as events that occurred before a historical record. Given that there are few recorded events, frequency and predictive research is difficult. The ability to model and examine palaeoevents will help research.

A wide variety of methods and identifying features have been developed to identify palaeoevents such as geological (e.g. grain size, anisotropy of magnetic susceptibility, heavy minerals), macro- and micropalaeontological (e.g. shells, diatoms, foraminifera, pollen, nannofossils), geochemical, geomorphological, archaeological, anthropological, and palaeo-ecological evidence. However, it is noted that not all features have been explored at each site where palaeoevent evidence exists. Therefore the lack or existence of one or more features does not prove or refute the location, type of event or intensity of said event (Goff et al., 2011).

Disagreement should be expected in differentiating palaeotsunamis from palaeostorms. Research should continue with a multidisciplinary approach and the proxies used to identify palaeo-events should continue to grow. The key to identifying a palaeotsunami deposit is to improve on and integrate as many methods as possible. Even if it is not possible to confidently identify a deposit is of a palaeotsunami origin, palaeotsunami research still has the potential to enhance our understanding of magnitude and frequency to improve modeling of future events for reductions in hazard and risk.

**Literature Review**

Tsunamis and storm events both cause significant deposition, so criteria for distinguishing tsunami and storm deposits are necessary for areas where both events are common. Thus Tuttle et al. (2004) began a comparative study began between the 1929 Grand Bank earthquake and the 1991 Halloween storm.

The study concluded that the tsunami depositions occurred within a marsh or bog and landward of the tidal ponds, while the storm deposits occurred in marshes and tidal ponds immediately behind barrier beach bars but no more landward than the tidal ponds. The tsunami deposits are found further away from the shoreline and at higher elevation than the storm deposits. Tsunami deposits are composed of multiple subunits layered from massive to ever finer upwards. Storms deposits are more interbedded with coarse, medium and fine-grained sand (Tuttle et al., 2004).

Morton et al. (2007) also conducted a study to examine sand bed deposits for two tsunamis and two hurricanes that caused substantial coastal damage and had a high probability of preservation. The overall intent was to determine the most significant criteria that can be used to determine the origin of the sediment deposit. Characteristics of the sediment deposits that were reviewed were the deposit composition and thickness, transport distance, grain size distribution and sedimentary structures.

Tsunamis dominantly resulted in thin (< 25 cm) deposits of normally graded sand with a single structureless bed or a bed with a few thin layers. Presence of mud laminae near the base was an attribute that had strong favor in tsunamis. Lastly the thickest deposits were located 50 meters inland.

Hurricanes result in thicker (> 30 cm) sediment deposits and consist of multiple laminasets with the thickest deposits being nearshore. Shell fragments and alternating coarse and fine sediment layers are also attributes common with hurricanes.

**Model Validation**

Existing tools to assess the condition of beach dunes work well when applied to uniform shorelines using a 1D setting and with relatively undisturbed coasts. In cases with barrier islands, many
parameters must be considered and a 2D prediction tool using essential physics to model the nearshore response from a hurricane impact is required.

Studies done by Roelvink et al. (2009) aimed to model swash, collision, overwash, and inundation regimes. Xbeach, a computer model that solves equations for hydrodynamics and morphodynamics, solves for coupled 2D equations for wave propagation, flow, sediment transport and bottom changes. Xbeach also takes into account “surf beat”, variation in wave height in time, making it an innovative model that is better at modeling the development of dune erosion, the time when overwash and breaching occur and developments throughout the phases (Roelvink et al. 2009).

Applying this model to multiple case studies, LIP11D-2E, Deltaflume, Delilah, and Zwin shows that Xbeach is capable of simulating complex storm events. The hydrodynamics and morphodynamics of XBeach have been extensively calibrated and validated against (1D) flume experiments (Roelvink et al., 2008, 2009; van Thiel de Vries, 2009), and some (2DH) field cases (Roelvink et al., 2009). Responses include: dune erosion, from avalanching and infragravity motions, dealing with complex profiles and second order waves, generally shows the correct trends for profiles (erosion and overwash) and can qualitatively and quantitatively the breaching process.

McCall et al. (2010) investigates the ability of XBeach to predict post storm conditions on a barrier island during Hurricane Ivan. Specifically, the paper aims to gain insight into the effects of hydraulic parameters on overwash events with a 2DH (depth averaged) model that accounts for longshore variability and infragravity waves, rather than using current 1D models, which are limited to longshore uniformity and neglects infragravity waves.

The base simulation can be broken up into 3 main stages. In the first 6 hours, the barrier island is in the collision stage, which is characterized by low surge levels and wave heights. These do not exceed the foredunes, and is primarily limited to erosion of the foredunes and deposition near shore.

The second stage runs from the sixth to the twelfth hour and can be characterized by increased surge level and wave height, leading up to overwash. The foredunes are eroded further and small amounts of erosion and deposition occur on the back barrier.

From the twelfth hour onward the combined surge level and wave height exceeds the height of the foredunes, which leads to inundation overwash. Hourly-mean velocities are supercritical causing large amounts of sediment to be transported from the foredunes to the back barrier and from the back barrier bay creating two distinct washover fans.

Post storm LIDAR shows a magnitude of 1–3 meters of erosion on the foredunes and 1 meter of deposition on the back barrier along 3 main deposition channels. The results of the model are representative of this measured data with an average magnitude less than the measured data. Thus, the model correctly predicts the effects of overwash on Santa Rosa.

A quantification of how closely XBeach models the overwash is needed to further comment on the results and the sensitivity analysis. Skill and bias values calculated for the base simulation were 0.73 and -0.13 meters as well as 0 and 0.09 meters for a prediction of no change. A skill value of 1 would mean the model perfectly predicted the overwash values, so the base simulation is closely representative to the measured values and a null hypothesis is not realistic. XBeach predicts an average bed level of 0.13 meters lower than measured and is lower than the standard deviation for the bed level change (0.74). This error is comparable in magnitude to GPS navigation errors in the LIDAR data (McCall et al., 2010).

A sensitivity analysis was performed on a number of parameters to test the validity of values used in the base simulation. The wave forcing (wave height, periods), surge forcing, storm duration, sheet transport limitation parameters were varied in separate simulations, keeping all other parameters set to the base simulation values. The analysis shows that XBeach can simulate complex runup and inundation.
overwash over longshore terrain and that the model is capable producing morphological features (McCall et al., 2010).

**Problem Statement**

This paper will investigate the differences in sediment transport on an idealized barrier island between tsunamis and hurricanes. Using Xbeach to model each event we hope to produce distinct and realistic differences in order to aid the study of palaeoevents and improve frequency analysis to protect coastal regions in future work. With a larger set of data to predict events it will be possible to better warn and defend against the immense damage caused by hurricanes and tsunamis. However there will be many limitations in this papers methods. The barrier island profile is longshore uniform and waves will be cross-shore uniform. Also the hurricanes will vary in wave height, wave period, and surge level whereas the tsunamis will only vary in wave height in order to keep a consistent energy ratio between the events.

**II. Research Methods**

**Island Description**

Little data exists in literature for describing barrier island shapes, parameters, and realistic measurements. Figure 10* (*Shown in the appendix) shows a generic barrier island profile and Figure 10 - General Barrier Island Profile (Steven Keith 7/15/14)

Table 1* shows large gaps in the data found. Because of the lack of available data the best option was to extrapolate a profile with the LIDAR data from McCall et al. (2010), Figure 11* shows the profile of Santa Rosa Island. To extrapolate a longshore uniform profile a crude proportional line method was used (see Figure 12*), where 500 meters was approximately equal to 1.96 inches (Table 2*). Lengths used listed in Table 3* were averaged and converted into meters. The final bathymetry parameters used 380, 35, 30, 40, 1, 4, 1.25 for the back barrier length, back dune length, front dune length, berm length, back barrier depth, dune height, and berm depth respectively. The final island profile used can be seen in Figure 13* and Figure 14* shows the entire island including the back and front bays.

**Storm Description**

Similar difficulties were met when building a matrix of storm events to test. Xbeach accepts a multitude of parameters but we chose to very the wave height, period and surge levels to simplify the complexity that comes with describing a hurricane event. Wave height, wave period, and surge being the average height between the top and bottom crest of each wave, the distance in time between wave crests, and the over all increase in water surface elevation respectively. Table 4* shows information found from a literature review and after a discussion about the parameter values it was decided that values to be used would be those listed in Table 5*.

**Tsunami Description**

Dean et al. (2004) calculates wave energy using Equation 1, which relates the density of water, gravity and the height of the wave.
Wave energy:

Equation 1

\[ E_{\text{wave}} = \frac{1}{8} \rho g H^2 \]

Using the wave energy equation a proportion (Equation 2) is made to compare the energy between six-hour storms and one-hour tsunamis.

Ratio:

Equation 2

\[ \frac{E_{\text{storm}}}{E_{\text{tsunami}}} = \frac{H_{\text{storm}}^2 L_{\text{storm}}^2 N_{\text{waves,s}}}{H_{\text{tsunami}}^2 L_{\text{tsunami}}^2 N_{\text{waves,t}}} \]

Wavelength:

Equation 3

\[ L_{\text{storm}} = \frac{g}{2\pi} T^2 \tanh \frac{2\pi h}{L} \]

Equation 4

\[ L_{\text{tsunami}} = T \sqrt{gh} \]

Using Equation 3 and Equation 4, to calculate wavelength in terms of distance, with Equation 2 and forcing an energy ratio of 1:100 the wave heights of the tsunamis were solved for (Table 6).

Experimental set up

Once the beach profile and the storm and tsunami parameters were finalized a MatLab loop was used to build grids of all necessary data and the command `xb_generate_model()` was used to build data structures needed for Xbeach to run each simulation. The “Params.txt” file was edited to ensure consistency due to the matlab commands tendency to optimize each model independently. Parameters were also specified in this text file in order to limit the data collected (to speed up simulations) and to be sure that all necessary data is collected for an analysis. When all models were built and double checked, they were sent to a blueridge cluster (super computer) to run.

Data collection and Analysis

Upon completion each set of runs was compressed and transferred to a local machine to be analyzed. Matlab’s `xb_view` command was clunky and time consuming so a matlab script was written to create color plots of energy, forces, sediment transport, velocities and bathymetry throughout each event. These plots where used to analyze each set of simulations qualitatively as they did not show specific values that could easily be identified. This allowed us to make decisions on how chosen parameters performed, their relevance, and any mistakes that may have been made. When the qualitative analysis was approved work began on the quantitative analysis. Another script was made to plot sediment transport and bathymetry for storms and their respective tsunamis against one another.

III. Results

Figure 8 and Figure 9 both show Sediment transport (top) and Bathymetry (bottom) of a tsunami (blue), a comparable hurricane at minimum (pink) and maximum (green) surge level and the initial island profile (black). These two sets of events were chosen because they best represent the data.
Figure 8 - Sediment Transport And Bathymetry For Storm 17&20 And Its Respective Tsunami

Figure 9 - Sediment Transport And Bathymetry For Storm 29&32 And Its Respective Tsunami

IV. Discussion

Generally speaking, the data matches what is said from previous studies. Hurricanes have thicker shorter deposits while Tsunamis have thinner and longer deposits.

Figure 8 shows that at the lowest surge level the hurricane does not erode the dune while the largest surge level does. The tsunami deposits is nearly 3 times longer than the hurricane deposit but
roughly 25% thinner. However, Figure 9 shows both surge levels eroding the dune with deposits about twice as thick as the tsunami deposit and the largest surge level is nearly as long as the tsunami’s.

It is clear that the surge level plays a large role in sediment transport for hurricanes but currently does not play a role in our method for calculating the respective tsunami height from an energy ratio of a storm event. We believe that while these results can tell us much about hurricane and tsunami sediment overwash events much more work must be done to consider the effects of surge to better compare the two events.

V. Conclusions

Our results confirm what is said in previous studies that use field data and geological evidence. The hydrodynamic and morphodynamic model, Xbeach, can simulate sediment transport for hurricanes and tsunamis.

Hurricanes are huge wind driven events that last for hours to days and result in short thick sediment deposits. Tsunamis are large waves driven by massive displacements that result in longer thinner deposits. Nothing more can confidently be said about the differences between the two events because of the limitations of the project.

Our assumptions and limitations include: Uniform barrier island, cross-shore uniform waves, limitations on tsunami wave description (shape, period, height), number of tsunami waves, duration of hurricane and tsunami events, and that surge was not accounted for when calculating each hurricanes respective tsunami wave height.

Because surge played a huge in how a hurricane eroded the barrier island it must be considered when finding a comparable tsunami wave height. More research should be done to distinguish hurricanes from tsunamis with a focus on the role of surge and its contribution to energy or a semi-empirical method must be developed to compare the two events.

VI. Acknowledgement

Thank you Dr. Jenifer Irish and Dr. Robert Weiss for advising me throughout the NSF/REU program and to Stephanie Smallegan and Wei Cheng for mentoring me and giving me all the help needed to be successful this summer.

We also 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 author(s) and do not necessarily reflect the views of the National Science Foundation.
### Appendix

**Figure 10 - General Barrier Island Profile (Steven Keith 7/15/14)**

**Table 1 - Barrier Island Profile Values (Steven Keith, 7/11/14)**

<table>
<thead>
<tr>
<th></th>
<th>D1</th>
<th>D2</th>
<th>D3</th>
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<th>L2</th>
<th>L3</th>
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<td>-</td>
<td>-</td>
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Figure 11 - LIDAR Data Of Santa Rosa Island Pre Hurricane Ivan (McCall et al., 2010)

Figure 12 - Close Up Of Santa Rosa Island LIDAR Data (McCall et al., 2010)

Table 2 - Proportion Base Measurements From Excel (Steven Keith, 7/11/14)

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Table 3 - Calculations For Idealized Island profile (Steven Keith, 7/11/14)

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Meters 40.5328798 64.5604396 383.017493 Sum 488.110812

D1 D2 D3 L1 L2+L3 L4
14m 1.25 383 65 40

Figure 13 – General Island Bathymetry (Steven Keith, 7/11/14)
Figure 14 - Full Barrier Island Profile (Steven Keith, 7/11/14)

Figure 15 - Surge Level Example (Steven Keith, 7/15/14)
### Table 4 - Storm Parameter Review (Steven Keith, 7/15/14)

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<th>T (wave period)</th>
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### Table 5 - Storm parameters (Steven Keith, 7/15/14)

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### Table 6 – Tsunami Parameters (Steven Keith, 7/15/14)

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References


Google maps. (2014) [Barrier Islands along the Eastern United States] [Barrier Islands]. Retrieved from https://www.google.com/maps/@26.1186656,-97.177888,11903m/data=!3m1!1e3 https://www.google.com/maps/@30.0969011,-85.6938419,1097m/data=!3m1!1e3 https://www.google.com/maps/@29.6567972,-84.8743024,3017m/data=!3m1!1e3 https://www.google.com/maps/@33.9254453,-78.3079116,4845m/data=!3m1!1e3 https://www.google.com/maps/@34.3683914,-77.6297089,2714m/data=!3m1!1e3 https://www.google.com/maps/@34.5667391,-77.2803108,784m/data=!3m1!1e3 https://www.google.com/maps/@35.1170146,-75.9305776,3793m/data=!3m1!1e3 https://www.google.com/maps/@35.4667305,-75.4773935,922m/data=!3m1!1e3 https://www.google.com/maps/@36.2261893,-75.774244,1009m/data=!3m1!1e3 https://www.google.com/maps/@38.0693563,-75.2254622,4075m/data=!3m1!1e3 https://www.google.com/maps/@39.5978083,-74.215393,1067m/data=!3m1!1e3


Fog Capture: Drop in the Bucket or Meaningful Source for the Driest Most Remote Communities

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**Department of Industrial Design, Virginia Tech

Abstract

Can fog capture make a difference in people’s potable water needs, specifically in third world countries? According to UNESCO “783 million people do not have access to clean water.” Given these figures fog capture activities should be advanced to help address these challenges. This paper will identify regions of fog capture opportunity, and to propose appropriate, cost sensitive design improvements that would improve water yield and human usability. Our conclusion is a proposal for a design that is adaptable on site to wind conditions, expandable as needed or as funds allow while improving the water capture performance and reducing maintenance.

Keywords: fog capture, design, impact

I. Introduction

The need for water is clearly already great, but will only increase overtime. It is predicted that the demand for water will outstrip the supply of clean, safe water in the very near future. (Patrick, 2012) Water issues are already evident worldwide with several droughts occurring in areas of South America, Australia, Asia and even the United States. Water issues can be attributed to demographic pressures with growing populations, declining fresh water supplies and poor water management. (Patrick, 2012) All of this information supports why the process of fog capture should be investigated more as one solution for the water issues. The United Nations Educational, Scientific and Cultural Organization (UNESCO) has predicted that water scarcity will grow by the year 2025.

Figure 1: Figure On Water Availability In 2025
(Schemenauer, Cereceda, Osses, 2005)
Fog capture is a low-tech way of extracting water for those who have no ability to have wells, desalination plants, and aquifers. In many ways it emulates a process known as “Fog Drip” whereby Redwood trees convert coastal fog to liquid water which drips to the ground and is in turn absorbed by the tree roots. As part of a simple explanation fog capture starts with “a frame that supports a section of mesh in a vertical plane” (Eytan). Then the fog capture process consists of fog entering from one side of the net, and water collecting in the net in the form of droplets. These droplets then fall into a trough due to gravity and from there are funneled into a cistern. Fog capture can be purposed as a viable type of solution to the current water issues because the technology uses no energy, produces drinkable water that meets World Health Organization (WHO) standards, and requires minimal maintenance and repair. Also due to the simple design of most fog capture devices they can be used in the various terrains worldwide. Although fog capture has shown to be a viable technological tool in addressing the water shortage issue, there are areas that could be improved. Fog capture use has a great deal of potential and promise but only with more investigations into the need, as well as the designs could it have the greatest impact. Currently projects impact is minimal, fog capture devices are employed in rural areas. Depending on the size of a fog capture project it can support around 150 people daily with the amount of water it produces. (FogQuest)

II. Research Methods

To learn about fog capture and find possible design improvements (for increased usable water collection) research included a literary review, analysis of current designs, and development of proposed design ideas.

Literary Review

Fog Capture Survey

Understanding fog capture first began with a literary review of where fog capture currently is practiced, what are good conditions for fog capture, and where fog capture could potentially be put in place. Many fog capture devices currently in use are from a company called FogQuest. This company currently has devices in over 17 countries, showing the potential wide-scale global use of fog capture.

Figure 2: Locations With Fog Collections Present Since 1987
(Schemenauer, Cereceda, Osses, 2005)
Before employing devices FogQuest had potential areas evaluated. Fog collection works best in arid or semi-arid climates that can be dry or humid sometimes, in an area with a higher altitude and little precipitation. To collect the most water these factors must be considered: Mountain ranges, Altitude, Distance to the sea, Corridors of fog penetration, Wind, Relief and slope orientation, Vegetation, and Accessibility. (Schemenauer, Cereceda, Osses 2005) After taking into consideration the factors that make a potential site for fog quest devices possible, new areas of opportunity were considered. Comparisons of various climate, terrain, and water availability around the globe, provide an indication that there are several new areas that could benefit from fog capture devices. Considering the perimeters Bolivia, California, India and Sudan are specific places of interest that could benefit from fog capture.

Figure 3: Recent Fog Collection Studies
(T. Hess, 1998)

Possible Places
Fog collection studies have been conducted at or near the proposed sites believed to have potential benefit from fog capture. Bolivia could benefit from fog capture because though water issues are not as bad as during the “Water Wars in Cochabamba” (PBS) there are still problems. Challenges in South America related to water are desertification, and loss of water supplies used for drinking and irrigation due to industrial pollution. (Central Intelligence Agency) The terrain varies with the rugged Andes Mountains, plateaus, hills, plains and Atacama Desert nearby which is a good environment for fog devices. FogQuest already has devices employed in nearby Chile and there is a company called Fogua using fog capture to produce bottled water to be sold individually and in Europe. Fog devices could be beneficial in rural areas near Cochabamba such as Arani, San Benito, Villa Rivero.

Fog capture devices could also be of use in the United States more so in California or semi-arid West coast areas. Fog collection studies have been conducted as can be seen in Figure 3. California is currently going through one if its worst droughts but has great potential for fog harvesting. California experiences many fog days depending on the location. Watsonville, California recorded 241 days of fog between 1998 and 2008 for example. (Western Regional Climate Center, 2009) This information has importance when considering the impact that water shortages caused by droughts can have on daily living. Santa Cruz, California is 17 miles away from Watsonville and has been dealing with water restrictions due to the current drought. (Association of California Water Agencies, 2014)
India’s tap water is not potable throughout the country, and places such as Rajasthan receive little water. Rajasthan also is an area that has been dealing with droughts lately so fog capture should be considered for this area. With India being one of the top ten areas for wind power (Danigelis, 2013) investigating the benefits of fog capture could also be impactful. Sudan is another area with fog capture potential. Its water issues are that 50 percent of people do not have access to improved water resources (World Bank Group) and that droughts have been causing crop loss in turn causing famine. FogQuest does have fog devices in Eritrea and due to its proximity to the Red Sea; the question rises if Sudan could improve its water supply too with fog capture.

**Analyze**

There are several water collecting devices used around the world. The first device examined was that of FogQuest due to its predominating use around the globe. Additionally a fog structure in Oman, a billboard in Peru, and a device named Airdrop were also examined.

FogQuest large devices use 40m2 netting that is suspended between two posts. The mesh netting is made of polyethylene or polypropylene, which are types of plastics.

A. FogQuests most successful project to date can be found in Guatemala using 30 large collectors and producing 5 liters per m2. Evaluating this device led to the identifying design issues and problems:
1. Flimsy mesh
2. Algae Growth and Dust
3. Water Transportation can be difficult to population areas
4. Changing Conditions hard to adapt to
5. Water Entrapment
6. Eyesore

![Figure 4: Fog Capture Device In Guatemala (FogQuest)](image)

B. This Oman structure consist of four nets together each 60 m2 and has the potential to hold 400 cubic meters of water. When analyzing this design it was noted that the devise had a different structure with concrete footings and two panels connecting creating a confined space. This device was also being used to irrigate nearby land to reverse desertification that had occurred.
C. The University of Engineering and Technology in Peru partnered with a publicity agency to install a billboard that converts fog into drinking water by using a reverse osmosis process. Located in the Bujama Desert, this area of Peru has an annual precipitation of .51 inches while its humidity is 98%. (Smith-Strickland) The billboard designed to capture water took on another purpose besides providing water but also became a tool for education. It cost $1200 to develop and produces 96 liters of water per day. (Smith-Strickland)

D. Airdrop, winner of the 2011 James Dyson Award, is another design that produces water from air. Edward Linacre, the designer, created this device to address the growing water issues in Australia. Australia recently has suffered droughts in some parts that subsequently have had a negative effect on crops. Linacre’s Airdrop device extracts water from the air and uses it to irrigate the ground through pressure. This device can produce 11.5 milliliters of water per every cubic meter of air with approximately 64% humidity. (A. Moses)
Scientific Solutions

Previous studies on fog capture have addressed the more scientific aspects of fog capture, namely performance, water yield and so on. However more recent studies are doing investigations into the use of nature and it’s processes in order to generate ideas or solutions to issues. This process known as Biomimcry or Bio-Inspiration has become a foundation for investigations into new water technologies or improving past technology. Many of these studies are ongoing with universities from around the globe. Universities are studying potential materials that assist with the process of converting nature’s fog into usable water. In Australia researchers at the University of Sydney have invented a synthetic surface with two polymer layers (similar to cell membrane) one hydrophilic to attract water and one hydrophobic to repel water. Similar to this study, in the Netherlands, Eindhoven University of Technology joined with Hong Kong Polytechnic University turning cotton fabric into a water collecting material by coating the fabric with a polymer. (Winston 2013) This “polymer” again functions just like the natural processes found in a cell membrane. In another study Chinese scientists have been studying the impact of the use of spider silk in the design of fog capture devices. Researchers from MIT in Massachusetts have conducted another fog capture “improvement” study. They recently published their work on a new material designed that is more efficient than materials used by common fog capture devices. This study looked at producing a mesh much like the shell of the Namib beetle that survives due to its shell surface ability to attract and repel water. MIT’s netting uses a window screen pattern made of thin stainless steel fibers. This is different from other methods such as those used by FogQuest (a company that produces majority of fog capture devices), who use polyethylene or polypropylene (plastic) mesh. MIT’s new netting differs in that it can capture 10 percent of water from fog (12 liters per square meter) compared to FogQuest 2 percent, the gaps in netting are smaller, and it is coated with different coatings. (McKinley 2013) With a predominate amount of studies being conducted on new possible materials for fog capture netting, the design of the whole structure, netting and frame, has not been considered that much, this is what was considered more in this research.

Opportunities for Design Improvements
From our analysis of existing designs we concluded that the Fog Quest ‘style’ of Fog Capturer is the best one to investigate for design improvements because it is the most widely used and is the least expensive to deploy. Following the problem areas we uncovered with the current designs we established some of the following design criteria to address in our design exploration:

1. Increase mesh water yield efficiency
2. Reduce or prevent algae growth
3. Enable customization for site specific wind direction variability
4. Improve frame structural strength and mesh durability
5. Facilitate expansion if possible
6. Help transport water more easily from the site to the population it serves

Design Solutions Exploration

After defining some of the significant problems, we began to brainstorm potential solutions. New ideas or questions that arose were what if the device was a plane versus confined space, or rotated to produce electricity? Could the new design incorporate a frame that has a “natural” curve, a fold, have more structure or be an installation? From these different ideas there was a narrowing step to ensure we were addressing the criteria defined above.

Initial Concept Ideas

![Sketches Of Design Ideas That Had a Different Structure, Rotated, Could Be Installations Or Curved](S. Cranford, 2014)

Figure 8: Sketches Of Design Ideas That Had a Different Structure, Rotated, Could Be Installations Or Curved

(S. Cranford, 2014)

III. Results and Discussion:

Ideas Revised

Narrowing down design ideas led to focusing on the materials, configuration and structure. While costs are very sensitive, averaging from $100-$150 USD for an iron structure, cables and mesh of 1 meter x 1 meter and installation costs (varies from country to country) our belief is that the benefits of improved structure and materials will outweigh the additional cost.
Suggestions for Possible Design Improvements

Structure and Configuration

This new form for the fog capture device would be supported by three stock steel I beams (or equivalent) fixed in the ground. This would result in greater support for the mesh (the material that actually collects the fog/water). Using I beams and a metal mesh would create a more stable robust device, which addresses the issue of flimsiness seen in fog devices today. The V shape of the netting could be adjusted to the conditions, which the device is placed to encompass the fog that passes through from multiple angles. This could potentially lead to an even greater collection of fog water. These design changes are still quite simple allowing the device to also be a modular so that it could possibly be extended/expanded to meet growing need.

Materials

There are two options for the mesh to improve performance and usability. The first would be to use a material like MIT’s polymer stainless steel netting, whose benefits we discussed before. This polymer coated metal netting would be connected to I beams and because it is metal should withstand high winds and avoid tearing better, but needs to be tested further. Another untested possibility would be to use a thicker, more rigid punched sheet metal mesh. Despite increased cost, such a mesh could be scored and folded for transport to the site and could certainly last longer than polyethylene meshes that are commonly used now.

An additional feature that could be added is a micro etched pattern or film akin to Sharklet Technologies products, which has shown the ability to repel Algae on the hulls of Naval vessels. If this technology could be deployed successfully in this application, it would reduce the cumbersome, time-consuming need to clean Algae from the mesh.

Costs

Determining the final design was an iterative process but it was also necessary to remind ourselves that these devices represent ‘appropriate technology,’ meaning they are constrained by local costs and available materials, not aesthetics. After researching current fog capture designs, climates and regions in different hemispheres that use or could benefit from use of the devices, and materials in use for fog capture devices, we concluded that additional costs would be justified if their lifespan and decreased maintenance was considered.

Proposed Design
Design Features (Details)

In the new design the structure supporting the device are three metal I beams. These I beams will provide more structure and stability than previously. The stainless steel netting would be two layers, one on each side of the I beam and bolted on. Altogether 16 nuts and 16 bolts would be used to connect the netting and trough. Using nuts, bolts and I-beams would eliminate the use of cables. Using a metal netting instead of plastic addresses the issue of tearing. Though we are suggesting MIT’s stainless steel netting an antimicrobial netting could also be possible such as copper to eliminate the dust and algae growth. These materials have other benefits besides the added structure, they are also easy to procure and create a sleeker design. The trough would be square instead of curved like the ones used currently enabling it to be installed between the I beams’ flanges. The trough would also be installed at an angle allowing for water to flow down into the cistern. The new design also creates a module that can be expanded upon to create a larger fog collecting system.

Material Option 1: Polymer-coated steel mesh (Developed at MIT)

Material Option 2: Perforated steel sheet with micro scale etching to provide hydrophobic/anti-algae properties (Sharklet)
Figure 11: Drawing of Purposed Design Detail in Plan  
(S. Cranford, 2014)

Figure 12: Purposed Design Folded  
(B. Kennedy, 2014)

Figure 13: Possible Design Configurations Of Changing Angles Or Expansion From Original Module  
(B. Kennedy, 2014)
IV. Conclusions:

Potable water availability continues to be a concern around the globe. Science has been addressing this concern through research and the development of various means of water collection. The fog capture process of collecting water has been shown to address this concern. Our purposed design respects the cost sensitivities of deploying appropriate technologies in countries with limited budgets. For this reason, our design proposal appears on the outside seems to be minimally different from existing solutions but in reality altering a seemingly minute detail or using newer, promising advanced materials could have a great effect. With additional investigations into the various designs of the device that collects the greatest amount of water with the least amount of economic hardship, the fog capture process could be the solution to the water shortage experienced in many areas around the globe. From this study on fog capture use and design, the research showed that there are many more places of need and opportunity for fog capture. Presently the water yield from fog capture devices needs to increase to demonstrate a greater impact. However with studies such as MIT’s this can hopefully be possible in the near future. Our research was restrained due to the environment/conditions of Virginia. The next step in our work would be to construct our device and test it in an environment conducive to fog collection. For progress to be made with fog capture more research studies need to be conducted. Studies to do this would either need to take place in regions that experience a great deal of fog, and/or in a controlled environment in which fog and the fog capture process can be simulated. Future studies to propel work in the fog capture area would be to see the difference of water yield with a V shaped net versus a flat net in the conditions best for fog capture. Investigating other designs that can integrate dew capture would be another area of exploration. Another design idea of a rotating fog capture device that could produce not only water but also electricity would be beneficial. To have a hybrid device that had the features of a fog capture device and wind turbine that used electricity for pumping or UV sterilization could have great impact potentially.

![Figure 14: Future Design Of Hybrid Fog Capturer/Wind Turbine](B. Kennedy, 2014)

Lastly, creating more devices that not only produce water but also continue to promote awareness of alternative methods for water capture (like the Peruvian Billboard) could be an additionally beneficial pursuit in the future. Many amazing technologies like fog capture suffer from being overshadowed by intense media coverage of the high tech, new and different in places like Silicon Valley and the Bay Area. Ironically, such a place is a perfect location for deploying a low tech, bio-inspired solution like fog capture. San Francisco is famous for its fog and is now becoming famous for its water shortages. While fog capture will not curb California’s drought issues, it does present a paradigm for rethinking the problem. After all, local Redwood and Sequoia trees have been supplementing their water supply with fog for millions of years. Thus, with increased awareness and continuous performance improvements, fog capture stands to have meaningful human impact. Hopefully continued efforts to develop this technology will contribute to helping meet global water demands in the coming future.
V. Acknowledgments

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References


High Frequency Environmental Monitoring Using A Raspberry Pi-Based System

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** Department of Engineering Education, Virginia Tech

Abstract

The Learning Enhanced Watershed Assessment System (LEWAS) is a high-frequency water and weather monitoring lab on Virginia Tech’s campus with three primary environmental sensors: an Acoustic Doppler Current Profiler, Water Quality Sonde and a Weather Station. The Goal of this study is to develop and implement a Linux based system with a Raspberry Pi that will allow users to access high-frequency real time LEWAS data for education and research.

Shell scripting on a Raspberry Pi controls modular Python programs for each sensor that start data collection, parse received data streams and store data points in a local database on the Raspberry Pi in real time before terminating data collection. A local database on the Raspberry Pi utilizes a mirroring process to replicate the local database to a remote database established for the LEWAS data. Users will access the remote database using various utilities to use the LEWAS data for research and education. Use of the Raspberry Pi system allows the LEWAS team to use common hardware and software environments to collect, process, store and manage high frequency data and thus giving advantages over using the individual proprietary software for each sensor.

Keywords: Raspberry Pi, High Frequency Data Acquisition, Python, Watershed Assessment

I. Introduction

The Learning Enhanced Watershed Assessment System (LEWAS) is a high frequency data acquisition system established to promote water sustainability education at Virginia Tech. The LEWAS lab is located on a portion of the Stroubles Creek near West Campus Drive, North East of the Virginia Tech Duck Pond. The water that flows through the LEWAS Lab field site is part of the Stroubles Creek watershed. Ninety-five percent of the land coverage of the Stroubles Creek watershed that flows through the labs site is urban, this results in a high quantity of pollution and manmade debris in the stream (Dymond, Lohani, Brogan, and Martinez, 2013). The ability to collect, analyze and store this real-time water and weather data for sustainability research and education has been a goal of the lab since its conception. (Delgoshaei, et al., 2012; Dymond, et al., 2013). With this data the lab has the ability to document pollution and use it in educational case studies.

The LEWAS Lab achieves this through the use of a weather station, flow measurement device and water quality measurement device. The Vaisala Weather Station captures the barometric pressure, air temperature, relative humidity, amount of precipitation and speed along with the direction of wind. The stage and velocity of the water moving through the field site is gathered through a Sontek Argonaut SW (Argonaut). Finally, a Hydrolab MS-5 Sonde (Water Sonde) gathers the water temperature, pH, conductivity, turbidity and dissolved oxygen (Martinez, et al., Rogers, 2012; Welch, et al., 2011)
Combined these three sensors give a detailed picture of the stream health at the LEWAS field site and surrounding environment of the watershed.

Figure 1. LEWAS Lab Field Site

During the summer of 2013 Arun Rai worked on implementing a remote data logging system that utilized a database. The goal of the project was to develop a weather monitoring system with an interactive web-based user interface using historical and real-time weather data recorded at the LEWAS site (Rai, Brogan, Guest, and Lohani, 2013). The previous project utilized LabVIEW, a graphical user interface driven programing language. The real time version of LabVIEW that was to be utilized was to run on a compactRIO, a modular embedded computer produced by National Instruments. The data collected by the system was to be sent over a local area network connection to a remote database. Data was then to be retrieved from the MySQL database and displayed on a web-interface for educational purposes.

This previous system was not fully implemented for several reasons. Firstly, the compactRIO, provided many difficulties when it came time to install the LabVIEW Virtual Instruments (VI’s). Second, the system was not able to connect to the host computer to load the VI’s. Third, compiling the VI’s failed several times before the method was changed. Finally, once the connection was established the files were too large for the compactRIO due to an upgrade to a newer version of LabVIEW. An open source system on chip solution has the ability to address these problems with the previous system along with several other issues.

II. Research Methods: System Overview

Raspberry Pi and Software Languages

Migrating to a modular open source Raspberry Pi-based environmental monitoring system will provide a large array of tools for collecting data and storing the data points. A Raspberry Pi is a system on chip computer that is about the size of a wallet and has all the main characteristics of a full desktop computer. A system on chip Linux computer will reduce the power consumption by fourteen watts compared to the compactRIO (Brogan, 2014). The compactRIO used in the previous project had the ability to connect up to three sensors at a time during real time data collection (Brogan, 2014). The system on chip computer to be implemented will not be constrained to using LabVIEW and will be able to connect more than six sensors during real time data acquisition.
In this implementation the Raspberry Pi is running a derivative of the open source Debian Linux Distribution called Raspbian. Raspbian is a Linux distribution that has been optimized to run on a Raspberry Pi. In this implementation communication with the sensors is carried over a RS-232 serial connection. Individual Python programs specifically developed for each sensor connect and perform data acquisition over the serial connections. After the data has been read from each sensor, python functions parse the data lines and insert the data into the MySQL database through queries. Finally, the data inside the local database is to be automatically mirrored into a remote database for later use by researchers, students and the general public.

The Linux distribution chosen for this is not as significant as the other components. The reasoning for choosing Raspbian is that it is well optimized to run on a Raspberry Pi and has a large amount of documentation. Python is an interpreted language, as the compiler moves through the code it compiles and adds the line to execution stack before compiling the next line. This is different from other C-style languages that are compiled before running. Python was utilized in this implementation because it abstracted away many of the system considerations that must be taken into consideration in C or C++. Python has a garbage collector, allowing the developer to ignore memory management unlike lower level languages traditionally used for system applications. C and C++ are lower level languages than python making them a better option for serial communication than Python is. I implemented a python library, PySerial, to resolve this handicap that python initially had. With PySerial I retained the abstraction that is inherent to the language while not forgoing any benefits of a C-style language because of the serial communication specific modules in PySerial. Finally a MySQL database is utilized as the storage engine because of the large amount of documentation about the engine and it also being the de facto standard for open source projects.

Data Flow

Figure 2 depicts the role that each device will play in the final implementation. The three inputs; the Water Sonde, Weather Station and Argonaut collect data in real time for the processing unit to retrieve. The processing unit or Raspberry Pi reads data for the devices once it becomes available. As each line is read the python code parses the data values from each line that it reads. In some cases it truncates certain values that are not needed. After this, post data processing SQL insertions store the data in the local database (a backup measure before mirroring the data into the remote database). A background setting in the local database allows it to automatically update additions that it receives to the remote database. The remote database stores the data for accessing near real time data or archived data through user interfaces like the Platform-Independent Remote Monitoring System (PIRMS) (Brogan, Lohani & Dimond, 2014).
Sensor Implementation

The three sensors share very similar components in their software structure, the method that they communicate with the Raspberry Pi and the methods used to store the data values. Each sensor receives commands, sends data for python code to read and finally be inserted into the local database.

In the final implementation a Linux shell script will start a program that will cause the local database to confirm the safe transmission of data to the remote database before each data collection deployment.
During this operation depicted by the blue blocks the local database will verify through queries that all the lines of data it contains are also located in the remote database. In the event that they were not mirrored during deployment they will be appended to the remote database. Once it is confirmed that the remote database contains the most recent points the local database on the Raspberry Pi will have all of its data values removed from the local database. This is done because of the limited amount of space that will exists on the Raspberry Pi and the possibility that it will eventual be fully occupied.

After the data preservation steps are completed the green Python blocks start data acquisition. Each of the three communication programs first established a connection to each sensor and opens a connection to the local database. Each sensor has a different command for stating data acquisition, but all the sensors require acquisition to be initialized. For the sensors that need to be directed to start data acquisition commands the Python programs send start acquisition commands after establishing a connection. Each program reads data from the sensors output buffer when it becomes available. After a line of data has be acquired from a sensor it is parsed apart into its components that represent the individual data parameters. These parsed values are then inserted the local database. As a background operation, after the local database detects a new insertion it will mirror that action over to the remote database. This action is not initialized by the python code but happens nearly instantaneously after the values are added to the database table. The acquisition, parsing and inserting of data values continues in each Python program for a user defined period of time, the deployment period. Each program stops after this deployment period individually.

Connections with all the devices happens through TTY connections in the Linux kernel. TTY or Teletype are terminals for interacting with the Linux kernel. The kernel is the lowest piece of software in a computer system. A kernel manages the flow of data from the hardware and further up layers of software that utilize abstraction. Commands and data acquisition flow through this TTY connection with the Linux system kernel.

III. Sensor Software Development

Weather Station

The Vaisala Weather Transmitter WXT520 or Weather Station that the LEWAS Lab has implemented at the field location has a serial object in its python code that represents the connection between the device and the Raspberry Pi. The python object has fields for the port location, baudrate, bytesize, parity, stopbits, read timeout, hardware and software flow control. The baud rate, bytesize, parity and number of stop bits that are required to communicate with Weather Station are dependent upon the communication standard chosen. The Weather Station supports ASCII, NMEA and the SDI-12 communication standards. The NMEA standard named after the Nation Marine Elections Association uses special proprietary ASCII commands as does SDI-12. NMEA was not implemented due to the fact that the commands are not well documented along with not knowing how much the device would support the standard. The SDI-12 standard is not directly compatible with Serial RS-232 communications due to the voltages that represent a binary one and zero. The voltage range of a RS-232 connection travels too far for it to be implemented with a SDI-12 device. The ASCII interface uses a baud rate of 19200, a packet size of eight data bits, no parity bits and one stop bit. The weather station does not use an implementation that responds to or require a break signal to be sent be commands can be sent.

The device supports automatic or polled measurements of weather parameters. In a polled deployment each measurement is only reported when the program requests a data point. In the automatic
mode data points are measured, calculated and written to the output buffer on the device for another device to read from. The serial object behaves similarly to a file that can be written to and read from by the rest of the program. The current implementation loops over the file and reads each line of data that is produced in the weather station. Each has the first three characters parsed off to determine what parameter set the line contains. The code excerpt below is an example output for the Precipitation Data Message.

```
0R3,Rc=0.0M,Rd=0s,Ri=0.0M,Hc=0.0M,Hd=0s,Hi=0.0M,Pr=0.0M,Hp=0.0M
```

The “0R3” characters in the beginning of the string represent that this line is precipitation data. Each data point follows this identifier, the data points are comma separated and follow the equals symbol of their exact field. The units, carriage return and line feed are also parsed off before the points can be put into the database and cast to a float.

The Weather Station has an automatic error reporting system that will include a pound symbol instead of a data point when it is unable to measure or calculate a specific value for a field. Subsequently the system looks for that symbol and will stop the current data insertion into the database, close the database, update the crash log and exit. This prevents a type cast error when trying to cast from a string to a float for the SQL insertion. Further error detection is built into the program to catch instances where the device does not respond to a signal or is unable to interpret a command. Every twenty four hours the system resets its internal counter for the accumulation of rainfall and hail. To accomplish this the python code sends two commands, one for each field, successively to the weather station and reads the next the lines in the buffer for the response to the commands. A confirmation from the weather station that acknowledges the reception of the commands is written to the output buffer of the device. The python code reads the next three lines from the weather station looking for a confirmation. A confirmation may not be the next line in the buffer of the weather station so the python code reads the next three lines to account for a slight buildup of data in the buffer. If the command reception is not located in those three lines then the system halts data collection, writes those lines to the crash file and closes up connections with the sensor and the database.

**Water Sonde**

Communication with the Hydrolab Water Sonde is executed over a TTY Connection like the other devices. However, the Water Sonde must be put into a data acquisition mode that reports data in manner that a terminal can utilize.

At the beginning of a deployment of the Water Sonde the device is connected to a Windows laptop and a connection is established with the proprietary software Hydras 3 LT. The connection with the proprietary software is established to create a deployment file in the water sonde to start data collection. After data collection is set to start the device is put in TTY mode. Throughout the duration of the deployment the device will automatically put data in the output buffer for a program or terminal to read from. During deployment the python code enters a loop that reads lines of ASCII formatted data separated by newlines. Each line of data is broken apart at the white space character and then imputed into the database. At the end of the deployment the python code exits TTY mode by sending a quit command. Quite commands can also be sent from a Windows Hyperterminal or Linux Terminal Program. Without the inclusion of the quit command the device cannot reconnect to Hydras 3 LT to start a new deployment.

**Argonaut Flow Device**
A break transmission is required to terminate the ongoing operation of the Argonaut and notify the device that a new stream of commands will be coming. The break lasts for a duration of eight hundred milliseconds during which time the transmission cable is held at the opposite voltage of idle state. After the termination of the break the device is ready to receive commands or settings. The start of data collection without internal storage is initialized by sending the command “start\r”. The ‘\r’ or carriage return is the ASCII character that notifies the sensor that no more commands will be coming in the current line. After a reception of a carriage return the device starts to internally process the command and start data collection.

A vertical plane is cut out of the water by the Argonaut’s sonar. From this the Argonaut is able to detect the velocity of clusters suspended particles moving through the vertical plane. A blanking distance exists between the device and closest proximity to particles where it is unable to measure water depth and speed. Above the blanking distance the device breaks the water column apart into nine cells. Internally the device finds the average velocity of the particles in each cell. Often at base flow only one or two of the cells will be below the waterline. The device reports the velocity in each cell and also reports an average velocity for the entire water column. The integrity of the data for the entire water column is not compromised due to some cells being above the waterline because the device can calculate the stage of the water and select from only the valid data points below the stage.

When capturing the data points the python program looks for the value that flags what number cell is the first cell below the water, it then flags all the cells below that depth as valid and all the cells above it invalid. The valid and invalid cells along with average velocity are stored in the local database. Two tables are allocated to the Argonaut data, one for average values and a second for individual cell values. Special queries can be executed to report only lines back with valid cells or to report all the cells. At the end of execution the database is closed, and a second break command is sent to terminate data collection to reduce system power consumption.

IV. Data Storage

A backup of the measured data that the sensors collect in real time is kept on the Raspberry Pi local system storage in a MySQL database. The local database utilizes an InnoDB storage engine. This storage engine supports commit, rollback and crash-recovery options that promote data integrity. InnoDB is fully compatible with other database storage engines and contains underlying processes that prevent inconsistencies in tables. A table is similar to a spreadsheet, these tables combined make up database. The local database on the Raspberry Pi has seven tables: two for the Argonaut, four for the weather station and one for the Water Sonde. The Argonaut has a table for the average velocity of the stream along with stage, temperature and power consumption. The second table contains a column for each cells vertical and horizontal velocity, signal strength and the validity of the cell for all nine cells. A single tale exists for the Water Sondes water temperature, pH, conductivity, turbidity and dissolved oxygen. There is a table for the Weather Station’s precipitation, PTH (pressure temperature humidity), wind and a self-check of system power consumption and internal heater.
Table 1. Weather Station Pressure, Temperature and Humidity Database Table.

<table>
<thead>
<tr>
<th>Index</th>
<th>Time</th>
<th>Temp (˚F)</th>
<th>Humidity (%RH)</th>
<th>Pressure (inHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2014-07-29 14:25:03</td>
<td>71.9</td>
<td>41.6</td>
<td>27.85</td>
</tr>
<tr>
<td>2</td>
<td>2014-07-29 14:26:03</td>
<td>71.7</td>
<td>41.8</td>
<td>27.85</td>
</tr>
<tr>
<td>3</td>
<td>2014-07-29 14:27:03</td>
<td>71.9</td>
<td>42.6</td>
<td>27.85</td>
</tr>
<tr>
<td>4</td>
<td>2014-07-29 14:28:03</td>
<td>72.1</td>
<td>45.8</td>
<td>27.85</td>
</tr>
<tr>
<td>5</td>
<td>2014-07-29 14:29:03</td>
<td>72.3</td>
<td>44.3</td>
<td>27.85</td>
</tr>
<tr>
<td>6</td>
<td>2014-07-29 14:30:03</td>
<td>72.6</td>
<td>43.9</td>
<td>27.85</td>
</tr>
</tbody>
</table>

Table 1 is an excerpt of the data collected on July 29, 2014 at the LEWAS field site. The far left column, index, is the row index by which a line of data can be referenced and is known as the primary key. The index or primary key auto increments for each new line of data this is inserted into the database. A time stamp is inserted into each line of data to signify when it was collected. Column two is dedicated to timestamps that are generated when the data is inserted into the table. Moving further to the right the remaining columns are reserved for the pressure, temperature and humidity observed during the deployment. All of the tables in the local and remote database have an index that serves as the primary key, a time stamp from the system time followed by the data values. The data values are stored as floating point numbers to preserved data precision. Storing the values as doubles would make the database unnecessarily large for the Raspberry Pi and using decimal data type numbers would truncate part of the data value reducing its precision.

V. Linux Development

The Raspberry Pi does not have a native RS-232 serial connector that the sensors in the system utilize. To resolve this each connection passes through a USB to RS-232 connector. The Linux kernel does not, though, automatically understand what the converter device is when it is connected to the system, instead the TTY connection is designated as ttyUSB0. The naming for these devices will continue to auto increment as more are connected. These names are assigned to the devices at random. The python programs need to know which directory to point at each time to send and receive data form the correct sensor that they are developed for. To overcome this issues each converter is has a custom rule written for the Kernel to interpret what the device is. These rules are written in the `/etc/udev/rules.d` as .rules file type.

```
SUBSYSTEM=="tty", ATTRS{idVendor}=="12d0", ATTRS{idProduct}=="1001", SYMLINK+="converter"
```

Placing the above line in a rules file in the rules.d directory would tell the Linux kernel that the device with the idVendor identifier of 12d01 and idProduct identifier of 1001 to always be recognized in
the /dev/ directory where the TTY connections exist as “converter”. Python code then consistently references /dev/converter as the location the serial object points to.

When the Raspberry Pi is installed in the field it will not have many peripherals connected to it including a keyboard, mouse and monitor. The Raspberry Pi has a static IP address assigned to it by Virginia Tech network services. When controlling the device in the field a Linux laptop is directly connected to the computer through an Ethernet cable. The Linux laptop is also given a static IP address and then the user of the computer can SSH into port 22 on the Raspberry Pi. SSH is a tool for remotely gaining access to the Raspberry Pi terminal. From the terminal any number of programs or shell scripts can be started. When running a program over SSH the user appends an ampersand to the end of the command to notify the terminal to run the command in the background. When programs run in the background the user is free to run other commands or disconnect.

At the time of this document the Linux shell script has not been implemented for the Raspberry Pi data acquisition system. The shell script will need to accomplish two tasks. First, the script will need to initialize the operations that have the local database check for mirroring in the remote database and then clearing of the local database. Second, each Python program must be started in the background to insure that they do not execute after each other and one program hanging does not cause another to also pause. After these two steps are accomplished the shell script will terminate and the Programs will run until completion.

VI. Implementation Improvements

In the current Water Sonde implementation, the data acquisition program is able to read data and exit the mode that allows the device to output the data lines. The LEWAS lab is currently looking to purchase an intermediate chip produced by the environmental monitoring company Vegetronix. The product will act as an intermediate translator between the Raspberry Pi and Water Sonde. The new chip will accept SDI-12 commands over a serial connection and then convert them to the voltages required for the SDI-12 bus that the Water Sonde will be on. The chip has a transparent mode where neither device can recognize that it is there. The Water Sonde will output data as it would for a SDI-12 data logger and the python code would read from chip as if it was reading form any of the other sensors. This implementation though could have three possible drawbacks. The first would occur if the chip does not function as described or the Python code cannot interact with it. The second is that a new wire is required to convert between the SDI-12 data bus and the Water Sondes external connection. It is possible that the connection between the chip and cable may be underground. It is possible that the connection spot is under a concrete slab at the LEWAS Field site. Finally, both the chip and new cable will have some cost to the lab and Virginia Tech.

The Raspberry Pi system on chip computer is built to a certain quality control standard as well as certain operating constraints. The onboard SD storage card houses the local database and Raspberry Pi system settings. Both of these pieces of hardware will exceed their rated operating parameters as well as mean time before failure. The lab is also looking to upgrade the onboard storage to preserve the work on the Raspberry Pi. The new storage will have a longer rated lifetime for continuous operation as well as hardware error detection and prevention. Due to the size limitations of the SD card the local database might also be moved to external solid state hard drive that would connect over USB to the Raspberry Pi. Both of these hardware upgrades would preserve and extend the life of the hardware in the field and the data located on the devices.
VII. Conclusion

A high frequency environmental monitoring using a Raspberry Pi-based system to acquire data in real time is an effective way to monitor the overall health of a stream. Using Python with the library PySerial is an effective way to communicate and control scientific devices over a RS-232 serial connection. Functionality that can be built into the Python programs is highly dependent upon the communication standards that the sensors support and the number of commands built into them. The Water Sonde initially does have a wide variety of commands to allow the developer of a system to create programs automatically control the device well. With the addition of more equipment it should have the same level of automation as the other devices. The other two sensors worked quite well out of the box comparatively. Expanding upon a system like this require the designer to carefully examine the sensors to be implemented to insure that they will function as well as the Weather Station or Argonaut. During the summer REU the LEWAS lab was able to develop code the acquire data form the sensors and store it in a local database on a Raspberry Pi. The remote database has not been built and the automatic mirroring process untested in this context. Full system completion will require that functionality. Once the remote database is created and the link is established the system will be ready to be utilized by the LEWAS Lab.

VII. Acknowledgements

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Release Potential and Mobility of Sediment Phosphorus in a Periodically Oxygenated Reservoir

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Abstract

Phosphorus (P) is a limiting nutrient for cyanobacteria, bloom-forming phytoplankton that threaten drinking water quality because of their scums, toxins, and odors. Excessive P in water can cause cyanobacteria to bloom. Oxygen, which controls P availability, is consumed in the decomposition of cyanobacteria. The cycle of oxygen depletion by cyanobacterial decomposition, P release into water due to low levels of dissolved oxygen, and further bloom proliferation due to increased P in the water column is called eutrophication. Release of P from sediments to water is thus a critical process to quantify for evaluating potential for cyanobacterial blooms. P can be bound to different sediment fractions, including minerals and organic matter. The concentration and affinity of P to these fractions influence P release into the water column. For this study, I analyzed P fractionation in sediment cores from Falling Creek Reservoir, a drinking water source in southwestern Virginia. The reservoir is periodically oxygenated. Cores were collected under both oxic and anoxic conditions. At selected depths in each core, I analyzed the following P fractionations: mobile, bound to iron and aluminum, associated with organic matter, and bound to calcium, carbonates, and apatite. Results of my work will shed light on the mobility of P in sediments under different controlled oxygen conditions, with the ultimate goal of preventing cyanobacterial blooms in reservoirs.

Keywords: phosphorus, sediment, P-fractionation, reservoir, oxygenation

I. Introduction

Problems with cyanobacteria

Cyanobacteria can cause a host of water quality problems in surface water. For example, *Anabaena*, a nitrogen-fixing cyanobacterium that exists as plankton, forms surface scums and produces toxins harmful to mammals. These toxins include microcystins (hepatotoxins that target the liver), anatoxin-a (a neurotoxin), and saxitoxins (neurotoxins). Anatoxin-a produced by *Anabaena flosaquae* has been shown to be the cause of death of cattle and waterfowl in Canada (Carmichael and Gorham, 1978; Pybus and Hobson, 1986).

Several factors influence cyanobacterial toxin production, including temperature, light, nutrient availability, salinity, and pH. Phosphorus (P) is the primary limiting nutrient for cyanobacterial growth (Schindler, 1974). Because of this, P levels can also influence toxin production. In a laboratory study, Rapala et al. (1997) showed that toxin concentrations in the cells of *Anabaena* spp. increased with P. The authors concluded that reducing P loads in bodies of water could curb health hazards caused by cyanobacterial scums and their toxins. Paterson et al. (2011) investigated if controlling inputs of nitrogen (N) would also decrease algal biomass. However, the authors suggested that cyanobacterial blooms
remained proportional to annual P loading in the experimental Lake 227, regardless of decreased N input. This study contributes to the idea that P is the primary limiting nutrient for cyanobacterial proliferation.

Another water quality problem related to cyanobacterial blooms in surface water bodies is a depletion of dissolved oxygen. When *Anabaena* and other cyanobacteria or organic matter decays, dissolved oxygen (DO) is consumed. This depletion of oxygen (anoxia) at the sediment-water interface allows for release of iron (Fe) and manganese (Mn) from sediments into the overlying water column. Under anoxic conditions, microbes in sediment can reductively dissolve Fe and Mn hydroxides, releasing Fe and Mn from sediment into water. Because phosphate adsorbs strongly to Fe and Mn hydroxides (McBride, 1994), reductive dissolution of these minerals under anoxic conditions also results in P release to water. The release of Fe and Mn causes problems with drinking water treatment, such as rust-colored or metallic-tasting water, while P release into water under anoxic conditions provides nutrients for cyanobacteria, fueling additional blooms.

Cyanobacteria not only produce harmful toxins and deplete the water body of oxygen through decay, but they also decrease biodiversity in bodies of water. The oxygen depletion resulting from cyanobacterial blooms threatens fish and larger animals and diversity of microorganisms decreases due to the dominance of cyanobacteria (López-Archilla *et al.*, 2003). López-Archilla *et al.* (2003) observed abundance and diversity of phytoplankton in a hyper-eutrophic shallow lake in Spain. The authors found that cyanobacteria dominated the lake’s phytoplankton. It was also observed that as organic P (g m$^{-3}$) increased, so did cyanobacterial biomass (López-Archilla *et al.*, 2003, Table 1).

**P fractions and mobility**

As discussed above, P mobility plays an important role in water quality and is particularly relevant for drinking water reservoirs. P can enter the water column of a reservoir via nearby streams, geological deposits, and surface soils. P input into reservoirs is strongly influenced by land use, as use of commercial fertilizer and animal manure for supplying nutrients to crops can result in high P loads to nearby surface water bodies. Other influences on P mobility include the mineralogy of sediment. P input from the surface will sink through the water column to the sediment water interface and is available to adsorb to minerals and organic matter (Boström *et al.*, 1988; Rydin, 1999). Release of P back into the water column depends on how it is chemically associated with sediment. Many studies on P mobility in lakes have utilized a sequential extraction approach to determine how P is associated with sediment (Psenner *et al.*, 1988; Rydin, 1999; Rydin, 2000). In these studies, sediment P is separated into the following fractions: labile P, iron-bound P, calcium-bound P, aluminum-bound P, organic P, and residual P (Table 1). Each of these fractions has a degree of mobility that depends on environmental conditions such as redox potential within the hypolimnion, the sediment-water interface, and within the shallow sediment (Rydin, 1999).

Table 1 displays the general mobility and bioavailability of each fraction. “Labile” refers to a fraction that contains P that is immediately available for uptake by phytoplankton, or could easily become available in a reduced condition. “Refractory” refers to a P fraction that is inert and subject to become buried in the sediment. Also included in table 1 is the solvent with which each fraction was extracted for this study.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Mobility</th>
<th>Bioavailability</th>
<th>Extracted with</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loosely adsorbed P</td>
<td>Easily released under all redox conditions</td>
<td>Labile</td>
<td>Ammonium chloride (NH4Cl)</td>
</tr>
<tr>
<td>Iron-bound P (Fe-P)</td>
<td>Released under reduced conditions</td>
<td>Labile</td>
<td>Bicarbonate dithionite (BD solution)</td>
</tr>
<tr>
<td>Exchangeable with OH- and aluminum oxides (Al-P)</td>
<td>Not sensitive to redox</td>
<td>Refractory</td>
<td>Sodium hydroxide (NaOH)</td>
</tr>
</tbody>
</table>

95
<table>
<thead>
<tr>
<th><strong>Organic P (nonreactive P)</strong></th>
<th><strong>Released under reduced conditions</strong></th>
<th><strong>Labile</strong></th>
<th><strong>NaOH, persulfate microwave digestion, and calculation</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>P bound to apatite and carbonates (Ca-P)</td>
<td>Not sensitive to redox</td>
<td>Refractory</td>
<td>Hydrochloric acid (HCl)</td>
</tr>
</tbody>
</table>

**Research objective**

The objective of this study was to examine P fractionation in sediment collected from Falling Creek Reservoir (FCR), a primary drinking water source for Roanoke, Virginia (see below for more description of the field site) under both oxic and anoxic conditions. To accomplish this, sediment cores were collected in May (oxic) and June (anoxic). I then performed sequential P fractionation on slices of the sediment cores to determine concentrations of P at each depth. P fractionation was carried out by separating fractions of P (see Table 1 above) with each fraction’s respective extraction agent (solvent).

My overarching hypothesis was that the oxygenated sediment would contain more P than the anoxic sediment because under anoxic conditions, certain P fractions are more mobile and thus more likely to be released into the water column. I also hypothesized that concentrations of P would differ the most between oxic and anoxic sediments in the redox-sensitive fractions, specifically Fe-P and organic P.

**Field site**

Sediment cores were collected for this study from Falling Creek Reservoir, a primary drinking water source for Roanoke, Virginia. Constructed in 1897, this reservoir can store up to 169 million gallons of water and covers 21 acres (Bedford County Public Service Authority, 2008). Situated about 1 mile northeast of Falling Creek reservoir is Beaverdam Reservoir (BVR), which holds 435 million gallons of water and covers 69 acres (Figure 1.1). Beaverdam Reservoir feeds Falling Creek Reservoir through a downstream pipeline (not shown in Figure 1.1).
Figure 1.1 Right: Geological Map of the area between Falling Creek reservoir and Beaverdam Reservoir; Left: Land cover map of the area between Falling Creek reservoir and Beaverdam reservoir (Z. Munger, July, 2014)

Geologic and land use maps for the area surrounding the reservoirs are shown in Figure 1.1. On a larger scale, Figure 1.2 illustrates the two reservoirs in relation to the entire surrounding reservoir system (Southeast Aquatic Resources Partnership, 2013).
Falling Creek Reservoir has high nutrient levels in bottom sediment and is prone to cyanobacterial blooms (Bedford County Public Service Authority, 2008). The Western Virginia Water Authority (WVWA), who operates the reservoir, has also measured elevated concentrations of Mn and Fe in the hypolimnion of the reservoir. The release of these metals and the proliferation of cyanobacterial blooms indicate that the reservoir was eutrophic, and possibly oxygen-depleted. P, the limiting nutrient for cyanobacterial growth, is released when phosphate-containing Fe oxides are microbially reduced (Beutel, et al., 2007). The reduction of these Fe oxides allow phosphate and soluble Fe(II) to diffuse from the sediment and into the water (Golterman, 2001). Once in the water column, P becomes bioavailable, thus exacerbating cyanobacterial growth.

In 2012 a side stream super-saturation (SSS) oxygenation system was installed to mitigate nutrient release of Fe, Mn, and P in Falling Creek reservoir (Figure 1.3). The SSS system removes water, injects oxygen into the water, and pumps the super-saturated (oxygenated) water to the bottom of the reservoir. High pressure dissolves oxygen to higher, more optimal levels. The SSS system also employs a line-diffuser to destratify the water column, actively mixing the surface waters (Gantzer Water Resources, 2012). The oxygenation system installation at Falling Creek was a collaborative project between the Western Virginia Water Authority, Mobley Engineering, Gantzer Water Resources, and Virginia Polytechnic Institute and State University. It was the first successful deployment of a hypolimnetic aeration system into a shallow reservoir.
P release linked to anoxia

In a 2013 preliminary study of the effects of oxygenation on water column chemistry, Virginia Tech scientists observed low dissolved oxygen (DO) levels, and elevated total P, total Fe, and total Mn in the water column before and after the oxygenation system was active. It was found that, when the system was off (anoxia), P and Fe concentrations increased in the water column near the sediment-water interface. An increase in Anabaena (a toxin-producing cyanobacterium) biomass was observed shortly after the release of P and Fe (Carey, 2014, unpublished).

Figure 1.3
Clockwise From Top Left: Side Stream Bubble Plume, Installing The Line-Diffuser, Compressor Station, The Full SSS System
(Mobley Engineering, 2012)

Figure 1.4 Depth Profiles of A) Dissolved Oxygen, B) Total Fe, C) Total P, And D) Total Mn In Falling Creek Reservoir In Summer 2013 When Oxygenation Was ON And OFF. Color Refers To The Concentration Of Each Species. (C. Carey, 2014)
II. Methods

To collect sediment cores, a core sampler suspended from a cable was deployed from a boat into the water column of Falling Creek reservoir. A core catcher is fitted at the bottom of the sampler to hold the sediment in place within the tube (Rickly Hydrological Company, 2009).

Figure 2.1 Eggshell Core Catcher
(Rickly Hydrological Company, 2009).

Cores were collected for this study on two dates: May 28, 2014 (oxic conditions) and June 23, 2014 (anoxic conditions). Figure 2.2 shows the general vicinity of core collection.

Figure 2.2 Core collection Location, Falling Creek Reservoir
(Z. Munger, July 14, 2014)
Oxic core collection

Five cores were collected on May 28, 2014 when the oxygenation system at Falling Creek reservoir was operational. After transporting the cores from Falling Creek reservoir to the laboratory, they were labeled sliced in 1.27 cm intervals. Slices were stored in individual plastic bags at 4 °C. Cores T4 and T5 were selected for P-fractionation due to their deep depths and similar sediment consistency and water content (Figure 2.3). T5 slices were stored at 4 °C for 13 days before beginning P-fractionation on June 10, 2014. Slices from T4 were stored at 4 °C for 28 days before beginning P-fractionation. Storing samples at 4 °C prevents release of organic P and fractional composition changes (Psenner et al., 1988).

Anoxic core collection

Three cores were collected on June 23, 2014 when the oxygenation system at Falling Creek Reservoir was off. In the laboratory, the cores were sliced in 1.27 cm intervals. Each slice was then stored in individual plastic bags at 4 °C. Core T1 was chosen for P-fractionation due to its depth (Table 2). T1 slices were stored for 7 days at 4 °C before beginning the extraction procedure.

Details of the cores analyzed for this study are shown in Table 2.

<table>
<thead>
<tr>
<th>Core Label</th>
<th>Date Collected</th>
<th>Oxygenation System</th>
<th>Sediment Core Depth (cm)</th>
<th>Deepest Sampled Depth (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T4 528</td>
<td>5/28/14</td>
<td>On</td>
<td>11.43</td>
<td>11.43</td>
</tr>
<tr>
<td>T5 528</td>
<td>5/28/14</td>
<td>On</td>
<td>15.24</td>
<td>12.7</td>
</tr>
<tr>
<td>T1 623</td>
<td>6/23/14</td>
<td>Off</td>
<td>11.43</td>
<td>11.43</td>
</tr>
</tbody>
</table>

P-fractionation

Fractions of P were determined by a sequential extraction scheme modeled after Rydin, 2000 (full procedure in appendix A). The sequential extraction of P characterizes fractions of P with varying degrees of mobility by using different solvents and digestion techniques in each step. Each of the solvents was prepared following the solution preparation procedures in appendix B. Approximately 1 mL of wet sediment from each depth of each core was collected and weighed before beginning the extraction scheme. Duplicates of each depth were also extracted. Another 1 mL of wet sediment from each depth was weighed and oven-dried to find the dry weight.

In the first step, sediment is extracted with ammonium chloride (NH₄Cl). This step dissolves the labile P fraction and amounts for P that is immediately available, “loosely bound,” or labile (Psenner et al., 1988).

The next step in the sequence employs a bicarbonate dithionite solution (referred to as BD) to dissolve P that is adsorbed to Fe and manganese (Mn) compounds. The supernatant of step 2 is left to oxidize overnight at 25 °C, following Psenner et al., 1988.

Step 3 requires two substeps: First, NaOH is used to dissolve P that is exchangeable with OH⁻ and that which is adsorbed to metal oxides, mainly aluminum (Al) oxides such as Al₂O₃ (Psenner et al., 1988). P bound to Al is also referred to as reactive NaOH-extractable P. Step 3 also involves an acid (HCl) digestion with 5% potassium persulfate (K₂S₂O₈).
NaOH-extractable P and is used to calculate nonreactive NaOH-extractable P, as shown in Equation 1 (Psenner et al., 1988). Nonreactive NaOH-extractable P represents organic P (Rydin, 2000).

$$\text{NaOH-nrP} = \text{NaOH-Total P} - \text{NaOH-rP}$$

Equation 1 can also be expressed as Organic P = NaOH-Total P – Al-P.

The last extraction (step 4) in the scheme is performed with HCl and represents P bound to apatite and carbonates. Mobility of apatite P is not affected by redox, however this step can contain traces of redox-sensitive P bound to Fe or hydrolyzed organic P (Psenner et al., 1988). The dissolution of Fe oxides during this step results in formation of visible orange precipitates.

**Quality Assurance/Quality Control (QA/QC)**

To examine heterogeneity in the reservoir sediment, five cores were collected for both oxic and anoxic conditions. However, due to limited time, only two oxic cores and one anoxic core were extracted. Of the cores that were extracted, duplicates of each sediment extraction were conducted to examine the influence of sediment heterogeneity on results. To determine if extraction solutions contained P or caused interference with the analytical method, blank extractions (extractions without the sediment) were conducted. Replicate phosphate analyses were also conducted to ensure precision of the analytical method.

**Flow injection analysis and calculations**

Concentrations of phosphate (PO$_4$-P) from the extractions were determined colorimetrically with a Lachat QuikChem 8500 Flow Injection Analyzer (FIA). A 13 cm sample loop was used in order to analyze small volumes of supernatant. As a carrier solution, deionied water was used in the analysis; all supernatants except those in step 1 were diluted with deionized water. The supernatant from step 1 was comprised of NH$_4$Cl and any dissolved labile P. In the first trial, all supernatant from this step was below detection. After running this fraction again with NH$_4$Cl as the carrier solution, concentrations of PO$_4$-P were still below detection.

Several problems occurred during the first run of the FIA. First, there were visible precipitates in Step 3 (reactive) and Step 4 (Ca-P), which clogged the FIA tubes. Additional HCl was added to Step 4 solution, which effectively dissolved the precipitates, allowing for analysis. However, the precipitates in Step 3 could not be dissolved. Thus, phosphate concentrations from this step could not be determined.

Raw data from the FIA (included in appendix C) was corrected with equation 2 to account for wet weight and expressed as µg P/g dry weight. This correction follows Rydin, 2000.

$$
\text{P (µg/g dry weight)} = \frac{C \cdot V}{m \cdot dw}
$$

Where:
- $C$ = concentration of PO$_4$-P as given by the Lachat
- $V$ = volume of extraction agent (L)
- $m$ = original weight of wet sediment (g)
- $dw$ = dry weight content (g dry weight/g wet weight of sample that was oven-dried)

Corrected concentrations of P (µg/g dry weight) are shown in appendix C.
III. Results

Figure 3.1 shows how the different P fractions are distributed with depth for both the anoxic (T1) and oxic (T4, T5) cores. Loosely exchangeable P was below detection and is thus not shown on the plot. Fe-P is next the smallest fraction, Ca-P (apatite P) is the second largest fraction, and total NaOH-extractable P (the combined fraction of reactive and nonreactive NaOH-extractable P) is the largest fraction.

![Figure 3.1 P Fractionation With Depth On A Log Scale](image1.png)

![Figure 3.2 P Fractionation With Depth on A Linear Scale](image2.png)
Figure 3.2 shows the fractional concentrations of P on a linear scale. Concentrations of Fe-P, Ca-P, and total NaOH-extractable P declined with sediment depth in both oxic and anoxic cores (Figures 3.3, 3.4, 3.5). In redox-sensitive fractions (Fe-P and total NaOH-extractable P) concentrations of P are higher under oxic conditions.

**Iron bound P**

Under oxic conditions (May), Fe-P decreased in core T4 from 7.92 µg P/g DW at 0.635 cm (average of slice interval) to 2.51 µg P/g DW at 5.72 cm, then declined to 2.35 µg P/g DW at the deepest sampled depth of 10.8 cm (Figure 3.3). Fe-P decreased in core T5 (oxic) from 7.34 µg P/g DW at 0.635 cm to 2.29 µg P/g DW at 5.72 cm, then increased at the deepest sampled depth (11.43 cm) to 3.19 µg P/g DW. Oxic average Fe-P decreased from 7.63 µg P/g DW at 0.635 cm to 2.40 µg P/g DW at 5.72 cm, then increased to 2.77 µg P/g DW at the deepest average depth (11.1 cm). Both oxic cores decrease with similarity from the shallowest depth to the middle, however T4 continues to decrease in Fe-P while T5 increases slightly in the deepest sample.

Under anoxic conditions (June), Fe-P decreased from 4.78 µg P/g dry weight (DW) at 0.635 cm to 2.09 µg P/g DW at 5.72 cm, then decreased to 2.02 µg P/g DW at 10.8 cm. In the shallowest sample (0.635 cm), the oxic sediment (on average) contained 37% more Fe-P than the anoxic sediment.

**Total NaOH-extractable P (organic P + aluminum bound P)**

Under oxic conditions (May), organic P + Al-P decreased in core T4 from 484 µg P/g DW at 0.635 cm (average of slice interval) to 274 µg P/g DW at 5.72 cm, then declined to 168 µg P/g DW at the deepest sampled depth of 10.8 cm. Organic P + Al-P decreased in core T5 (oxic) from 296 µg P/g DW at 0.635 cm to 152 µg P/g DW at 5.72 cm, and continued to decrease to 128 µg P/g DW at the deepest sampled depth (11.43 cm). Oxic average organic P + Al-P decreased from 390 µg P/g DW at 0.635 cm to 213 µg P/g DW at 5.72 cm, then decreased to 148 µg P/g DW at the deepest average depth (11.1 cm).

Under anoxic conditions (June), organic P + Al-P decreased from 235 µg P/g dry weight (DW) at 0.635 cm to 122 µg P/g DW at 5.72 cm, then decreased to 48 µg P/g DW at 10.8 cm. At 0.635 cm, the oxic sediment (on average) contained 40% more organic P + Al-P than the anoxic sediment.
IV. Discussion

The purpose of this study was to understand phosphorus (P) mobility under different water column redox conditions in Falling Creek Reservoir (FCR), which is periodically oxygenated. This study advanced that understanding by measuring concentrations of P in sediment core samples from various depths (between 0 and 12 cm). We found that redox sensitive fractions showed a higher degree of mobility into the water column under reduced (anoxic) conditions (Figures 3.3, 3.4). Some forms of P, particularly Fe-P and organic P, are more easily mobile into the water column than others.

In 2013, scientists conducted a preliminary study at FCR in which they measured dissolved oxygen (DO) and total P within the water column, finding that when the oxygenation system was on, lower concentrations of total P were found near the sediment water interface than when the oxygenation system was turned off. An increase in total P in the water during anoxia indicates that P was being released from the sediment (Carey, 2014, Unpublished). In this 2013 study, Carey also observed an increase in toxic cyanobacteria biomass shortly after the increase in total P (in the water column) was recorded.

While the 2013 study measured levels of total P in the water and the current study measured concentrations of sediment P fractions, the studies are mutually supportive and hypothetically consistent with respect to the influence of DO levels in the water. The current study extended previous knowledge by examining the sediment profile and better understanding the varying degrees of mobility of various P fractions; i.e., how various P fractions are released into the water column under different redox conditions. Knowing the concentrations of each P fraction offers a better overall view of the sediment profile in FCR.

While this study afforded unproblematic collection of sediment samples, it was limited by the flow injection analytical (FIA) method in that some fractions, particularly Al-P, contained solid precipitate that clogged the instrument. Thus, the concentrations for Al-P were not analyzed. Additionally, one fraction, labile (loosely adsorbed) P, was below detection using FIA, which may have confounded the results.

A number of research questions remain. How would anthropogenic nutrient (P) loading affect internal P levels? Better understanding this potential relationship can protect the drinking water supply against heavier land use (and potential run off) in the future that may increase external P loading.

In addition, finding a method for dissolving the particulate in sediment samples for accurate testing of Al-P is recommended for future studies to ensure accurate understanding of P mobility. Further
labile P testing is recommended, as well, with a more suitable standard operating procedure or a more sensitive instrument.

Critic of this study may assert that oxygen may not be the only control over phosphorous levels. Sediment retention capacity and other factors may influence P levels, and these factors were not in the scope of this study. Thus, a more expansive examination of the sediment profile is warranted to respond to such criticisms.

This study’s findings lead to the policy suggestion that the Western Virginia Water Authority (WVWA) develop systems for continuous monitoring of dissolved oxygen (a proxy measure that covaries with P levels) which should trigger the operation of the oxygenation system. The objective is to control dangerous P levels by modulating oxygen levels in the water.

V. Acknowledgements

I thank Dr. Emil Rydin, Uppsala University, Uppsula, Sweden, who helped to develop the P-fractionation procedure on reservoir sediment with Dr. Madeleine Schreiber. Dr. Schreiber has provided invaluable resources and guidance during this project. Dr. Cayelan Carey made possible the communication with Dr. Rydin and has also pushed my conceptual envelope; Carey communicates clearly how P fits into the big picture of reservoir health. I would like to thank Zack Munger, who seems to have a solution for any problem. Bobbie Niederlehner is an extraordinary lab technician, fluent in analytical chemistry, to whom I express gratitude for the quality of my results.

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References


Google Maps. (2014). [Falling Creek reservoir and Beaverdam Reservoir, Bedford County, Virginia] [Satellite map]. Retrieved from [https://www.google.com/maps/place/Falling+Creek+Reservoir/@37.309745,-79.831653,2072m/data=!3m1!1e3!4m2!3m1!1s0x884d1149b63c9e13:0xdf481d5f555bdf0](https://www.google.com/maps/place/Falling+Creek+Reservoir/@37.309745,-79.831653,2072m/data=!3m1!1e3!4m2!3m1!1s0x884d1149b63c9e13:0xdf481d5f555bdf0)


Appendix A

Written by M. Schreiber
Modified from Psenner et al. 1988, Rydin 2000, Rydin notes, Rydin email communication
All extractions done at 25 °C (room temperature) unless otherwise noted

Supplies
- Solutions (see Appendix B)
  - 15 ml centrifuge tubes (5 per extraction)
  - 50 ml centrifuge tubes (6 per extraction)
  - 0.7 um GF/F filters (4 per extraction)
  - HCl-washed filter holders (1 per extraction, rinse in between steps with HCl and DI)
- 10 ml syringes (4 per extraction) & 60 ml syringes (1 per extraction)
- Plastic scoops for sediment (1 ml)

Equipment
- Shaker table or tube rotator
- Centrifuge (IEC Clinical – set to #6 for ~3000 rpm)
- Microwave digester

Day 1 (start in morning)
On balance, tare scoop
Measure ~1 ml fresh (or refrigerated) wet sediment, weigh, record mass
Put sediment into 50 ml centrifuge tube
Also scoop for dry weight:
  - Scoop ~1 ml wet sediment into clean aluminum tray
  - Record wet weight and let dry in oven overnight
  - Record dry weight for calculations after Lachat analysis

Step 1: Labile
Add 25 ml 1 M NH4Cl to tube, rinse off scoop in solution to get all sediment in tube.
Mix on shaker table for 2 hours
Centrifuge at 3000 rpm for 10 min
Remove supernatant (should be able to pour off), and store in clean 50 ml centrifuge tube
Repeat step:
Add 25 ml 1 M NH4Cl, stir up a bit, mix for 2 hours on shaker table, centrifuge
Remove supernatant, add to supernatant tube (should now have 50 ml)
Take 10 ml, filter, put filtrate in 15 ml tube
Freeze sample for measurement of DRP (Label: 1R; fridge ok if only for a few days)

Step 2: Adsorbed to Fe/Mn (BD-P); BD = bicarbonate dithionite solution
To pellet leftover from Step 1, add 25 ml BD solution, mix on shaker table for 1 hour
Centrifuge at 3000 rpm for 10 min
Remove supernatant, store in clean 50 ml centrifuge tube
Repeat step:
Add another 25 ml BD, stir up a bit, mix for 1 hour, centrifuge
Remove supernatant, add to supernatant tube (now have 50 ml), filter
  - Take 50 ml, filter 40 ml into new 50 ml tube, freeze samples for measurement of TDP (Label: 2T)
  - Filter ~5 ml supernatant into clean beaker. Pipette 2 ml into 15 ml tube, add 8 ml DI, let 10 ml diluted sample stand overnight in open bottle to oxidize
Freeze 10 ml sample for measurement of DRP (Label: 2R; fridge ok if for a few days)

Step 3: Exchangeable with OH (mainly Al oxides) and organic P
To pellet leftover from Step 2, add 25 ml of 0.1 M NaOH in 50 ml centrifuge tube, mix on shaker table for 18 hours (overnight)

Day 2 – continue on Step 3 (morning: remember to freeze oxidized samples from Day 1, step 2)
Centrifuge at 3000 rpm for 10 min
Take out supernatant, store in clean 50 ml centrifuge tube
KEEP PELLET FOR STEP 4
Take 2 ml of supernatant, put in 15 ml cent tube, add 0.4 ml of 0.5 M HCl
Add 7.6 ml DI water to make 10 ml total volume
Filter the 10 ml, freeze (or fridge) for measurement of DRP (Label: 3R)
  - (This is NaOH-rP)
Take another 5ml of supernatant, put in microwave vessel, add 1 ml of 0.5 M HCl
Add 5 ml oxidizing agent (5% K$_2$S$_2$O$_8$)
Microwave (CEM MARSXpress) the 11 ml solution at 120 °C for 1 hour
Let cool, filter ~5 ml digestate into a clean beaker
Pipette 2 ml filtered sample, dilute with 8 ml DI in 15 ml centrifuge tube
Freeze (or fridge) for measurement of DRP (Label: 3T)
(This is NaOH-totalP)
[NaOH-NRP = NaOH-total P - NaOH-rP]

*Step 4: Bound to Ca (Ca-P)*
Using pellet from Step 3, add 25 ml 0.5 M HCl, mix on shaker table overnight

*Day 3 – continue on Step 4*
Centrifuge at 3000 rpm for 10 min (*longer if still cloudy*)
Take out supernatant, store in clean 50 ml centrifuge tube
Filter ~5 ml supernatant into a clean beaker. Pipette 2ml filtered sample into 15 ml centrifuge tube, add 0.5 ml 2 M NaOH to neutralize (*color may change from clear, pale yellow to dark brown—Fe?*)
Add 7.5 ml DI water (*Orange-brown Fe ppt may become suspended in solution after dilution*)
Freeze the 10 ml for measurement of DRP (Label: 4R)
Appendix B

1 M NH₄Cl
  Dissolve 53.5 g NH₄Cl p.a. in 800 ml DI in 1 L volumetric flask
  Put on stir plate with stir bar
  Measure pH on a subsample
  Correct pH of solution to 7 using 0.1 M NaOH

0.1 M NaOH
  Dissolve 4 g NaOH in DI, dilute to 1000 ml in 1 L volumetric flask

2 M NaOH
  Dissolve 40 g NaOH in DI, dilute to 500 ml in 500 mL volumetric flask

0.5 M HCl
  Mix 40 ml concentrated HCl with DI, dilute to 1 L in 1 L volumetric flask

Bicarbonate dithionite solution (0.11 M Na₂S₂O₄/0.11 M NaHCO₃)
  Dissolve 19.14 g Na₂S₂O₄ in ~500 ml DI in 1 L volumetric flask
  Put on stir plate with stir bar
  Add 9.24 g NaHCO₃, continue to dissolve
  Bring to volume with DI, store in airtight bottle to prevent oxidation

5% K₂S₂O₈ (solution comes prepared from Fisher)
  Ricca Chemical 6450-32
### Appendix C

Corrected µg P/g dry weight

<table>
<thead>
<tr>
<th>Depth Avg. (cm)</th>
<th>Fe-P (2R)</th>
<th>NaOH-totalP (3T)</th>
<th>Ca-P (4R)</th>
<th>Fe-P (2R)</th>
<th>NaOH-totalP (3T)</th>
<th>Ca-P (4R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T101 (anoxic)</td>
<td>4.78</td>
<td>234.665</td>
<td>21.124</td>
<td>44.4</td>
<td>122.329</td>
<td>12.221</td>
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<tr>
<td>T105 (anoxic)</td>
<td>2.086</td>
<td>47.52</td>
<td>7.646</td>
<td>5.715</td>
<td>167.8423</td>
<td>9.676</td>
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<tr>
<td>T109 (anoxic)</td>
<td>2.016</td>
<td>47.52</td>
<td>7.646</td>
<td>5.715</td>
<td>167.8423</td>
<td>9.676</td>
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<tr>
<td>T401 (oxic)</td>
<td>7.923</td>
<td>484.0051</td>
<td>20.354</td>
<td>0.635</td>
<td>71.8</td>
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<td>T405 (oxic)</td>
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<td>9.676</td>
<td>5.715</td>
<td>53.8</td>
<td>1160</td>
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<tr>
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Raw µg PO₄-P/L

<table>
<thead>
<tr>
<th>Depth Avg. (cm)</th>
<th>Fe-P (2R)</th>
<th>NaOH-totalP (3T)</th>
<th>Ca-P (4R)</th>
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<th>NaOH-totalP (3T)</th>
<th>Ca-P (4R)</th>
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<tr>
<td>T101 (anoxic)</td>
<td>71.8</td>
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<td>199</td>
<td>0.635</td>
<td>71.8</td>
<td>1160</td>
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<td>0.635</td>
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<td>not analyzed</td>
<td>167</td>
<td>10.795</td>
<td>41</td>
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</tr>
<tr>
<td>T401 (oxic)</td>
<td>53.8</td>
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<td>101</td>
<td>0.635</td>
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<td>T401 (oxic)</td>
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<td>T409 (oxic)</td>
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<td>1160</td>
<td>189</td>
<td>0.635</td>
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<td>1070</td>
<td>152</td>
<td>0.635</td>
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<td>1070</td>
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<tr>
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Benefits of Greywater Systems in Third World Countries: Special Focus on India

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Abstract

The lack of access to clean drinking water is a major problem; there are almost a billion people who currently don't have access to this vital resource. It is extremely important to find ways to provide clean drinking water to people around the world. One of the best ways to do so would be to use the water that is already available more efficiently. Greywater filtration systems are an efficient way to reduce the amount of potable water needed for various uses. This increase in efficiency could lead to more clean water being available to more people. The purpose of this research is to determine the possible costs and benefits of installing greywater systems in the third world countries of Africa and Asia, while using India as an example.

Keywords: Greywater Systems, Sustainability, Reuse, Third World, Water Scarcity

I. Introduction

Lack of Clean Drinking Water

Clean drinking water is one of the most important factors in regards to quality of life, and according to (WHO/UNICEF, 2014) there are over 700 million people that lack access to clean drinking water. Access to clean drinking water allows people the opportunity spend time pursuing other aspects of life, such as education and employment, which are necessary in order to work toward a higher standard of living. Little to no access to clean drinking water means that individuals must spend a large portion of their time trying to find or gain access to this extremely vital resource. The lack of clean drinking water also causes issues when people are forced to resort to unsafe sources of water. A report published in 2009 by (UNICEF/WHO, 2009) estimates that 1.5 million children under the age of 5 die every day from diarrheal diseases which are attributed to the lack of clean drinking water, sanitation, and hygiene. That means that approximately 4,110 children die every day due to diarrheal diseases, which in the developed world would be both easily curable and preventable.

The amount of time lost through travelling to locate and collect clean drinking water, transporting it back to where it is to be used, and the time that people lose from illness due to unclean water, makes it extremely difficult for individuals to spend the time needed to improve their quality of life or that of their family. This is a tragedy which could potentially be rectified by making a few changes in the way people use water.

Developed vs. Undeveloped

The availability of clean drinking water and the reality of water usage and treatment in third world countries, such as India, is astounding when compared to developed countries such as the U.S.A. A report published in 2005 by the USGS (USGS, 2005) states that the national average for domestic water use in the U.S. is 99 gallons per day, whereas in India the average use according to (Shaban & Sharma, 2007) is 24.3 gallons per day. That is a huge difference in the amount of water used per person.
between the two countries. However, this is not the only large discrepancy between the two nations with regards to water. A comparison of water storage capacity was published in 2006, which stated that “India can still store only relatively small quantities of its fickle rainfall. Whereas arid rich countries (such as the United States and Australia) have built over 5000 cubic meters of water storage per capita…India’s dams can store only 200 cubic meters per person” (Briscoe & Malik, 2006). This lack of storage capacity coupled with the seasonality of India’s rainfall, with “50 percent of precipitation falling in just 15 days and over 90 percent of river flows in just 4 months” (Briscoe & Malik, 2006) will lead to serious challenges in the future. Without extreme measures of capture and storage, the majority of the water will be lost. The low storage capacity, in conjunction with climate change due to changes in temperature, rainfall distribution, and the period of time that rainfall occurs, is contributing to the country’s growing water crisis. Together these issues make it extremely difficult for India to provide water to its vast and growing population. To make matters worse, India has a population of approximately 1.21 billion with 377 million people living in urban areas. The urban population alone is larger than that of the entire population of the U.S. (a population of 317 million), and yet according to (International Institute for Population Sciences, 2007) only 50.7% of the urban population has water piped into their dwelling or on the premises.

**Reality of Water in India**

Statistics alone do not convey the gravity of the situation and the crisis individuals face every day when trying to obtain clean drinking water. Even with a connection to a water system on the premises there is no guarantee that the water will actually be available. In many cities water is only available for 4 hours per day, or in some cases it might only be available for as little as 30 minutes per day. This has resulted in many wealthy Indians installing water storage tanks in their homes. When water becomes available, they divert water into storage, so that it will be available for later use. However, this is not an option for the majority of the population who must rely on the limited water when it is accessible. In addition, those individuals who are not fortunate enough to have a connection in their home or on the premises, must travel to public water stands or wells to get their drinking water. The (International Institute for Population Sciences, 2007) indicates that 7% of the urban population have to travel more than 30 minutes round trip, per day, to obtain water. That means that over 26 million people have to travel more than half an hour every day to get their drinking water. However, not only is availability a problem, but also water quality. In many cases, those who do not have an official connection to the water system will create their own connections, which leads to contamination and degradation of quality, and damages the infrastructure.

Having water pumped into a home or having it available at a public stand or well is not always sufficient to provide enough water to the local Indian population. In many areas water must be delivered in tanker trucks, requiring people to stand in line for a long time with whatever storage containers they have available to them. In some cases they may be required to bring their own hoses as well as storage containers, so that they can siphon the water from the tanker trucks themselves. It is a first-come, first-serve system, and if the tanker truck runs out of water before it reaches the end of the line, than those individuals at the end must go without water until the next truck arrives, which most likely isn’t until the next day.

Indians who must cope with the lack of clean drinking water every day are those who typically live in the slums of urban India. Data from the Indian census conducted in 2011 (Primary Census Abstract Data for Slum, 2011) reported that a startling number of Indian citizens live in slums, 17.2% of the population to be exact; which means that 65 million Indians live in slums in urban India. These citizens also make up the majority of those who must travel long distances to obtain clean drinking water or stand in long lines waiting on delivery trucks to bring in water. These people are also the ones most likely to use whatever water is available around them, despite the poor quality, just so that they can survive another day.

For almost a billion people, the lack of clean drinking water is a scourge that must be dealt with the utmost haste and conviction because the current status and the results of inadequate action are
appalling. Based on data from (UNICEF/WHO, 2009) of the 1.5 million children under the age of 5 that die from diarrheal related diseases 390,000 of those deaths occur in India, and 343,000 of those are due to lack of clean drinking water, hygiene, and sanitation. These are deaths that could be easily prevented with access to clean water and proper sanitation.

In contrast, some of the benefits of having access to clean water are quite obvious, such as: less disease, and fewer needless deaths; however there are many other benefits which result from access to clean drinking water, such as an increase in education or employment. The lack of clean drinking water can prevent people from obtaining an education or from obtaining employment, simply due to the fact that so much time is spent trying to secure this vital resource; or due to sickness from water related diseases. “An estimated 73 million working days are lost due to water related diseases” (UNICEF, FAO, and SaciWaters, 2013). Access to clean drinking water allows individuals the opportunity to improve their quality of life. An education makes it possible for individuals to find jobs, so they can provide for themselves and their families, thereby increasing their standard of living. An increase in individuals able to pursue an education or gain employment would also boost the overall productivity of India, resulting in a positive cycle with India having more revenue to increase the standard of living for many Indians, as well as funds to build or update current infrastructure, or to fund other public environmental projects.

Ways to Provide Water

There are several methods used to supply water to a large population or increasing population. Tapping new sources of water can be an effective method of supplying water to the population, such as boring into aquifers to pump groundwater, installing dams in rivers to create reservoirs that can provide water, or it might be as simple as running pipes into an existing lake. Installing new pipes or infrastructure, or maintenance of a system already in place, can provide more water due to a decrease in inefficiency. Data from (McKenzie & Ray, 2009) indicates that as much as 50% of potable water in India can be lost before it ever reaches its destination, with the norm being between 30% and 40%. Therefore an extremely large amount of water could be gained simply by increasing the efficiency of the system already in place. However, installing new infrastructure or repairing the existing infrastructure would be extremely expensive.

Another frequently proposed method for increasing water accessibility is desalination. Desalination systems are a popular method used to remove the salt from seawater, turning it into fresh water available for consumption. Desalination however, is extremely energy intensive and can be expensive. Also because most sources of energy produce large amounts of carbon gas, desalination would most likely make environmental issues worse by increasing greenhouse gases.

Rainwater harvesting is sometimes used as a means to supplement existing water supplies. Rainwater harvesting allows for the collection and storage of precipitation so that it can be repurposed for uses like irrigation or aquifer recharge. Rainwater harvesting is cheap and requires minimal skills for installation. However, its uses are limited without a system to clean the rainwater of contaminates.

Recycling water is another method of supplying water to more people through an increase in efficiency. A specific example of a recycling water method is through the use of greywater systems, which have the potential to decrease the amount of clean water used, thereby increasing the amount of water available for others. It is greywater systems which have the capability to provide water to more people cheaply and efficiently.

I. Research Methods

A literature review was conducted in order to determine the different types of greywater systems, the efficiency of greywater systems in reducing the amount of clean water initially used, and the costs and benefits of these systems in a third world country such as India.
II. Results and Discussion

Greywater Systems

Greywater systems are a way of recycling wastewater, in this case grey water. Greywater is wastewater that comes from within a home from: kitchen or bathroom sinks, laundry, bathing or showers. Toilets are not included because the water from flushing is considered black water and is usually contaminated with bacteria from human waste. Greywater systems recycle grey water by removing coarse materials, lowering turbidity, and destroying harmful bacteria; thereby making the water reusable for purposes such as toilet flushing, irrigation, groundwater recharge, and washing cars.

The type of greywater system to be used depends both upon the intended use of the recycled water generated by the system, and the incoming greywater. A simple system might be used if the only purpose is to supply water to be used for flushing a toilet; whereas a more complex system might be used if supplying water to both the toilet and an irrigation system for a garden. Greywater from a kitchen sink or a dishwasher might not be used depending on the recycled water use due to the higher concentrations of bacteria and organic matter (Allen, Christian-Smith, & Palaniappan, 2010).

Types of Greywater Systems

According to (Allen et al., 2010) there are three main types of greywater systems. These include: diversion systems, physical/chemical greywater treatment systems, and biological greywater systems. A diversion system does not store water but might, depending on the use, send it through a simple treatment system before it can be used immediately. A physical/chemical systems allow greywater to be stored where it is physically and chemically treated before it is reused. Finally a biological system uses biological processes, such as helpful bacteria, to treat water before it is used again.

One example of a simple diversion system would be to take water directly from a household sink and divert it into a small filtration system which would remove coarse materials before it is sent into a toilet flushing tank where it can be used in place of clean water. Figure 1 and Figure 2 are both examples of greywater diversion systems.

![Figure 1. A Toilet That Uses Greywater From The Sink That Sits On Top Of The Flushing Tank Made By Caroma](http://www.caromausa.com/database/images/profile_smart_eh_elg_1.jpg)
Physical/Chemical greywater treatment systems can store water for long periods of time. This water has to be treated due to stagnation of the water, which allows for bacteria to grow. These systems filter the grey water coming into the system to remove particulate matter and use chemicals to kill harmful bacteria within the water. These systems are useful when dealing with larger amounts of grey water that might accrue over time. A system of this nature might be used in larger residential buildings that house a large number people. Figure 3 is an example of a physical greywater system.
Biological greywater systems use aerobic activity to treat water. There are three types of biological greywater treatment systems according to (Santasmasas, Rovira, Clarens, & Valderrama, 2013)). These include Wetlands, membrane bioreactors, and rotating biological contractor. An example of a biological treatment system might look like Figure 4 below, which is an example of a membrane bioreactor.
Another example of a biological greywater system is a slow sand filter, which contains a biolayer within the top few millimeters of the filter. A thick sand layer that sits atop two different gravel layers of various diameters as shown in Figure 5. This system requires an almost constant infusion of water to support the biological activity within the sand.

![Figure 5. An Example Of A Biosand Filter, Which Is A Type Of Slow Sand Filter.](http://www.indiawaterportal.org/sites/indiawaterportal.org/files/image.png)

A Case Study

As mentioned earlier the type of system used depends on the intended scale and use of the treated greywater. In Nagpur, India a greywater filtration system was installed at NEERI Colony in a study to determine the effectiveness of greywater systems in conserving clean water (Mandal et al., 2011). The system that was installed was designed for a family of 5 and only used grey water from the bath/showers, close washing and sinks. The system was capable of reducing clean water usage by approximately 48% if treated greywater was used for irrigation, gardening, and toilet flushing.
The study calculated that the greywater system could be scaled to treat greywater for all 800 of the residences at NEERI Colony at an initial construction cost of $10,000, and an annual savings of $6230 based upon the amount of clean water saved. As stated by the researchers, a system of this nature would pay for itself in approximately 1.6 years.
Benefits

The benefits of installing greywater systems could be quite substantial based on the amount of clean water that could be saved due to the increase in efficiency from greywater systems.

<table>
<thead>
<tr>
<th>Activity</th>
<th>All 7 cities</th>
<th>Delhi</th>
<th>Mumbai</th>
<th>Kolkata</th>
<th>Hyderabad</th>
<th>Kanpur</th>
<th>Ahmedabad</th>
<th>Madurai</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bathing</td>
<td>28.2</td>
<td>31.7</td>
<td>23.7</td>
<td>37.1</td>
<td>25.6</td>
<td>29.1</td>
<td>22.8</td>
<td>26.6</td>
</tr>
<tr>
<td>Washing clothes</td>
<td>18.6</td>
<td>14.2</td>
<td>24.3</td>
<td>14.0</td>
<td>20.9</td>
<td>16.3</td>
<td>21.4</td>
<td>18.9</td>
</tr>
<tr>
<td>Drinking</td>
<td>4.2</td>
<td>5.0</td>
<td>4.2</td>
<td>2.6</td>
<td>4.3</td>
<td>3.8</td>
<td>4.9</td>
<td>4.9</td>
</tr>
<tr>
<td>Cooking</td>
<td>3.0</td>
<td>3.7</td>
<td>1.7</td>
<td>2.3</td>
<td>3.1</td>
<td>2.2</td>
<td>3.3</td>
<td>4.2</td>
</tr>
<tr>
<td>Toilets</td>
<td>20.0</td>
<td>16.5</td>
<td>21.6</td>
<td>15.9</td>
<td>24.1</td>
<td>20.1</td>
<td>19.1</td>
<td>25.7</td>
</tr>
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<td>Cleaning house</td>
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<td>7.0</td>
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<td>5.7</td>
<td>12.4</td>
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<tr>
<td>Washing utensils</td>
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<td>17.4</td>
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<td>16.5</td>
<td>15.4</td>
<td>15.2</td>
<td>16.1</td>
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<tr>
<td>Others</td>
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<td>0.5</td>
<td>0.3</td>
<td>2.0</td>
<td>0.9</td>
<td>0.7</td>
<td>1.7</td>
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<tr>
<td>Total</td>
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<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
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</table>

Figure 8. This Table Shows The Distribution Of Water Usage In A Household By % Of Total Consumption Per Day.

(Shaban et al., 2008)

<table>
<thead>
<tr>
<th>Cities</th>
<th>Per Household</th>
<th>Per Capita</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Std. Deviation</td>
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<tr>
<td>Delhi</td>
<td>377.7</td>
<td>256.8</td>
</tr>
<tr>
<td>Mumbai</td>
<td>406.8</td>
<td>158.6</td>
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<tr>
<td>Kolkata</td>
<td>445.2</td>
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<tr>
<td>Hyderabad</td>
<td>391.8</td>
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<td>Kanpur</td>
<td>383.7</td>
<td>286.2</td>
</tr>
<tr>
<td>Ahmedabad</td>
<td>410.9</td>
<td>224.1</td>
</tr>
<tr>
<td>Madurai</td>
<td>363.1</td>
<td>182.1</td>
</tr>
<tr>
<td>Total</td>
<td>398.3</td>
<td>220.20</td>
</tr>
</tbody>
</table>

Figure 9. This Table Provides The Average Household And Per Capita Water Usage For 7 Cities In India

(Shaban et al., 2008)

A study conducted in 2008 (Shaban, Islamia, & Delhi, 2008) revealed that the combined average water usage per capita for the following 7 cities, Delhi, Mumbai, Kolkata, Hyderabad, Kanpur, Ahmedabad, and Madurai to be 92 liters per day. Based on the average water usage per capita of 92 liters per day (lpd) and an urban population of 377 million, 50.7% of which have water connections in their home and the data contained within the table above it is possible to estimate the amount of water that could be saved by implementing greywater systems on a large scale in urban India. 191 million urban Indians have access to water in their home or on the premises. Using the % of clean water used for toilet flushing and the average per capita water usage of 92 lpd, toilets account for 18.4 liters. If simple greywater systems that only diverted greywater into toilets were installed, a total of 3.5 billion liters of water could be saved daily. This 3.5 billion liters of water could supply another 38.2 million people with water every day. This 38.2 million people represents more than half of India’s slum population. What if the minimum daily water requirements of 50 liters per day, as stated by Peter Gleick in (Gleick, 1996) was used, then that represents 70.2 million people that could have access to clean water, which is more than the current 65 million people living in the slums of urban India.

Installing greywater systems for the 50.7% of Indians that have water connections on the premises is unrealistic. To get a better understanding of the amount of water that could be saved on a smaller scale, calculations were done to determine the amount of water that could be saved in household with 5 members, a neighborhood of 3000, and finally a city with a population of 100,000. A household of
5 would use approximately 460 lpd, just using the percentage for toilet flushing, greywater systems could reduce clean water usage by 92 lpd. This is enough water to supply an entire day’s worth of water to another person. A neighborhood of 3000 people uses 276,000 lpd. With greywater systems installed to supply water to toilets, a savings of 55,200 lpd could be achieved, which is enough water for 600 people. Finally a city of 100,000 uses 9,200,000 lpd. The amount of water saved with greywater systems is approximately 1.8 million lpd, which is enough water to supply an additional 20,000 people.

The amount of money that could be saved depends on the amount of reduction in clean water usage and the rates that are charged for water. Water rates vary widely by region. The price of water supplied by the Nagpur Municipal Corporation to NEERI Colony in 2010 was 12 Indian Rupees (Rs) per 1000 liters (Mandal et al., 2011), where residential users in Mumbai pay Rs 4.5 (Pay 8 percent more for water starting July). An individual in Mumbai could expect to reduce water consumption by 20% using a greywater system to supply water to the toilet for flushing. This would result in the reduction of clean water usage by 6716 liters, leading to a savings of Rs 30.15. A person in NEERI Colony who uses 165 liters per day could save at a minimum 15% of water consumption due to toilet flushing which means they would use 24.75 liters less per day, resulting in 9033 liters per year in water reduction with a savings of Rs 108.

The benefits of installing greywater systems in third world countries are quite obvious after looking at the research. Greywater systems can increase how efficient water is used, thereby decreasing the amount of clean drinking water that is used. This decrease means that there is more clean water available to supply to those who are not currently served or who do not receive enough water. Increasing the availability and amount of clean water that people have access to can lead to less disease, hospitalizations, and deaths. Another advantage of clean water availability, is that individuals spend less time trying to obtain this precious resource, giving them more time for education and employment. Less money spent on clean water, through the efficient use of water, means financial resources can be invested back into their lives to help increase their standard of living. More efficient water use results in a healthier, more educated, and more productive population that can take advantages of opportunities that will continue to elevate their standard of living.

**Barriers**

The benefits of efficient water use are quite clear, but the question that seems most relevant is why aren’t these systems being utilized or why aren’t they more prevalent? There are several possible explanations. First is public awareness; the majority of the population may not know that these systems exist. This lack of knowledge could result in the lack of adoption of greywater systems. A second possible reason is a negative public perception of recycled water that is similar to the toilet to tap argument common in some areas in the U.S. Expense could be another reason for the lack of widespread adoption or knowledge of greywater systems, and there are a couple of aspects to this. Greywater systems can be a cost that many individuals or communities might not be able to afford. A second expense related reason could be due to how cheap water actually is in India. According to (Mathur & Thakur, 2003) “Water in most Indian cities and towns is underpriced”. Low prices may not provide incentive to invest money into a greywater system. Because the water is so cheap, individuals or communities may wonder why they should be bothered to spend money on improving the efficiency of their water usage.

Installation of greywater systems might prove to be another barrier to using greywater systems, an individual might be able to install a small system like a diversionary greywater system that takes water from the bathroom sink to the toilets flushing tank, but a more complicated system would probably require a professional to install. Installation of larger systems that might serve an entire residential building are more difficult to install in an existing structure, not to mention more expensive.

Finally, water policy in India might also be another reason that adoption of greywater systems has not been more successful. The national water policy in India states “Direct use of rainfall, desalination and avoidance of inadvertent evapo-transpiration are the new additional strategies for augmenting utilizable water resources” (NATIONAL WATER POLICY ( 2012 ), 11.4 2012). Rainfall is a positive step in the right direction, but greywater systems are not mentioned in the policy, only that “Recycle and reuse
of water…should be the norm…Recycle and reuse should also be incentivized through a properly planned
tariff system…reuse of urban effluents from kitchens and bathrooms…in flush toilets should be
encouraged” (NATIONAL WATER POLICY (2012), 2012). There is some hope however, Brihanmumbai
Municipal Corporation in Mumbai has, according to (Mhaske, 2010), since 2002 required all new
buildings to install rainwater harvesting and then in 2010 required all new residential and commercial
buildings to recycle greywater “for non-potable purposes”

III. Conclusion

The benefits of increased efficiency of water usage from greywater systems in third world
countries are quite considerable. Greywater systems have the ability to provide additional clean drinking
water to more people, resulting in a decrease in water-related diarrheal diseases and deaths. It would also
provide an increase in opportunities for education and employment, due to less time spent gathering water
and from getting sick from water related diseases. This would therefore lead to increases in productivity
and earnings to spend on other goods and services to potentially increase their standard of living. There
are some barriers and misconceptions which seem to be preventing widespread adoption of greywater
systems in third world countries, along with policies that don’t adequately promote the implementation of
these systems. Further research needs to be conducted in order to determine what can be done to
overcome these barriers so that greywater systems are implemented on a large scale as a means to provide
clean drinking water to those in need.

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Greywater Systems to Aid Sustainable Water Management. Oakland, CA.


due to greywater treatment and reuse in urban setting with specific context to developing countries.

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Hormones in the Stroubles Creek Watershed

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Abstract

The use of animal manure to fertilize soil has been a common practice, but its environmental impact has not been thoroughly questioned. Our study focuses on soil samples that were collected over the period of one year from animal manure-applied to a Virginia Tech field to determine the impacts of such a practice. Eleven hormones are suspected to be in the soils due to the application of manure including: Estrone, 17α-Estradiol, 17β-Estradiol, Estriol, Progesterone, Estrone-3-Sulfate, Estrone-3-Glucorinide, Estradiol-3-Sulfate, Estradiol-3-Glucorinide, 1,4-Androstadiene-3,17-dione, and 4-Androstene-3,17-dione. The effects of hormones on our environment can be detrimental to fishes including various health issues such as sex changes and birth defects. Also the overall health of the streams and waterways directly affects the health of the surrounding human population. It is thought that these hormones accumulate in depressions as they are being washed away from ridges and swales of the field. The field is also located directly along the side of Stroubles Creek in Blacksburg, Virginia; thereby possibly affecting the health of the nearby stream and the watershed. Our study determines the concentration of the hormones and where they are in relation to run off. High Pressure Solvent Extraction and Solid Phase Extraction were used for sample extraction and cleanup. High Performance Liquid Chromatography/Triple Quadrupole Mass Spectrometry was used for analysis of compounds of interest. Hormones were found to be traveling via runoff but too few samples were analyzed to provide statistical evidence in support thereof.

Keywords: Steroid hormones, Stroubles, manure, soil

I. Introduction

Stroubles Creek Background

The Stroubles Creek Watershed is a small sub-watershed in the New River Watershed located in southwest Virginia. The watershed is fed by small springs found throughout the town of Blacksburg. Stroubles Creek has alluvium-flood-plain deposits of stratified unconsolidated sand, silt, and clay with beds and lenses of pebbles and cobbles (StREAM Lab). The watershed is also undergoing many restoration projects to better its health. Restoration projects such as Adaptive Livestock Exclusion Strategies for Reducing Nutrient Loads and Stroubles Creek Restoration are in progress with local authorities to clean up the watershed (Center for Watershed Studies at Virginia Tech). Stroubles Creek connects to the New River in Virginia, which merges into Kanawha River, which then runs into the Ohio River, followed by the Mississippi; making the health of the stream imperative (Parece et al.). Additionally Stroubles creek has encountered pollution ever since Blacksburg has been populated; coal mining waste water pollution, and chemical and fuel spills have been some of the major cases for pollution, however, sediment runoff is the major source of pollution. (Stroubles Creek Steering Committee).

Our study focuses on the health of Stroubles Creek specifically tackling the problem of hormonal deposits from manure used as fertilizer. It has been found that hormones can cause reproductive problems in fish at very low amounts (US EPA). Our study focuses on a part of Stroubles Creek downstream from
the duck pond located just adjacent to a corn field receiving annual animal manure application. Dairy cow manure from the Virginia Tech Dairy and drystack compiled from all of the Virginia Tech livestock operations were applied to the field. The geography of the field is gradually sloping with ridges and swales running into Stroubles Creek. Figure 1 shows the field in relation to Stroubles Creek.

According to Young People’s Trust for the Environment, “Most fresh water pollution is caused by the addition of organic material which is mainly sewage but can be food waste or farm effluent.” Runoff from rainfall may cause farm wastes or effluent to make its way to a water source. Today there are regulations to protect our environment put into action by government agencies like the Environmental Protection Agency and state governments like the Virginia Department of Environmental Quality. However, runoff is not fully understood proposing that more scientific data from studies needs to be given to adopt changes to better the effects humans have on the environment.

**Objectives**

To understand the fate of hormones associated with animal manure applied to fields.

**Literature review**

The effects hormones have on wildlife.

The hormones investigated for this study are classified as steroid hormones. Steroid hormones are active biological compounds formed from cholesterol and share a common cyclopentan-o-perhydrophenanthrene ring. Each play important roles in mammals including: the maintenance of tissues from androgens; the maintenance of reproductive tissues, breasts, skin and brain from estrogens; and some are hormone regulators like progesterone, which specifically regulate estrogens. Natural forms of these hormones come from the adrenal cortex, testis, ovary, and placenta from mammals. Hormones that are of main concern to wildlife in our study, in particular, fishes, are 17β-Estradiol, Estrone, Estriol, Androgens, Progesterones and their conjugates (Desbrow et al.).
The effects hormones can have on fish populations are varied based on species. However, certain effects have been noticed including vitellogenesis and feminization of male fish. Vitellogenesis is a plasma vitellogenin induction process impacted by estrogens (Desbrow et al.). The process induces the production of a precursor protein responsible for the production of egg yolks (Tyler et al.). Vitellogenesis was also found to occur in male fathead minnows, specifically (Pimephales promelas) by exposing them to concentrations as low as 30ng/L of 17β estradiol for 21 days. It was also observed that when temporally exposed to the hormone male fathead minnows underwent vitellogen production (Panter et al., 2000).

Androgenic steroids have been supported to be steroidal in nature and are actively deconjugated by biological organisms such as E. coli. However, E. coli only deconjugates the glucuroinide conjugate (Gomes, Meredith, Snape, & Sephton). It can be speculated that if the correct microorganisms were present in the field they would aid in converting the glucuronide conjugates found in the manure into a biologically active form leading to fewer amounts of the glucuronide form and more unconjugated forms.

**Hormone Concentrations in Animal wastes**

Through various studies it is known that hormones are present in animal wastes. This section looks at the various types of wastes and shows what has been found with studies regarding specific types of animals found in various types of CAFOs.

**Poultry**

Estradiol and Testosterone are found in poultry litter at varying levels of concentration. Testosterone levels in poultry litter range from 133±12 ng/g in males and 133±13ng/g in female broiler chickens. Adult Roosters have 670±95 ng/g of testosterone in their litter and egg layers have 533±30 ng/g of estrogen in their litter. Testosterone levels in poultry litter that are allowed to ferment are slightly lower; however, when antibiotics are applied during incubation testosterone levels increase significantly from 96±4 ng/g to 578±80 ng/g (Shore et al. 1993).

**Cattle**

Cattle excrete steroidal hormones in varying degrees based on their age, sex, pregnancy status and what type of implant they have received also (Lange et al). Concentrations of steroidal hormones from castrated cattle are usually an average of 3 ng/g of estrogens and 30ng/g of androgens (Arts et.al.1991, Lange et al. 2002, Johnson et al 2006). Bulls usually range 3 times more in concentration levels of estrogens and androgens. In pregnant cattle their concentrations in what they excrete are 100 times more than males and non-pregnant females (Ying et al.), leading to concentrations of 240 ng/g estradiol possible in dairy cow waste (Hanselman et al.). Implanted cattle with trenbolone acetate and 17β-estradiol have increased amounts of hormones relative to non-implanted cattle which have 200% more androstenedione, 500% more 17β-estradiol, and 700% more estrone (Sellin et al.). Furthermore, 17α-estradiol is not studied as regularly as 17β-estradiol. It is known that cattle are also able to convert 17β-estradiol to 17α-estradiol before passing it (Rico); therefore, higher levels of 17α-estradiol may be likely when cattle are implanted with 17β-estradiol (Mansell p. 6). Roughly 90% of cattle are implanted with hormones to promote fast weight gain which makes the animal go to slaughter sooner promoting a more tender meat. Six steroidal hormones are used including estradiol, testosterone, progesterone, zenanol, melengesterol acetate, and trenbolone acetate. The later three are synthetically derived hormones, whereas the first three are naturally occurring. (Balter p. 1455). In general hormone concentrations have been reported by Lange et al. 2002 to be present in cattle in amounts of 329 mg of estrogens excreted per cow annually, 3800 mg of progesterones per cow excreted annually and 255 mg of androgens excreted per cow annually on average.

**Swine**

Swine produce varying degrees of hormonal levels based on their age, sex and pregnancy status as is commonly found in the above mentioned animals. Swine operations have their own terminology to describe at what level in production they are. Farrowing facilities are where swine are born and weaned by their mothers. Nurseries are where swine are kept for 40-70 days to mature and finishing facilities are where the swine reach a specific market weight (Fine et al. 2003, Lorenzen et al. 2004, Raman et al.)
According to Fine et al. study it was found in tested lagoons of waste storage for different types of swine (i.e. sex age and pregnancy status) that the different lagoons had maximum concentrations including: a finishing lagoon with 74.7 ug/l estrone found, a farrowing lagoon with a maximum concentration of 25.7 ug/l estrone found, and a nursery lagoon with 0.58ug/l of estrone found (Fine et al. 2003).

Concentrated Animal Feeding Operations (CAFOs) are a major source of manure. At Virginia tech the field is being fertilized with manure from its own operations including various animals. The concentrations of hormones all vary depending on the facility and the amount of types of animals present. Furthermore, the field being studied has been fertilized with drystack and dairy cow manure not being dispersed over a uniform area.

**Manure production in the United States**

Nationally as of 2002 there were 12,000 CAFOs in operation with each CAFO able to produce more than 1.6 million tons of manure annually (Report to Congressional Requesters). CAFOs, where a majority of cow manure comes form, are required to have management plans to lessen their impact on the environment. Current practices involve applying manure to fields as fertilizer, allow liquid wastes to infiltrate into soils, composting, and treating wastes in lagoons or wetlands (USDA). Typically a combination of the above mentioned plans are used (Combalbert et al.). These plans, however, are primarily focused on nutrients and pathogens and not hormones (US EPA 2000).

**Hormonal Characteristics**

Each hormone has its own characteristics and favorable environmental conditions. Table 1 describes the physicochemical characteristics of Estrone, 17β-Estradiol, Estriol, Progesterone, and 4-Androstene-3, 17-dione. Data was gathered from the National Center for Biotechnology Information’s website, PubChem. Figure 2 shows the chemical structure of each hormone being analyzed. Physiochemical data was not available for Estradiol and Estrone’s conjugates, 17α-Estradiol, and 1, 4-Androstadiene-3, 17-dione due to lack of known physicochemical data. However, steroidal hormones excreted by urine are conjugated with glucoronide or sulfate groups. Glucoronide and sulfate groups are found on the c-3 or c-17 positions. The polarity of these groups makes them more soluble than their counterparts and less biologically active until deconjugated (Hanselman et al.). The Table lists various values to give data on the physicochemical properties of the steroidal hormones. Vapor pressure values are used to determine at what pressure the substances evaporate. The photolysis values give information on how long the compounds can be exposed to sunlight before degrading. The Koc or soil organic carbon-water partitioning coefficient values listed are used to predict the mobility of the organic compounds. The higher the value is the less mobile the compound is in soil and the lower the value is the more mobile the compound is in soil. Henry’s Law Constant shows the compounds relative concentrations in air as compared to in water at equilibrium. The absorbance to suspended solids is based on the Koc values, but shows if the compound of interest can sorb to particles found in the soil. Bioaccumulation refers to the potential of being ingested and accumulating in wildlife. Lastly, hydrolysis shows whether or not the compound can be broken apart and transformed with water.

**Fate of Hormones in our Environment**

The different chemical structures of the hormones in study play an impact on their fate in the environment. 17β- estradiol was observed to be able to stay intact for at least 7 days if not longer in the field (Nichols et al., 1997). 17β-estradiol also requires biological activity to be transformed into estrone-3-sulfate. It however, does not require interactions from organisms to transform into estrone (Goeppert et al 2014). Furthermore, it can be gathered from table 1 that the mobility of the hormones included in the
table are based on the Koc values. It can also be gathered from the table that the hormones are going to be able to last in the aquatic environment since they lack functional groups that can be hydrolyzed. As for the androgens their fate in water is to sorb to suspended particles based on testosterone’s Koc value of 2,188 (Pub Chem. 2004).

Processes not expected to contribute much to the fate of hormones in the environment are volatilization from water because it is not a major fate process based on their Henry’s law constant values. Processes expected to make an impact on the fate of hormones in the environment are leaching, photolysis (in the water), sediment runoff, degradation from microorganisms and sorption to soil particulate.

Table 1 Physicochemical Properties of hormones tested for in Hethwood Fields.
<table>
<thead>
<tr>
<th>Hormone Physicochemical Characteristics</th>
<th></th>
<th></th>
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<th></th>
<th>Henry's Law Constant</th>
<th>Adsorbancc to Suspended Solids</th>
<th>Bioconcentration</th>
<th>Hydrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vapor Pressure</td>
<td>Photolysis</td>
<td>Koc Range</td>
<td>Mobile in soil</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17α-Estradiol</td>
<td>6.4x10^1^mmHg at 25C</td>
<td>half-life of 2 hours in river water and 41.7 hours in air-saturated purified water</td>
<td>30,000</td>
<td>no</td>
<td>3.6x10^1^atm-cu m/mole</td>
<td>no, based on Koc range</td>
<td>BCF of 200 suggests potential - moderate</td>
<td>Lacks functional groups that hydrolyze under environmental conditions</td>
</tr>
<tr>
<td>Estriol</td>
<td>9.9x10^1^mmHg at 25C</td>
<td>half-life of 2.9 hours in river water and 36.2 hours in air-saturated purified water</td>
<td>1,200</td>
<td>somewhat</td>
<td>1.3x10^1^atm-cu m/mole</td>
<td>yes, based on Koc range</td>
<td>BCF of 19 and 50 suggests potential - low to moderate</td>
<td>Lacks functional groups that hydrolyze under environmental conditions</td>
</tr>
<tr>
<td>Estrogen</td>
<td>2.5x10^1^mmHg at 25C</td>
<td>half-life 2.3 hours in river water and 47 hours air-saturated purified water</td>
<td>457-10,000</td>
<td>somewhat</td>
<td>3.8x10^1^atm-cu m/mole</td>
<td>yes, based on Koc range</td>
<td>BCF of 54 suggests potential - moderate</td>
<td>Lacks functional groups that hydrolyze under environmental conditions</td>
</tr>
<tr>
<td>Progesterone</td>
<td>3.6x10^4^mmHg at 25C</td>
<td>Progesterone will exist in both the vapor and particulate phases in the atmosphere. Vapor-phase progesterone will be degraded in the atmosphere by reaction with photochemically-produced hydroxyl radicals; the half-life for this reaction in air is estimated to be 1.2 hours. Particulate-phase progesterone will be removed from the atmosphere by wet or dry deposition. Progesterone absorbs light at wavelengths &gt;290 nm, and therefore may be susceptible to direct photolysis by sunlight.</td>
<td>2.800</td>
<td>somewhat</td>
<td>6.5x10^3^atm-cu m/mole</td>
<td>yes, based on Koc range</td>
<td>BCF of 130 suggests potential - moderate</td>
<td>Lacks functional groups that hydrolyze under environmental conditions</td>
</tr>
<tr>
<td>4-Androstene-3,17-dione</td>
<td>1.8x10^6^mmHg at 25C</td>
<td>Androstenedione will exist in both the vapor and particulate phases in the ambient atmosphere. Vapor-phase androstenedione will be degraded in the atmosphere by reaction with photochemically-produced hydroxyl radicals; the half-life for this reaction in air is estimated to be 3.5 hours. Androstenedione does not absorb light at wavelengths &gt;290 nm and therefore is not expected to be susceptible to direct photolysis</td>
<td>760</td>
<td>somewhat</td>
<td>3.7x10^6^atm-cu m/mole</td>
<td>yes, based on Koc range</td>
<td>BCF of 26 suggests potential - low</td>
<td>Lacks functional groups that hydrolyze under environmental conditions</td>
</tr>
</tbody>
</table>
Figure 2: Eleven Hormones Suspected To Be In Soil Tested At Stroubles Creek.

(James von Dollen 2014 (Structures gathered from Pub Chem))
II. Methods and Materials

Site/Sample description

Twenty sites are located on the field for this study each following either a ridge or drainage swale. Sample sites A1-A4, and A7-A9 are located along a ridge of the farm whereas A5, A6, B1-B4, D1-D4 are on drainage swales. C1-C3 sample sites are located in an area that bridges between a swale and a ridge. Each sample was collected on an interval basis for a year. A water sample was collected during each visit where the drainage runs into Stroubles Creek and two sets of samples were collected prior to application of manure. An additional sample, E, was collected across from Stroubles Creek during each collection period to be used as a control for the experiment and to be used for matrix standards for instrumental analysis. The time frame in which samples were collected was September 2012- November 2013. Manure was spread in the spring of 2013. This study focuses on roughly 700 samples gathered from the field to build statistical evidence on how these hormones travel. Figure 2 shows a map of the sample sites and the topography of the area.

Sample collection involved taking two samples at each site one at a depth of 0-5 cm and the other at a depth of 5-20 cm. The collected samples were put on ice in the field and frozen immediately upon return to the lab at -10 °C or lower.

Throughout the study eleven hormones were analyzed, all of which can be found in manure. The eleven hormones being analyzed are: Estrone, 17α-Estradiol, 17β-Estradiol, Estriol, Progesterone, Estrone-3-Sulfate, Estrone-3-Glucorinide, Estradiol-3-Sulfate, Estradiol-3-Glucorinide, 1, 4-Androstadiene-3, 17-dione, and 4-Androstene-3, 17-dione. It is suspected that interactions between hormones and microorganisms and interactions between other hormones present might cause a varying degree of hormonal travel through the soil via runoff.

Sample extraction, cleanup, and instrumental analysis
The method for analyzing the samples includes sample extraction using high pressure solvent extraction, cleanup using solid phase extraction (SPE), and finally analysis using ultrahigh performance liquid chromatography coupled with triple quadrupole tandem mass spectrometry (UPLC/MS/MS).

**Sample Extraction**

Before the samples can be processed they first have to be freeze dried to ensure there is no water in the sample, one gram of hydro matrix (treated at 200 °C for 12 hours and stored in a desiccator) is then added to keep the samples dry. 5.00 grams of the sample is then placed in stainless steel cells with the remainder of the space being filled with Ottawa sand (0.3-0.9 mm, BUCHI) leaving 1 cm of space at the top. The cells are then placed on a high pressure solvent extractor (BUCHI Speed Extractor E-916) to separate the hormones from the soil. Samples were extracted at 75 °C under 100 Bar. The flush volume is 30% and the nitrogen purge lasts for 120 seconds. Two 3 minute cycles of Methanol/Acetone (1:1 v/v) followed by two 3 minute cycles of methanol/water (1:1 v/v) are run on the samples. Extract is stored at -20 °C in a freezer until the cleanup using solid phase extraction.

**Sample extract cleanup**

The sample extracts were each reconstituted to 50 mL with Distilled De-ionized (DDI) water because the speed extractor does not always produce the same volume of solution during the extraction process. This allows us to be able to take a known amount. Once the samples have been reconstituted to 50 mL they are placed in a centrifuge to separate the unwanted sediment from the extract. 25 mL are then taken and diluted further to 500 mL with 500 μL of 5 molar hydrochloric acid to lower the pH to approximately 2, because the Solid Phase Extraction system method works optimally with an aqueous, acidic mobile phase. The samples are then run through Oasis HLB cartridges (60mg/3cc, 30um particle size, Waters) in an Agilent SampliQ 20-position Vacuum Manifold. The cartridges on the SPE are conditioned with 3 mL ethyl acetate/methanol (9:1 v/v), 3 mL methanol and 3mL DDI water. After all the sample has passed through the Oasis HLB Cartridges the HLB SPE cartridge is rinsed with 5 mL of water/methanol (95:5, v/v) and allowed to dry under a gentle vacuum for 20 minutes. Test tubes are then prepared for elution and placed inside the vacuum manifold. The samples are eluted with 3 mL ethyl acetate/methanol (9:1, v/v) and 3 mL of 2% ammonium hydroxide in methanol. The samples are then evaporated to dryness using the TurboVap evaporation system under a stream of nitrogen at 45 °C. The residue is then dissolved in 0.5 mL of acetonitrile followed by 0.5 mL of water. Samples are stored in a freezer at -20 °C for short term and -80°C for long term until UPLC/S/MS analysis.

**UPLC/MS/MS analytical conditions**

The mobile phases for the UPLC are Acetonitrile/5mM Ammonium Acetate in water for the androgen and estrogen conjugate procedure and Acetonitrile/0.2mM Ammonium Fluoride in water for the estrogen procedure.

**Data Collection**

Data was generated using Quantitative Analysis with the UPLC. A total of 78 samples were processed. 8 E site samples were processed with every sample set to build a standard curve matrix comparison. Data gathered is incomplete and only represents a small fraction of the study. Only two sample sets were able to be analyzed and these were the sample sets taken before the application of manure at depths of 0-5cm and 5-20cm.
III. Results

Results of the study are shown in the graphs below depicting the concentration at each sample site with varying diameter sizes representing the concentration levels of the hormone tested for. Each pound mark shows where samples were but were not analyzed in the time of the program. Each star represents where samples were and had hormone levels below detection limits. The colors of the circles depict a specific sample set on a certain topographical feature. Blue represents samples along a swale, green shows samples along a ridge and purple shows samples along a bridge connecting a ridge and a swale. The circles on graphs 1 and 2 indicate where the buffer zone is located that is highly saturated in water and close to Stroubles Creek. Graphs 1 and 2 depict sample sets taken at a depth of 0-5 cm. Graphs 3 and 4 represent the same sample sets at depths of 5-20 cm.

![Graph 1](Theresa Sosienski 2014)

![Graph 2](Theresa Sosienski 2014)

![Graph 3](Theresa Sosienski 2014)

![Graph 4](Theresa Sosienski 2014)

The largest concentration of progesterone six months after application of manure was 2.41 ng/g and the lowest was 0.44 ng/g. One year after the application of manure the highest concentration of progesterone was 3.3 ng/g and the lowest was 0.4 ng/g. This is seen on graphs 1 and 2. Graphs 3 and 4 show that where the highest concentration of progesterone was in depths of 0-5 cm the hormone was only detected in those sample sites at depths of 5-20 cm.
IV. Conclusions

The fate and occurrence of hormones in the watershed have an impact on fish populations found within. This study focused on the concentrations of hormones and how they travel through soil through runoff and other chemical processes including biological intervention and soil hormone interactions. Samples were collected over the period of September 2012- November 2013 and data was analyzed in the summer of 2014. During the 10 week REU program 78 samples out of roughly 700 were able to be analyzed due to complications with the instrumentation. Quantitative analysis needs to be completed to gather further information on the matter and draw more relevant conclusions. The data shows that hormones are traveling via runoff by the larger concentrations located downhill on both graphs in the buffer zone. Also samples at depths of 5-20 cm in the buffer zone show that leaching is occurring because of the presence of progesterone at that depth at that site and nowhere else in the sample set. Because the samples in total includes over 700 samples, the samples processed only provide a snapshot of what is happening on the field and do not provide enough evidence to make any predictions on the fate of the hormones in question.

V. Acknowledgements

I would like to acknowledge the NSF-REU program for making my research possible and allowing an undergraduate to participate in such a grand opportunity to build a sense of what research really is; which gives the student the ability to make an educated decision on their perusal of graduate school.

I would also like to thank my mentors involved in the project who helped me understand to the best of my knowledge what I was to do, who guided me to develop safe practices in the lab, and who oversaw the creation of my paper to present the facts as coherently and accurately as possible.

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References


Legionella Pneumophila Growth in Simulated Water Heaters Under Stagnant Conditions

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Abstract

Legionella pneumophila is an opportunistic pathogen which can thrive in pipes and fixtures at the building level of the distribution system (premise plumbing). L. pneumophila exposure hospitalizes 8,000-18,000 people annually with a fatality rate of 5-30%. The goal of this experiment was to determine during a stagnation period whether the amount of total organic carbon affects L. pneumophila growth, specifically when carbon is removed by a granular activated carbon filter. The experiment was performed using previously established simulated glass water heaters inoculated with L. pneumophila and other organisms typically found in a premise plumbing microbiome.

Keywords: Legionella Pneumophila, Opportunistic pathogens, Premise plumbing

I. Introduction

Background Information and Exposure

In 2009 the World Health Organization announced that waterborne diseases were the world’s leading killer, taking 3.4 million lives annually. (Berman, 2009) Many of these deaths occur in underdeveloped countries, but developed countries have reason to worry as well. Opportunistic pathogens are infectious microorganisms that can lead to disease in certain at risk populations. Despite disinfection at the drinking water plant, opportunistic pathogens can thrive in our plumbing systems and Legionella pneumophila is a particularly concerning one.

Exposure to the pathogen can lead to two diseases; Pontiac fever and Legionnaire’s disease. Both of these can be grouped under the term Legionellosis. Pontiac fever develops in a healthier individual and will go away untreated. Legionnaire’s disease occurs in exposed immunocompromised populations (Center for Disease Control, 2013) and can lead to hospitalization with a 5-30% fatality rate (Marston, 1994). There are an estimated 8,000 to 18,000 people in the United States hospitalized with Legionnaire’s Disease each year. (Center for Disease Control, 2013) These statistics are believed to be an underestimation since symptoms for both include pneumonia or flu-like symptoms and especially if the person is contracts Pontiac fever rather than Legionnaire’s disease, cases of contamination may often go undiagnosed.

To contract the disease, one must breathe in a vapor or aerosol with the pathogen in it. For example, this could happen in steam from unclean hot tubs or showers where the bacteria are in the water systems. There are groups of people that are more susceptible to become seriously ill such as smokers, those above age fifty, people with chronic lung disease and anyone with a weakened immune system. (Center for Disease Control, 2013)

Outbreaks
Legionnaire’s disease got its name from its discovery after a large outbreak at a Philadelphia American Legion conference in 1972 that caused thirty four deaths (Occupational Safety and Health Administration). A recent outbreak that gained a lot of attention was at a Pittsburg Veteran’s Affairs Hospital in 2012. (Office of Inspector General, 2013). The outbreaks tend to be more common in hospitals because they have an extensive premise plumbing system of their own in each building to maintain, and also because they have such a high level of immunocompromised individuals that would contract the harsher form of Legionellosis.

Why Stagnation in Premise Plumbing is Important

Opportunistic pathogens in premise plumbing have been shown to be a growing problem for the developed world. Premise plumbing involves the pipes and materials at the individual building level not including the distribution systems owned and maintained by the water authority. While distribution lines are flushed regularly, areas of premise plumbing may remain unused or stagnant for long periods of time. This increase of water age also leads to a loss of disinfectant residual (Lautenschlager, Boon, Wang, Egli and Hammes, 2010) and overall a change in the microbiome. Also, premise plumbing has smaller pipes with a high surface area to volume ratio so growth within biofilms may have a greater effect on the water quality in pipes (Zhang, Edwards, Pinto, Love, Camper, Rahman and Baribeau, 2009).

There are periods where premise plumbing lines may stay stagnant longer than the normal. This can occur in schools, student facilities and dorms that may be left for the summer by students of all ages. Another scenario would be parks and vacation facilities that work on seasonal schedules. Also, those with vacation homes that are only used for a portion of the year would have their plumbing systems go stagnant.

Total Organic Carbon

Total organic carbon (TOC) is a laboratory measurement of all organic forms of carbon from simple sugars to complex molecules secreted from dead or live organisms. A small portion of this is easily assimilated by heterotrophs found in drinking water and is referred to as assimilable organic carbon (AOC) (Haddix, Shaw and LeChevallier, 2004). Maintaining low levels of AOC is one option for reducing regrowth in the distribution system and many areas of the world have applied this strategy in order to use lower levels of residual disinfectants. Europe is an example of this. A strategy for controlling AOC levels is the application of granular activated carbon (GAC) filters.

GAC filters directly remove organic matter by sorption and provide a high surface area for attachment of microbes which can biodegrade AOC going through the filter leaving the effluent with stable and low organic carbon levels. GAC filters can be used at every level of the distribution system. At the treatment plant they have been used successfully to consume biodegradable carbon and give biological stability. In premise plumbing, they can improve taste and odor of drinking water and can be applied for a whole building or at the point of use. The consumer can actually purchase them in the form of a filter for an individual tap or to store the water in pitchers.

GAC filters do have some negative aspects which is one reason why they are not universally applied. They remove the disinfectant residual (Sorlini and Collivignarelli 2005), leaving the system downstream more vulnerable to microbial growth. The GAC itself can provide a growth surface and house high levels of microbes, including pathogens such as Yersina enterocolitica, Salmonella typhimurium and Eschericia coli (Camper, Lechevallier, Broadaway and McFeters, 1985). It was suggested after a recent L. pneumophila outbreak in Florida that GAC filtering can actually intensify opportunistic pathogen proliferation (Wang, Edwards, Falkinham and Pruden, 2013).

The majority of research on AOC and its removal through methods similar to GAC filtration has not focused on L. pneumophila specifically but more of them look for total bacteria regrowth.
II. Research Methods

Simulated Glass Water Heaters

Simulated glass water heaters (SGWHs) were used in order to observe results from a variety of conditions and factors. SGWHs consisted of 125 mL French square borosilicate glass bottles with polytetrafluoroethylene caps and were incubated at 32°C, a temperature representative of the bottom of a conventional water heater where certain opportunistic pathogens are believed to thrive. SGWHs were originally inoculated with L. pneumophila at an approximate initial concentration of $2.03 \times 10^5$ gene copies/mL, Acanthamoeba polyphaga at $2,079$ gene copies/mL, Mycobacterium avium at $7.15 \times 10^5$ gene copies/mL and Hartmannella vermiformis at $1.46 \times 10^3$ amoeba/mL into each reactor. All SGWHs were operated for four years before the present experiment.

This study used a variety of plumbing conditions in order to determine if GAC and AOC influence was constant across a relevant range of issues. Plumbing materials and conditions implemented in this study included (1) iron coupon to simulate iron plumbing system components including steel in water heaters, (2) cross-linked polyethylene (PEX) pipe sections, (3) magnesium to simulate magnesium anodes used for corrosion control, (4) iron (III) oxide sediment from unlined iron in many distribution systems, (5) ammonium sulfate additions at concentrations 1 mg/L free NH$_3$-N to simulate chloramine systems after residuals disappear, (6) combination of iron coupon, magnesium rod, and ammonium sulfate condition and (8) controls (no additional materials) at pH 7.5 and 10. In addition to the described materials, all SGWHs also contained 1.5 layers of 1mm glass beads, which served to increase the surface area to volume ratio and provide a range of redox zones similar to those found in premise plumbing sediment layers.

Figure 1: Simulated Glass Water Heaters
(Kara Harrison, July 2014)

Water Preparation

Prior to the beginning of the stagnation period, an 80% water change was conducted three times a week to simulate infrequent use of a water heater, having 100 mL be discarded and replaced with freshly prepared modified Blacksburg drinking water. Town of Blacksburg, Virginia, tap water is disinfected with chloramines. Water was collected in the lab from the cold water tap. The lines were flushed for ten
minutes prior to collection in order to ensure any water that had been stagnant in the pipes was not used. The collected water was break-point chlorinated (BPC) with addition of a diluted hypochlorite solution. The water was then heated to 90 °C for ten minutes to remove most disinfectant residual.

For the SGWHs receiving GAC treated water, the cooled water was subject to biofiltration with a point of use GAC filter. All influent water was pre-treated by passage through a .45 µm polyvinylidene fluoride (PVDF) filter to remove microbes. Water was adjusted to pH 7.5 ±0.1, except in the case of the ‘high pH control’ which was adjusted to pH 10.0 ±0.1. pH was controlled with additions of 1 M or less NaOH and HCl using an Oakton pH 10 series meter (Oakton Instruments, Vernon Hills, IL). Water for half of the reactors underwent GAC biofiltration to reduce organic carbon (GAC Water), and the other half did not undergo this filtration step and was simply breakpoint chlorinated as described earlier (BPC water). This could allow for direct comparisons to be made between both the water types and the plumbing conditions.

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### Table 1: Experimental Design

<table>
<thead>
<tr>
<th>Condition</th>
<th>GAC Water</th>
<th>BPC Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>1 2 3</td>
<td>1 2 3</td>
</tr>
<tr>
<td>High pH Control*</td>
<td>1 2 3</td>
<td>1 2 3</td>
</tr>
<tr>
<td>Iron Coupon</td>
<td>1 2 3</td>
<td>1 2 3</td>
</tr>
<tr>
<td>PEX pipe sections</td>
<td>1 2 3</td>
<td>1 2 3</td>
</tr>
<tr>
<td>Magnesium Rod</td>
<td>1 2 3</td>
<td>1 2 3</td>
</tr>
<tr>
<td>Iron(III) oxide sediment</td>
<td>1 2 3</td>
<td>1 2 3</td>
</tr>
<tr>
<td>Ammonium Addition**</td>
<td>1 2 3</td>
<td>1 2 3</td>
</tr>
<tr>
<td>Combination of iron, magnesium rod and ammonium**</td>
<td>1 2 3</td>
<td>1 2 3</td>
</tr>
</tbody>
</table>

*pH adjusted to 10.0±0.1 rather than 7.5±0.1

**Addition of ammonium sulfate at 1 mg/L free NH₃-N
(Each boxed number represents one simulated glass water heater)

(Kara Harrison, July 2014)

### Data Collection

The SGWHs had routine water changes three times a week until the stagnation process began. Samples were collected immediately before the stagnation process. Then simulated water heaters were left undisturbed for seven weeks and sampled again before water changes were resumed. All samples were collected through aseptic techniques and procedures inside a biosafety cabinet. TOC was measured with a Sievers 5310 C Laboratory TOC-MS Analyzer using the Data Pro 5310 C Computer Program. Thirty milliliter samples were collected by pooling ten milliliters from each triplicate SGWH. They were then acidified with phosphoric acid and sparged with Nitrogen gas in order to purge inorganic carbon prior to being analyzed.
Effluent water of 100 mL from each SGWH was filtered onto sterile 0.22 µm-pore-size mixed cellulose ester filters (Millipore, Billerica, MA). The filter was folded and torn using sterile tweezers and pushed inside a Lysing Matrix A tube from the Fast DNA® SPIN Kit (MP Biomedicals, Solon, OH). DNA extraction was conducted according to the manufacturer instructions.

Quantitative polymerase chain reaction (qPCR) was applied to quantify the macrophage infectivity potentiator (mip) gene specific to L. pneumophila. qPCR was carried out using a CFX96™ realtime system (Bio-Rad, Hercules, BA). All qPCR assays were previously validated for drinking water samples in terms of specificity and limit of quantification. A Taqman Probe Mix (Bio-Rad, Hercules, CA) assay was used. For each run of qPCR analysis a calibration curve was included with at least six points.

Samples were also cultured to confirm that the L. pneumophila colonies were still viable. 100 µL effluent samples were heated in a water bath at 50°C for 30 minutes and then directly plated on buffer charcoal yeast extract agar according to published methods (Leoni, De Luca, Legnani, Sachetti, Stampi and Zanetti, 2005).

III. Results and Discussion

In this experiment, simulated glass water heaters using GAC filtered water were directly compared to ones filled with breakpoint chlorinated water. The mean concentration levels of Legionella pneumophila before stagnation were six times greater in the GAC filtered water than in the BPC water. These levels were measured after reactors had been undergoing regular water changes. However, the difference between the levels of L. pneumophila in the two water types before stagnation was not statistically significant with t-tests at p>.05.

![Figure 2: Mean Concentrations before Stagnation](Kara Harrison July 22, 2014)

Post stagnation data suggested that GAC filtered water retained higher L. pneumophila growth, despite having lower carbon levels. A t-test confirmed that the results were significant with (p<.05). The only condition in which BPC water had higher levels of L. pneumophila was the combination reactors with iron, ammonium and magnesium.
Figure 4 shows that levels of *L. pneumophila* decreased during the stagnation period in almost all conditions. The magnesium reactors were the only condition that saw an increase in growth and further research should be done on why this may have occurred. These results do not agree with the expected results that *L. pneumophila* levels should increase with a stagnation period since the pathogen is known to proliferate in stagnant water.
IV. Conclusions

Results from this study strongly suggest that Granular Activated Carbon filtered water may have a greater ability to sustain L. pneumophila growth both during regular use and a stagnation process despite lower levels of Carbon. This does not mean that lower levels of carbon can be traced to higher levels of L. pneumophila. It is very likely that the characteristics of the Granular Activated Carbon filter encouraged the pathogen growth.

Results also suggested that L. pneumophila growth would decrease during a stagnation period across varying conditions. This was not what was expected and further investigation must be done on this subject.

Extended Research

Total Organic Carbon levels were measured for the experiment and are undergoing analysis. This data should be included in any further work.

Throughout all of the experiments mentioned here and previously, there were two other sets of simulated water heaters undergoing the same procedures. Also for all experiments, qPCR will analyze both L. pneumophila levels and the overall bacterial levels as recognized by the 16S rRNA gene. The second additional set of simulated water heaters involved water conditions with varying added carbon levels. Since these are controlled additions the goal is to be able to determine if there is a correlation between levels of L. pneumophila or overall bacterial growth and carbon levels. The third experimental set of SGWHs investigates the relationship between copper and bacterial growth, representing copper pipes and copper additions as a disinfectant. This third group also has simulated water heaters at varying pHs to look into that being a factor.

After the stagnation process on all three experimental sets, the SGWHs resumed regular 80% water changes three times a week for the next eight weeks. Then samples were taken to investigate if levels of both L. pneumophila and total bacteria remained stable after stagnation ended and regular use began. The question would be, if a premise plumbing system is allowed to stay stagnant and have the microbiome change, would levels remain at this stagnated point?

In order to establish a baseline within the SGWHs, the effluent from the reactors known to have L. pneumophila was pooled from each of the three experiments. A cross-inoculation was done by adding one milliliter of the pooled effluent to each reactor in that experimental subset. Two weeks after the cross inoculation, samples were taken again to gather information on which conditions may lead to a more welcoming environment for incoming L.pneumophila.

In all of these experiments there were no chlorine residuals added to the reacting water heater simulations. Current research involves adding different levels of chlorine residual to determine what levels of chlorine residual would control L. pneumophila growth.

V. Acknowledgements

I would like to heavily thank my mentors Dr. Edwards and Dr. Pruden, and my graduate students, Rebekah Hupp and Caitlin Proctor, for their trust, patience and guidance throughout all of my work with in this lab and with them. They truly taught me what a great work environment is like. I also would like to think Dr. Lohani and everyone who has worked to make this REU and overall undergraduate research program possible.
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 author(s) and do not necessarily reflect the views of the National Science Foundation.

References


NSF/REU Site Assessment Report
The following is an independent assessment of the level of success of the program conducted during the summer of 2014. As in 2007 through 2009 and in 2011-2013, 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. Most came to the program with some commitment to attend graduate school, though this group seemed more interested in part-time and master’s level study but wanting to use the experience as an opportunity to explore the matter further. The levels of commitment stayed the same or strengthened slightly over the summer. About half intend to go to graduate school immediately after their undergraduate programs, with one planning on attending medical school. The others plan on working and perhaps going to graduate school either part-time or after working for a while after graduation.

The students in the program reported the greatest gains in ability to conduct research in the library and understanding the processes used to monitor water quantity and quality. Other areas of reported growth include ability to communicate scientific concepts effectively to a scientific audience, confidence in understanding how to conduct scientific research, and being aware of the many ways in which scientists from different fields interact with each other in conducting research in water sciences. In addition, they seemed to genuinely enjoy each other’s company; the esprit des corps of the undergraduate students was quite obvious and came through in their comments. The suggestions for improving the program were modest and generally reflected logistical matters. On the positive side, they found a number of the seminar presentations interesting, especially the one by Dr. Edwards. Even though there was no direct question about field trips this year, several mentioned them, with the water and wastewater treatment plants being mentioned most often. There were a few suggestions for improving both the seminars and the field trips.

Entering Survey

There were ten students who completed the pre-test during the summer of 2014. Their responses are below, in order of the highest to lowest responses. (The questions were developed in cooperation with the faculty who are the Principle Investigators for the project. They were revised in 2014 by deleting some of the questions used during 2011-2013 that were not yielding useful results. This made for a shorter survey but still allowed for 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 research. – 4.70
I have an appreciation for the role of graduate students in research. – 4.70
I have an appreciation for the role of faculty in advising students. – 4.70
Water research can be challenging. – 4.70
I have a good understanding of the role of ethics in scientific investigations. – 4.20
I am aware of many ways in which scientists serve their communities. – 3.80
I plan on going to work soon after I graduate. – 3.70
I am aware of the many ways in which scientists from different fields interact with each other in conducting research in water sciences. – 3.60
I am aware of many opportunities for employment in the water field. – 3.60
I am confident that I understand how to conduct scientific research. – 3.50
I plan on attending graduate school soon after I graduate. – 3.20
I can communicate scientific concepts effectively to a scientific audience. – 3.10
I know everything that I need to know to conduct scientific research in the library. – 2.80
I understand the processes used to monitor water quantity and water quality. – 2.70

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 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 during this 10-week long NSF/REU program.

Exiting Survey

At the completion of the program the same ten students completed the same survey with the same questions. Their responses are below, again in order from the highest to lowest.

I have an appreciation for the role of faculty in research. – 4.80
I have an appreciation for the role of graduate students in research. – 4.80
• I have an appreciation for the role of faculty in advising students. – 4.80

• Water research can be challenging. – 4.70

• I have a good understanding of the role of ethics in scientific investigations. – 4.70

• I am aware of many ways in which scientists serve their communities. – 4.50

• I am aware of the many ways in which scientists from different fields interact with each other in conducting research in water sciences. – 4.50

• I am confident that I understand how to conduct scientific research. – 4.40

• I am aware of many opportunities for employment in the water field. – 4.20

• I know everything that I need to know to conduct scientific research in the library. – 4.10

• I can communicate scientific concepts effectively to a scientific audience. – 4.10

• I understand the processes used to monitor water quantity and water quality. – 4.00

• I plan on attending graduate school soon after I graduate. – 3.50

• I plan on going to work soon after I graduate. – 3.30

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.

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 know everything that I need to know to conduct scientific research in the library. – 1.30
- I understand the processes used to monitor water quantity and water quality. – 1.30
- I can communicate scientific concepts effectively to a scientific audience. – 1.00
- I am confident that I understand how to conduct scientific research. – 0.90
- I am aware of the many ways in which scientists from different fields interact with each other in conducting research in watershed sciences. – 0.90
- I am aware of many ways in which scientists serve their communities. – 0.70
- I am aware of many opportunities for employment in the water field. – 0.60
- I have a good understanding of the role of ethics in scientific investigations. – 0.50
- I plan on attending graduate school soon after I graduate. – 0.30
- I have an appreciation for the role of faculty in research. – 0.10
- I have an appreciation for the role of graduate students in research. – 0.10
- I have an appreciation for the role of faculty in advising students. – 0.10
- Water research can be challenging. – 0.00
- I plan on going to work soon after I graduate. – (0.40)

To summarize, the greatest reported gains over the summer were in the areas of conducting library research, understanding the processes used to monitor water quantity and quality, communicating scientific concepts effectively to a scientific audience, understanding how to conduct scientific research, and becoming aware of the many ways in which scientists from different fields interact with each other in conducting research in water sciences. 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 who participated in it. 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?
   - Getting to know about graduate work and the lifestyles of graduate students.
   - Having my own project, my first research paper and scientific talk; was able to relate the topic to my passions.
   - Enjoyed learning a lot about my topic; would like to keep in contact with my professor.
   - Enjoyed the field trips, which helped me visualize the interdisciplinary concepts, see scientific authorities, the jobs in the community, the work being applied, the careers (both ones that I might want to include as possibilities and ones that I might want to exclude as possibilities).
   - Doing presentations and critiques, seeing others become better presenters; the presentation on ethics was particularly good; the one by Dr. Edwards was especially moving.
   - Solidified the fact that I want to get a Ph.D., even though it showed me that not everything goes right.
   - Mentor allowed me to do different aspects of the project.

2. What concerns do you have about the program just ended?
   - The meal plans did not match up to the number of meals.
   - The meal plan is restrictive as to eating healthy; the hours are restrictive; they would prefer using their own money instead.
   - A money based plan versus a meal based plan would have been preferable for meals.
   - Use a campus van for group outings rather than private vehicles; students had to use their own money for gas.
   - There was a problem with food missing from the dorm refrigerator; would have preferred another, more private living arrangement.
   - Regarding the final paper, would have preferred submitting a draft first and getting earlier feedback on it; there seemed to be variation by program; there needs to be more structure in some cases and coordination between mentors and graduate students and undergraduates; there was a lack of communication between the three in some cases, which can get out of hand sometimes.
   - Should sit with mentors beforehand to lay out how the program works and deadlines and a schedule for the students.
   - In at least one case a student has a professor/mentor but not a graduate student.
   - Regarding activities, they were limited to the pure sciences and engineering, with none in computer science or design, but there were students in those fields in the REU program.
   - Better project descriptions would have been helpful to better understand what research is going to be like.

3. List the top three things that you learned (within and outside of your discipline) during this program.
   - Giving a scientific talk as a form of theater.
   - Getting to see how a lab is run and interaction of grad students with each other, e.g., in coordination of schedules.
   - Learned a lot about science.
   - Have to be really independent.
• Modeling is easy.
• Creating plots that represent something significant is very difficult.
• Even when stressed by deadlines, still must get enough sleep and recreation.

• Creating a deliverable in computer science, keep in mind that somebody else will be using it; design it as best solution for the end user.

• How vital the use of statistics is and how depressing it is that there is error in everything that we do.

• We take water and sewer for granted, but they are important scientifically.

• There is a need to make a personal connection to a mentor before going to grad school.
• There is a need to get funding for grad school.
• Have improved presentation skills.

4.a. How many of you are motivated to go to graduate school now? – did the NSF REU influence your motivation?
• Of 11, a total of 6 intend to go to graduate school, including one who intends to go to medical school.
• The NSF REU experience seemed to generally confirm preconceived notions and plans as much as anything. It provided a chance to simulate the experience and deepen the knowledge base but did not change minds very much one way or the other.

4.b. How many of you intended to go to graduate school at the beginning of the summer?
• Of 11, a total of 7 intended to go to graduate school, including one who intended to go to medical school.

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

6. In what ways, if any, did you find the field trips informative?
• Everything.
• Knowing what’s behind water quality and water treatment.
• What graduate school is all about.

7. How satisfied were you with your living environment at Virginia Tech? Your social/cultural environment?
• Lack of central air conditioning is a problem, but had window units.
• Came together socially.
• Would prefer a worse dorm and a better stipend.
• Would have preferred to have some direction regarding outing events such as hiking and tubing, especially due to transportation limitations.
• One mandatory group activity would have been nice.

8. Other comments?
Concluding Comments

The group in 2014 did not seem to have a high commitment to Ph.D. research when they began the program even though they claimed to have a strong appreciation of how graduate students and faculty conduct research upon entry. At the end of the summer they reported having learned a lot about how to conduct research in the library and understanding the processes used to monitor water quantity and quality in particular, and how to communicate scientific concepts effectively to a scientific audience, yet their commitment to doctoral research did not increase much. The rankings of the survey answers were remarkably similar to those of prior years, however, especially those of the past three years as can be seen in Appendix III. The student opinions about the program itself were generally positive.
Appendix I

Open Ended Questions – Beginning of the Summer

What suggestions do you have for improving the application process for this NSF/REU program?
- No suggestions at this time.
- None, I found the site and information very helpful.
- I would like to see the program advertised through more listservs.
- Attract more awareness to what REU is.
- N/A
- None, it was quite simple.
- The application process went smoothly but for some reason the emails didn’t work very well.
- It was wonderful actually! Choosing a project preference was easy because the descriptions were very detailed.
- More detailed project descriptions would be helpful in selecting first and second choice of project applying for.
- More accessible □ I had to go to many different links before finding it.

Do you have any concerns about the program that you are beginning now? If so, what are they?
- Yes. I’ve never conducted research beyond what was needed for a class paper. Not sure how to start, also not entirely sure what my research is right now.
- No.
- I have a concern about the comparability between hardware.
- [Left blank.]
- Coming from a design background I worry about the science aspect of the research, but look at it as a challenge.
- I feel a bit overwhelmed this first week.
- Other fellows are loud at night.
- No concerns.
- Bureaucracy! All the issues with forms, wi-fi, no hot water in the dorms, figuring out technical stuff, etc. There’s a lot of hoops to jump through.
• [Left blank]
• I’m having difficulty connecting to the network and 4-help/computing services have not been helpful.

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

#1
• [Left blank]

#2
• How to write a research paper.
• How to interact well with faculty.
• How to use databases for research articles.

#3
• USB/serial [???] and system programming.
• How to take lab work to research paper.
• Learn more about the natural and physical sciences my work is enabling.

#4
• GIS
• Solar Panels
• Awareness of VT agri-science projects & other REU programs to promote more interdisciplinary interactions among a wide array of studies.

#5
• How scientific research differs from other fields.
• The process of scientific investigations.
• How to apply what I learn at future jobs.

#6
• More careers in water resources in general.
• Field trips to see employees in a water resource field working.
• See something come out of this project i.e. some form of proof that I accomplished something during my time here.

#7
• Gain valuable experience.
• Learn some science.
• Make friends and connections.

#8
• How to present a research poster.
• How to draft proposals.
• Analytical chemistry techniques.
#9
- Writing to a scientific audience.
- Presentation skills.
- Taking data and drawing useful conclusions.

#10
- Working with faculty closely … to see if I want to pursue a PhD.
- Explore Virginia.
- Have good data.
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.

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.

- Social activities such as the lake picnic were very fun. However, the social interaction felt slow moving. Ice breakers are silly but sometimes bridge that gap more quickly.

- A weekly req. committee should be formed for the REU group so there is more group interactions.

- I enjoyed majority of the social activities because I learned something new every time. It would be nice if with the program extending its fields of study the activities could do the same to be more interdisciplinary. (Maybe visiting where each other works/site if possible)

- For field trips – REU should provide transport. 1 van would have fit us all and made the event feel more inclusive. Also the students who did drive never got reimbursed for gas.

- It was hard to be social as a group. After some time everyone had their own agenda/activities. Scheduled activities on Fridays could mitigate this however weekends should always be free.

- I would be open to changing the housing. If the REU rented a house and the students live there that would be unique.
  - There were several dining halls open on campus that we could not eat at. Can that be restructured?

- Social activities that we did as an entire group were great however, transportation to and from could have been better with a campus van.

- If field trips were schedule in the beginning of the program as an entire group (like Cascades, tubing, etc. the social bonding of the entire group may be better. There was a lot of bonding between the girls and among the guys but not as a full group.

- I think that more organized activities should be scheduled.

- Picnics were so fun & they were a great time to be ourselves & also film the YouTube video. I was fairly social with everyone, especially my girls! I will love them forever.

- Social activities were nice. The picnic at Claytor Lake was my favorite.

Please comment on the field trips you participated [in] during the past 10 weeks. Feel free to list the trips you liked and didn’t like. Suggestions for next year are most welcome.

- Liked
Did not like
   o Statistical modeling of watersheds.

Library meeting should be followed up on.

Taking a tour of the wastewater facility and learning about how they measure the amount of affluent and effluent water via flumes gave me a great appreciation of the project I’m doing on volumetric flow and I hope to continue my work in this field.

The seminars were interesting. I didn’t understand 100% of the material though. Dr. Edwards seminar was the best seminar to me.

Dr. Marc Edwards was amazing! The one seminar about GIS was not very valuable because it’s hard to grasp GIS and computer science in 45 min.

Seminars and field trips were great! Do more field trips?

As a VT student I did not get much out of the library trip.
I felt like a lot of the water sciences were well represented but my field, CS, was not at the seminar and trips.

Seminars during the program engaged me in thinking about interdisciplinary work so they accomplished their task even if they weren’t much fun.

Enjoyed a lot
   o Dr. Edwards.
   o DC water.
   o Water treatment plant.
   o Wastewater treatment.
   o Claytor Lake picnic.

Least favorite
   o National Weather Service.
   o Climate modeling.

For next year a suggestion for a Friday session topic would be water situation in lesser developed countries.

They were all very interesting.

LOVED: Dr. Marc Edwards’ talk & mostly: the grad student panel. I could have done without: the GIS modeling w/ Venkat (forgot last name). The field trips were enlightening, but not my personal cup of tea.

The weekly seminars were O.K. I’d like to see more faculty come and promote their research to us.

Please comment on the merit and frequency of presentations you made during the last 10 weeks.
• That was the most worthwhile thing of this program. The feedback I received was great and I now feel like I understand better the steps taken towards having a very prepared, fluid presentation.

• I enjoyed working on the ppt every 2 weeks. The practice really helped me especially the one on one interactions on Wed. meetings.

• We did a lot of presentations but not to many. I feel that the merit of the presentations grew as the occurred more. We presented 4 times before our final and I felt more well versed and capable to explain my topic each time. (The feedback helped too)

• I really liked the feedback cards during the presentations. I thought 3 presentations were too much, and we should have done 1 @ the beginning and 1 @ the end (not including the final ceremony).

• The presentation practice was beneficial because it made us continually think about our project, develop it and a train of thought, and lastly kept us updated with one another and the interdisciplinarity of the program.

• I really liked the amount of practice we got for our presentations the past 10 weeks. Presenting in front of our peers built confidence.

• It did become boring hearing the same 10 presentations so often. It would be interesting if in the earlier weeks we rotated off the group we presented to. This would not expose everyone to the same project so much. It would feel fresher and less tedious.

• During this program I felt that I was used as a lab assistant and not treated as an REU student. I processed samples for the final 7 weeks I was here and didn’t start on my paper until after then; and my presentation only really got off the ground after then too. I would recommend keeping the mentors on a strict schedule to guarantee students are going to the library at least once a week and are meeting with their mentors.

• I feel that the presentations were helpful in improving my communication skills. Presenting back to back (Thursday at Undergraduate Research Symposium then Friday at REU program conclusion) was a little much.

• I hate oral presentations. I did well the second + third times. When I actually do well I think I have a good presentation.

• My presentation transformed enormously. I took practice very seriously & the Friday practices were invaluable.

• Making presentations throughout the program was very helpful for the final presentations. I think maybe one-more presentation could have been done before the final practice.
NSF/REU Site Announcements
Short Announcement

**Summer 2014 (May 25 – August 2, 2014) - 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 1, 2014 (5:00PM, 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 25-August 1, 2014) 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 25, 2014 (arrival day) at Virginia Tech and end on August 2, 2014. 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 56 excellent undergraduate researchers from our site during 2007, 2008, 2009, 2011, 2012, and 2013. Application materials, details of Research Mentors along with summer 2014 research projects and other program activities are posted on the following website: [http://www.lewas.centers.vt.edu/](http://www.lewas.centers.vt.edu/)

Applicants are requested to upload their applications along with other required documents by the deadline (March 1, 2014, 5:00 pm, EST). Successful applicants will be informed by March 17, 2014. Please contact Dr. Vinod K Lohani (phone: (540)231-9545; FAX: (540) 231-6903; E-mail: vlohani@vt.edu) for questions.

**Titles of Summer 2014 Projects**

Project ID#1: Evaluating the Efficacy of Water Quality Treatment on Cyanobacterial Blooms  
Project ID#2: Water Quality for Human Health and Aesthetics  
Project ID#3: Hydrology and Hydraulics Impacts on Ecological Health of Streams and Rivers  
Project ID#4: Quantification of distinguishing features of tsunami versus hurricane sediment overwash events  
Project ID#5: Bio-Inspired Water Stewardship Lab  
Project ID#6: Development and Implementation of a Raspberry Pi-based System for Processing and Remote Access of Real-Time Environmental Data  
Project ID#7: Biogeochemical Controls on Contaminant Transport and Transformation  
Project ID#8: Designing empowerment: Development of a community level hydro power generation solution for impoverished communities  
Project ID#9: Investigation of the occurrence and fate of 4-nonylphenol, an endocrine disruptor, in urban-impacted watersheds  
Project ID#10: Mechanisms of Cupric Ion Control of Legionella in Premise Plumbing
Long Announcement

Summer 2014 (May 25 – August 2, 2014) - Undergraduate Research Fellowships
National Science Foundation - Research Experiences for Undergraduates (REU) Site
Interdisciplinary Water Sciences and Engineering
Virginia Tech, Blacksburg, Virginia
Application Deadline March 10, 2014 (Monday; 5 PM EST)

Program Description: Applications are invited from qualified and motivated undergraduate students (rising sophomores, juniors and seniors – engineering and science majors) 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. This NSF REU site has successfully hosted a total of 56 undergraduate researchers in summers of 2007, 2008, 2009, 2011, 2012 and 2013.

Successful applicants (hereafter referred to as REU fellows) will join one of the ongoing research projects in water sciences and engineering and conduct research under the supervision of Virginia Tech faculty and graduate students. Research projects address issues related to sustainable management of water resources and water infrastructure, and facilitate opportunities of field research, laboratory work and testing of theoretical concepts. See Appendices 1 and 2 for list of faculty advisors and typical 2014 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 10-week internship will begin on May 25, 2014 (arrival day) at Virginia Tech and end on August 2, 2013. The research internship includes a stipend of $450/week, housing (2 persons per room), $400 meal allowance and round trip travel expenses, limited to a maximum of $500 per person, to Virginia Tech.

Application: The deadline to receive all application materials is March 10, 2014. 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 and include 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 to Dr. Lohani (See email address below). Letters should address candidate’s motivation, enthusiasm, reliability, team-work and personality.
Successful applicants will be announced by **March 24, 2014**. 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**

<table>
<thead>
<tr>
<th>Name</th>
<th>Organization</th>
<th>Responsibility</th>
<th>Academic Discipline and Field of Study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dr. Carey</td>
<td>Virginia Tech</td>
<td>Research Mentor; Participant Selection</td>
<td>Biological Sciences; Freshwater Ecology</td>
</tr>
<tr>
<td>Dr. Hester</td>
<td>Virginia Tech</td>
<td>Research Mentor; Participant Selection</td>
<td>Civil &amp; Environ Eng.; Ecohydraulics</td>
</tr>
<tr>
<td>Dr. Edwards</td>
<td>Virginia Tech</td>
<td>Research Mentor; Participant Selection</td>
<td>Civil &amp; Environ Eng.; Water Infrastructure</td>
</tr>
<tr>
<td>Dr. Dietrich</td>
<td>Virginia Tech</td>
<td>Research Mentor; Participant Selection</td>
<td>Civil &amp; Environ Eng.; Analytical Chemistry</td>
</tr>
<tr>
<td>Dr. Xia</td>
<td>Virginia Tech</td>
<td>Research Mentor; Participant Selection</td>
<td>Crop &amp; Soil Environ Sciences – Soil Chemistry</td>
</tr>
<tr>
<td>Dr. Weiss</td>
<td>Virginia Tech</td>
<td>Research Mentor; Participant Selection</td>
<td>Geoscience; Coastal Engineering</td>
</tr>
<tr>
<td>Dr. Lohani*</td>
<td>Virginia Tech</td>
<td>Project Director (PI); Program Coordinator; Recruitment &amp; Selection; Assessment; Cohort Experiences/ Professional Development; Dissemination; Research Mentor</td>
<td>Civil and Agricultural Engineering; Watershed Instrumentation, Hydrology, and Engineering Education</td>
</tr>
<tr>
<td>Dr. Irish</td>
<td>Virginia Tech</td>
<td>Research Mentor; Participant Selection</td>
<td>Civil &amp; Environ Eng.; Coastal Engineering</td>
</tr>
<tr>
<td>Dr. Pruden</td>
<td>Virginia Tech</td>
<td>Research Mentor; Participant Selection</td>
<td>Civil &amp; Environ Eng.; Environmental Contaminants</td>
</tr>
<tr>
<td>Dr. Sharma</td>
<td>Virginia Tech</td>
<td>Research Mentor; Participant Selection</td>
<td>Architecture and Design; Industrial Design</td>
</tr>
<tr>
<td>Dr. Schreiber</td>
<td>Virginia Tech</td>
<td>Research Mentor; Participant Selection</td>
<td>Hydrogeosciences; Chemical Hydrogeology</td>
</tr>
<tr>
<td>Prof. Kennedy</td>
<td>Virginia Tech</td>
<td>Research Mentor; Participant Selection</td>
<td>Architecture and Design; Biomimicry</td>
</tr>
<tr>
<td>Dr. Muffo</td>
<td>Independent Assessment Consultant</td>
<td>Evaluation/Assessment</td>
<td>Academic Assessment</td>
</tr>
</tbody>
</table>

* Project Management
Appendix 2.
NSF REU Summer 2014 Research Projects
Virginia Tech NSF/REU Site: Interdisciplinary Water Sciences and Engineering
Summer 2014: Research Projects
REU Site Duration: May 25 – August 2, 2014

Project ID# 1: Evaluating the Efficacy of Water Quality Treatment on Cyanobacterial Blooms; Mentor: Dr. Carey
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. The REU participant will be involved in a project in collaboration with the Western Virginia Water Authority (WVWA) to evaluate the efficacy of two engineering systems recently deployed in a local drinking water reservoir. To combat cyanobacterial blooms, the WVWA has deployed a coupled hypolimnetic oxygenation system and a mixing system to prevent both nutrient release from the reservoir sediments and algal scum formation. The REU student will work with a graduate student mentor to conduct intensive field sampling to monitor the effects of the systems on water quality. Specific projects for the REU include: 1) determining the effects of the oxygenation and mixing systems on thermal stratification, algal blooms, and nutrient cycling; 2) conducting microcosm water quality experiments; and 3) conducting snorkeling surveys of in situ cyanobacterial recruitment traps. Experience and interest in field sampling, especially snorkeling, would be highly beneficial.

Project ID#2: Water Quality for Human Health and Aesthetics; Mentor: Dr. Dietrich
The increasing demands on the world’s water supplies has led to: 1) the need for using lower quality water sources for drinking water supplies; 2) water supplies being contaminated by potentially toxic and odorous chemical spills such as the one which occurred with the licorice smelling crude MCHM in Charleston, West Virginia. Unresolved issues related to use of these lower quality sources include increased treatment, concern about nutritional and aesthetic content of drinking water. Projects for the REU fellows could include: 1) evaluating human exposure to dissolved aqueous metals and aqueous particulates through inhalation from vaporizers and showers; 2) performing sensory evaluations with human subject to determine suitable mineral content of drinking waters and to determine the concentration range at which humans can detect and describe tastes and odors; 3) isolating and identifying the odorous chemicals in natural and engineered drinking water; 4) research related to communicating the value of drinking water for healthy living.

Project ID#3: Hydrology and Hydraulics Impacts on Ecological Health 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 urbanization, stream restoration, or mining 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; using geophysical techniques to monitor surface water or groundwater movement; installing, monitoring, or downloading hydraulic and water quality...
sensors; 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 4 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: Bio-Inspired Water Stewardship Lab; Mentor: Prof. Kennedy
Professor Kennedy's current research explores how the emerging field of Bio-Inspired Design can be used as a powerful tool for developing sustainable solutions to today's global resource challenges. His current projects are focused on ways Biological approaches to capturing and filtering potable water can be applied to designs benefiting communities across the income spectrum. According to the UN, more people die annually from water-based sickness than warfare, and yet many communities lack local solutions for addressing their water safety needs. Bio-Inspired Design projects will seek to tackle problems of critical global need as well as local water quality, such as the PCB contamination of the New River. By harnessing the 'Design Thinking' skills in students, coupled with the knowledge of biology and engineering students, we will explore solutions that are appropriate and responsive to their communities' needs. The REU participant will (i) conduct extensive preliminary research in the area of bio inspired water treatment/purification initiatives, (ii) work with an industrial design student to propose an appropriate solution to a specific problem and, (iii) document the project in the form of a research paper.

Project ID#6: Development and Implementation of a Raspberry Pi-based System for Processing and Remote Access of Real-Time Environmental Data; Mentor: Dr. Lohani
Dr. Lohani established a LabVIEW Enabled Watershed Assessment System (LEWAS) for remotely assessing real-time water quality and quantity data from a creek that flows through Virginia Tech campus. The LEWAS uses LabVIEW programming to enable the remote access to the real time environmental data collected through sensors. A water quality sonde provides the capability to sense temperature, conductivity, dissolved oxygen, turbidity, and pH of water. A flow meter measures the flow in 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. Six NSF/REU participants have worked in this lab since 2008. Currently, a new system in being developed to enhance the reliability of real-time collection and processing of data. This system deploys a Raspberry Pi, a single board computer with LINUX environment, to collect data from the LEWAS sensors and store these in a database. A user will be able to
access the data from this database through an interactive user interface. The REU participant will participate in integrating the hardware and software components of this new system using programming languages such as Python, PHP and SQL. He/she will be mentored by a PhD student along with Dr. Lohani and will be expected to write a research paper.

**Project ID#7: Biogeochemical Controls on Contaminant Transport and Transformation; Mentor: Dr. Schreiber**

This project’s goal is to examine the biogeochemical controls on trace element transport and transformation in natural waters. To do this, we utilize hydrologic, geochemical, and biological techniques in the field and laboratory to determine rates of reaction and properties of the medium/contaminant, in order to construct quantitative models that can be used to simulate transport and transformation. The REU participant would conduct field monitoring and lab experiments and compile results in the form of a research paper. Experience (and interest) in field sampling, analytical chemistry, and environmental chemistry would be highly beneficial.

**Project ID#8: Designing empowerment: Development of a community level hydropower generation solution for impoverished communities; Mentor: Dr. Sharma**

Prof. Sharma's research explores the role of design as a catalyst for empowerment of people living below the poverty line. The current project is looking at creating alternative sources of energy for people living in off the grid situations. One test location is the Himalayan region in India subcontinent which is home to approximately 40 million people. About half of the households have no access to electricity, and where 5 access is provided, the quality of power is erratic and poor, with electricity available no more than 40 percent of the time. The Himalayas “have some of the greatest potential to capture energy from the sun and water as it is home to fast flowing water streams. Most households in the Himalayas, if electricity is inaccessible, use Kerosene to light their homes. With the low cost availability of solar lights, PV panels and other solutions of this nature, why it is that kerosene is still the preferred choice for illumination. Is it possible to develop a community supported, hydro power generation system that would also support community engagement. The REU participant will: (i) conduct extensive literature survey and analyze existing alternative energy solutions, (ii) Will work with an Industrial Design student to develop a proposal for a solution that is inspired by the lifestyle of end users rather than driven by technology, and (iii) document research results and experiences in a paper for a conference / journal publication.

**Project ID#9: 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 Strouple’s 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 fate of 4-nonylphenol in sediments is also investigated. 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#10: Mechanisms of Cupric Ion Control of Legionella in Premise Plumbing; Mentors: Drs. Pruden and Edwards

Legionella pneumophila (LP) is an opportunistic pathogen found in building plumbing. LP can cause Legionnaire’s Disease (severe pneumonia) in immune-compromised individuals, hospitalizing 8,000 to 18,000 people each year. To explore the possibility of combating LP by selection of plumbing materials, the effectiveness of inactivation of LP by copper is being studied with eighteen simulated water heater reactors. Two plastic pipe materials, PEX and CPVC, are being utilized because past experiments have shown high levels of LP grow on PEX and there is concern of similar findings for PVC. Copper is being dosed as previous studies indicate a possible correlation between free Cu ions and LP inactivation. pH is controlled from 7 to 9, in different reactors. A more basic pH reduces the fraction of copper present as free copper ions, which might allow LP to persist. LP levels are being analyzed via qPCR and agar plating. TOC-MS, ICP, ATP, and AMP Index are also being monitored. The overall goal of this study is to show the relationship between free copper ion levels and LP inactivation, with the expectation that higher levels of free copper will reduce LP. The REU participant would first develop, and then execute, a sub-set of experiments to address this issue, in collaboration with a graduate student, under the direction of Drs. Edwards/Pruden. He/She would also write up the results and hopefully, present the work at a major research conference.
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 2014 REU Site

FIELD TRIPS

Wastewater treatment plant

NOAA National Weather Service forecast station

Water treatment plant
SOCIAL EVENTS

End of summer cookout at Claytor Lake

Enjoying at McAfee Knob

Fun at Claytor Lake

Barbecue in VT Campus