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COLLEGE OF EARTH AND MINERAL SCIENCES

DEPARTMENT OF GEOSCIENCES

**The Use of Water Sensors to Examine Water Chemistry
Related to Marcellus Shale Natural Gas Development**

A Senior Thesis in Geosciences

by

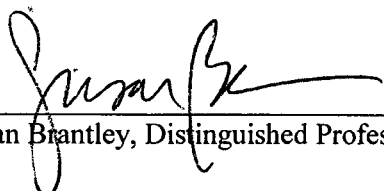
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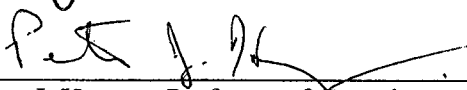
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ABSTRACT

With conflicting information about Marcellus Shale natural gas activities and resulting water contamination coming from pro versus anti-drilling sources, it can be difficult for Pennsylvania citizens to judge the safety of their water. Even after methane contamination has occurred, it has been difficult to prove whether the source was Marcellus drilling activities or something else such as natural seepage. This paper presents a quantitative analysis of what incidents of contamination have occurred along with what can be done to track future incidents and prove the source of contamination. Three water sensors were also tested for their accuracy and ease of use for scientists and nonscientists around Pennsylvania to collect background geochemical data for their wells and nearby streams. Results show that there have been sixty incidents of contamination to land and water in northern and western Pennsylvania from January 2008 to March 2013 but increased regulation correlates with a decrease in the number of major incidents of environmental impact since 2008. Also, improvements need to be made on all three sensors to improve their accuracy and handling of harsh Pennsylvania conditions including high sediment loads in streams and freezing winter temperatures.

It is recommended that more sensors with the ability to collect data such as total dissolved solids and possibly barium and strontium be tested out to determine their accuracy, ease of use, and ability to track Marcellus related contamination compared to the ones tested in this study. Once the best sensors are developed, it is recommended that these be deployed around Pennsylvania with citizens in areas where there is currently natural gas development or it is expected in the future. With public education about these sensors and collection of data from them, incidents could be found faster, background levels around Pennsylvania can be measured, and citizens could get involved in controlling their water's safety hopefully leading to a cleaner natural gas industry in Pennsylvania.

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Chapter 1

Introduction

“Marcellus shale” and “fracking” have become household terms in the past five years in Pennsylvania due to the exploration of a large domestic supply of energy and subsequent occurrence of associated environmental issues. While conventional drilling has been used to extract natural gas in Pennsylvania for many decades, unconventional gas wells have only been widely used since 2004. Conventional gas wells are drilled vertically and only access gas that has escaped from a source rock into a reservoir. Unconventional gas wells use horizontal drilling and hydraulic fracturing to access natural gas still trapped in the source rock so there are higher yields from these wells. Unfortunately, environmental incidents have occurred due to spilling of fracking and flowback fluids on the ground surface and fluids migrating into groundwater. Citizens often question how much danger their water is in. The purpose of this study is to get a more accurate picture of what incidents have occurred and to find sensors that can be used by scientists and non-scientists to collect more water quality data. This data would be useful input into the Shale Network (shalenetwork.org) to help capture incidents quickly and be able to prove them against background data.

1.1 Marcellus Shale Information

The Marcellus Shale is a black shale that was created over 350 million years ago and now lies up to 9,000 feet below the surface of the earth. It covers 95,000 square miles throughout southern New York, Pennsylvania, and into parts of Ohio, Maryland, and most of West Virginia (Soeder and Kappel, 2009). The Marcellus Shale is of particular economic interest because drilling for natural gas has brought hundreds of energy companies and hence significant

employment and business into Pennsylvania. Additionally, there is a lot of local and state investment, natural gas is being marketed as a “bridge fuel” in order to lower greenhouse gas emissions, the shale is close to the densely populated Mid-Atlantic and Northeast, and it is a viable source for domestic energy supply.

1.2 Hydraulic Fracturing

Since 2004, a combination of horizontal drilling and hydraulic fracturing (aka “hydrofracking”) has allowed drilling companies to efficiently extract natural gas as compared to using conventional wells. These natural gas companies drill down to the Marcellus formation vertically and then drill horizontally into it for a significant horizontal distance. According to David Yoxtheimer, a hydrogeologist at Penn State’s Marcellus Center for Outreach and Research, flexible steel is put down the hole to keep the well open, the top few hundred feet are cased in cement to prevent groundwater contamination, and a perforation gun is sent down into the horizontal part of the well to perforate the steel and fracture the shale. Then, millions of gallons of water are sent down accompanied by a proppant (usually sand) and fracking fluid which consists of friction reducers, antibacterial agent, and scale inhibitors and varies in composition depending on the gas company (Yoxtheimer, 2012). Fracking with this mixture opens and extends the fractures so that the gas can escape. It also transports the proppant along the fracture length and, in some cases, transports radioactive tracers through the fractures to determine the injection profile and track the locations of fractures (Harper, 2009).

1.3 Environmental Issues

1.3.1 Water Contamination

There has been surface water and groundwater contamination due to drilling of nonconventional shale gas in the northeastern USA. One type of contamination is due to methane gas that leaks into water systems. The two most common causes of natural gas contamination of

water wells as related to oil and gas development are annular buildup of gas in and around cement casing in the well, usually soon after drilling, and fractures that allow pre-existing gas to get into aquifers (Gorody, 2012). Entrekin et al. (2011) explored the various other pathways that contaminants from the fracking process have gotten into water supplies. One such pathway is through spills from transport trucks, near the well, or from overflow of storage ponds directly onto the land surface which can infiltrate to groundwater or runoff to surface water. Another pathway develops due to the treatment options for the water contaminated by the drilling process. Due to both the high volume and extremely high levels of total dissolved solids (TDS) and radioactive elements in contaminated waters collected at the land surface during shale-gas development, municipal water treatment facilities are not equipped to handle the challenge. Before 2011, gas companies were legally allowed to treat their water by discharging to rivers through these facilities but the facilities were not equipped for the very contaminated water. Nonetheless, the briny gas flowback water was discharged to streams without adequate dilution of the TDS or radioactive elements. A few facilities capable of treating flowback water have been constructed in the past few years. Now, many companies either inject the wastes underground in deep injection wells in Ohio or West Virginia, or they treat on-site and re-inject for ongoing hydrofracturing (Wilson and VanBriesen, 2012). In addition to these contaminants, water quality has also been negatively impacted by increased sediment loads into surface water due to the land use change from building a well pad, roads, pipelines, etc. (Entrekin, 2011).

Osborn et al. (2011) first revealed that deep, thermogenic methane was migrating to drinking water resources near Marcellus drilling wells in northeastern PA and southeastern NY. They found that methane concentrations in the ~60 wells tested in northeastern PA and southern NY were 17 times higher on average in shallow drinking-water wells near active drilling sites (within 1000 meters) than those farther away. Drinking water wells further away not only had lower methane concentrations but also an isotopic signature that was distinctive for a more

biogenic methane source. Osborn et al. claim that new fractures generated by hydraulic fracturing could enhance fluid migration from deep formations into shallow drinking-water aquifers. Although analysis did not include baseline measurements and sampling was not random or regionally spaced over Pennsylvania, this study nonetheless documents the potential for methane to migrate into drinking water resources due to drilling or hydrofracking of Marcellus wells (Osborn et al., 2011).

1.3.2 Flowback Waters

Hydraulic fracturing uses huge volumes of water, ranging between 3-5 million gallons per well, to fracture rock. The ingoing water is mixed with a proppant and chemicals creating a “frack fluid.” The proppant, which is usually sand, gets into the fractures and essentially props them open so that the gas can escape. David Yoxtheimer explains that 8-10 percent of the original frack fluid returns to the surface as “flowback water.” Although it does not seem like a high percentage, it ends up amounting to about 400,000 gallons per fracture (Yoxtheimer, 2012).

Flowback waters contain not only what was sent down the well but also what was weathered out of the formations. These added constituents include cations and anions and organic molecules from brines at depth. The origin of the brines at depth is seawater that was evaporated and then later reacted with limestones to form dolostones (Dresel and Rose, 2010). In addition, brines were often diluted, most often with freshwater but sometimes with seawater. The brines are thought to be present throughout the Appalachian basin at depth. Brines especially contribute Na, Ca and Cl, as well as lower concentrations of Mg, Ba, Sr and Br (amongst other cations and anions) to the flowback water. Dresel and Rose conclude that barium in flowback waters is not from drilling muds because drilling muds also contain high concentrations of sulfate, which flowback waters do not. They propose that barium was added to the brines due to silicate alteration of the original shale. Likewise, strontium was inferred to have derived from limestone in the subsurface (2010).

Warner et al. (2012) further emphasize that Na, Ca, Mg, Ba, Sr, Cl and Br in the flowback water are likely due to the deep brines. Warner also points out that elevated salinity in drinking water wells in Northeast PA was present prior to drilling and is likely unrelated to it. They explain that rebound after glacial retreat may have enhanced natural flow paths, which combined with high hydrodynamic pressure could allow the flow of deep brine fluids up into shallow aquifers. The possibility of drilling and hydraulic fracturing causing the rapid flow of brine to shallow groundwater in low hydrodynamic pressure zones is unlikely and has never been demonstrated. Nonetheless, areas of groundwater with elevated salinity could be at greater risk of contamination from Marcellus activities because of the preexisting network of cross-formational pathways.

Haluszczak et al. (2012) compares flowback water chemistry from Marcellus shale drilling to previous chemistry of oil and gas brines in PA and comes up with three main conclusions. First of all, high concentrations of TDS in flowback do not derive from dissolution of minerals in the shale – injection fluids have near neutral pH with low concentrations of Cl^- and SO_4^{2-} . Secondly, flowback water chemistry is similar to brine chemistry obtained from conventional oil and gas wells (contains a mixture of highly evaporated seawater and injection water). Lastly, high concentrations of Ra^{226} , Ra^{228} , and Ba are attributed to leaching from the rock (possibly due to low SO_4^{2-} levels), but during brine formation as opposed to during the hydrofracking process.

1.3.3 Tracing Contamination

In Pennsylvania, the dominant sources of water contamination are runoff from road salt, agriculture, mines, acid rain, and natural gas drilling activities (Fish and Boating Commission, 2013). We can tell the difference between these by differences in amounts of total dissolved solids, pH, and ions. In general, we can assume that the lower the pH and the higher TDS, the more impacted a sample is, as seen in Figure 1-1.

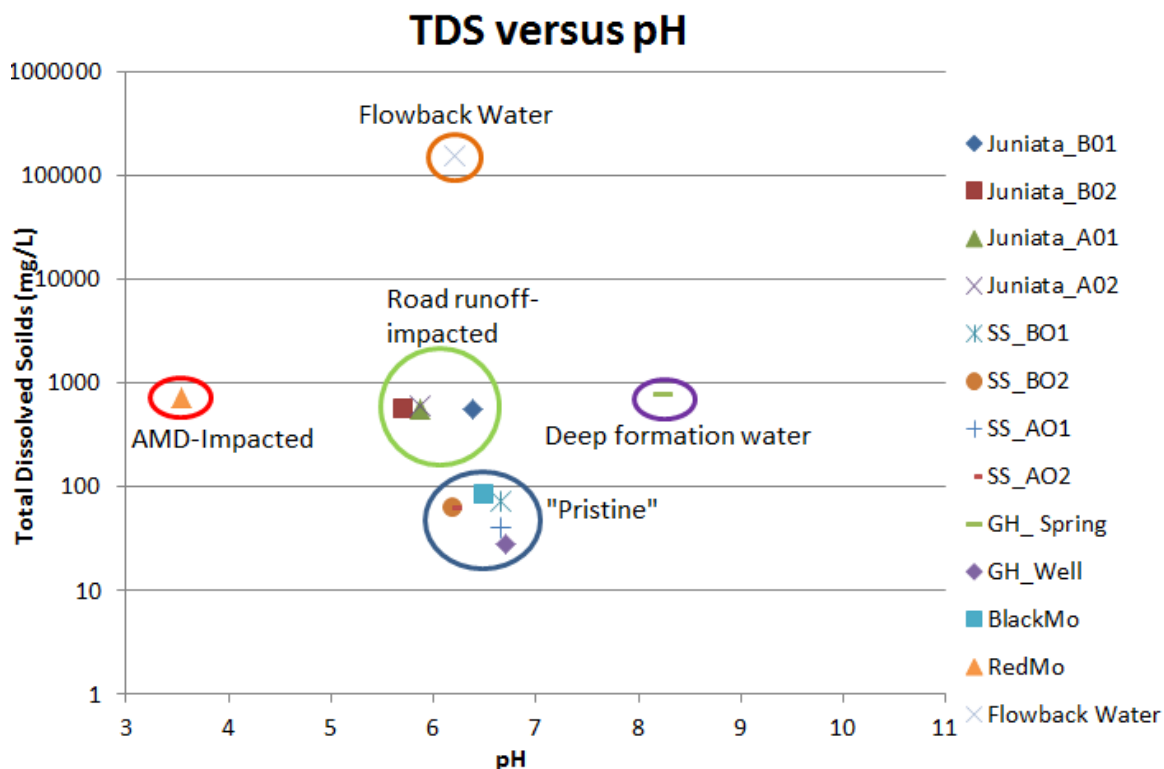
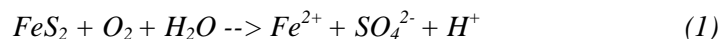


Figure 1-1. Human impact on streams seen via TDS plotted versus pH. The points in the “Pristine” circle are from samples of relatively clean streams including Standing Stone Creek and the Black Moshannon, and also from a pool of rainwater. The points in the “Road runoff-impacted circle” are Juniata River samples that came from right next to Route 22 in Hollidaysburg. The “Deep formation water” sample is from a spring next to an orphaned natural gas well in Grindstone Hollow, from the Red Moshannon (stream widely known as impacted by acid mine drainage), and the “Flowback Water” sample is the average of data from 7 horizontal drilling sites from day 14 of flowback (data from Haluszczak 2012). All data in this figure except the flowback water data was collected in September 2012 by the Geosc 413W class at Penn State (I. Gorski, *unpublished data*)

Acid mine drainage (AMD), acid rain, road salt, and flowback water can all introduce high TDS to a river. AMD and acid rain will decrease the pH to the 3-4 range but flowback and road runoff will not decrease it by much. Flowback will add the highest TDS of the three influences (Kirby, 2011).

The general reaction that causes low pH values in acid mine drainage is (Sams and Beer 2000):



In most AMD that has mixed with meteoric fluids, we expect high levels of sulfate and iron, either as solute or precipitate. Water impacted by road salt runoff is expected to have high levels of sodium and chloride and for agricultural runoff, high nitrate and phosphate and pesticides (Fish and Boating Commission, 2013). The key cations from flowback water include Sr, Ba, K, Li, Mg, and Mn, and their concentrations and isotope ratios can provide important chemical fingerprints for tracing contamination by this water (Blauch, 2009). Chapman et al. (2012) show that the isotopic ratio of radiogenic strontium-87 to the stable strontium isotopes ^{84}Sr , ^{86}Sr , and ^{88}Sr has been effectively used to identify and quantify sources of groundwater constituents in areas impacted by human activity. Strontium isotopes are particularly useful because their composition is not affected by evaporation or biological activity and it is found in highly soluble minerals (unlike Ba which cannot be considered a conservative element in aqueous systems with sulfate because barite often precipitates). There is a narrow range of Sr isotope compositions of Marcellus Formation produced waters which differ from the range of acid mine drainage values that are higher and from fly ash impoundment values which are lower and have very high Ba and Sr values. Therefore, Sr isotopes can be used to trace the source of high TDS in impacted waters (Chapman et al., 2012).

Taking a more quantified look at the difference between acid mine drainage and flowback water, Table 1-1 shows the values of several chemical parameters for the two. The AMD data is from the Fall 2012 Geosc 413W class sampling of the Red Moshannon at 41° 02.196' N, 078° 03.524' (Four samples of 20-25 milliliters (mL) were taken in HDPE bottles. pH and EC were measured directly in the Red Moshannon, anion concentrations were measured with

an Ion Chromatograph and cation concentrations with an Inductively Coupled Plasma Atomic Emission Spectroscope) and the flowback water data from Haluszczak et al. (2012).

Table 1-1. AMD vs. Flowback Water Chemistry

Chemical Parameter	AMD Concentration (milligrams per liter, mg/L)	Flowback Water Concentration (mg/L)
pH	3.53	6.2
TDS	727	157000
Cl	1.26	98300
SO ₄	449	50
Br	0	872
Al	3.23	0.5
Ba	0.03	1990
Ca	78.32	11200
Fe	0.47	47
K	1.39	281
Mg	37.32	875
Na	11.61	36400
Sr	0.26	2330

AMD pH is lower than that of flowback water; TDS and concentrations of Cl, Br, Ba, Ca, K, Mg, Na, and Sr are significantly higher for flowback water than AMD-impacted water. The two different sources of contamination can be distinguished by these differences, mainly the lower pH for AMD and higher TDS for flowback.

1.4 Use of Sensors to Detect Issues

1.4.1 Study Purpose

Environmental water quality issues have rarely been reported in peer-reviewed literature from Marcellus Shale natural gas problems (Considine 2012). While this may be because the industry is environmentally clean, it may also be because the density of our sampling network throughout Pennsylvania is too low in density to detect issues (Figure 1-2 shows all water analysis locations for PA that have been registered as HydroServers with the CUAHSI Hydrologic Information Systems). Increasing the density of sampling sites is difficult because it relies on funding for labor. In this research, I focus on addressing one aspect of this question by investigating use of chemical sensors that could be deployed, perhaps at lower cost. I also look at incident reports to investigate where water quality issues have already occurred to allow research into whether water quality data has already been collected that document these incidents.

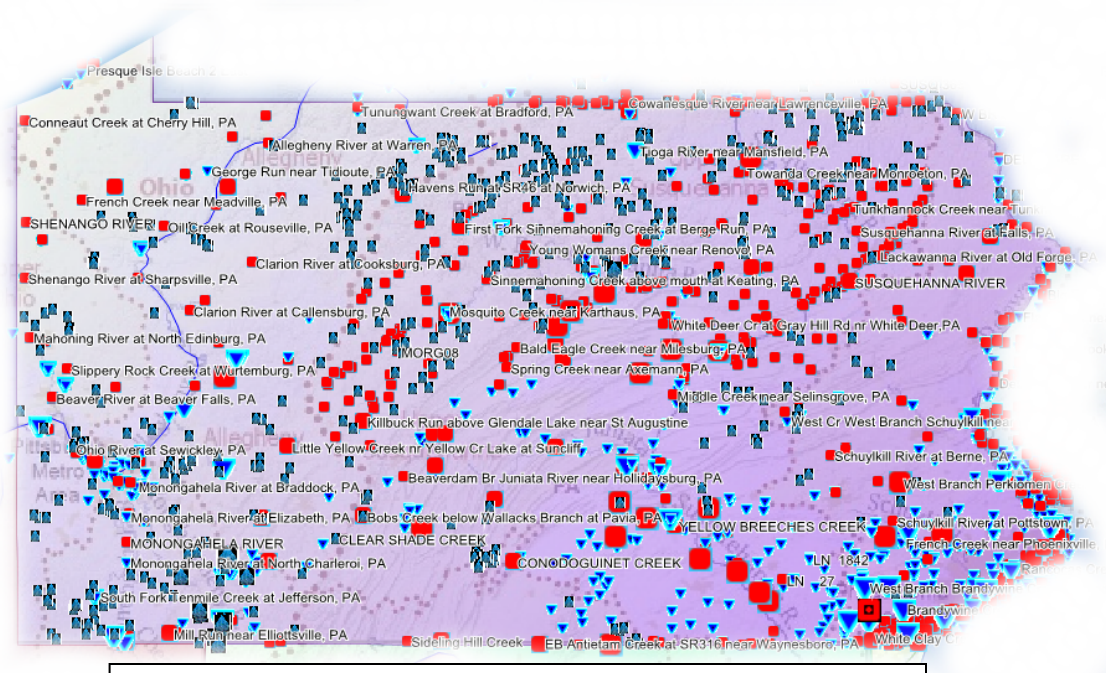


Figure 1-2. HydroDesktop map of sampling sites or sensor sites (for any analyte) currently in PA that are registered as Hydroservers in CUAHSI HIS, as well as USGS and EPA sites.

- ▲: Data from the USGS NWIS
- : Data from the US EPA
- : Data from the Shale Network

This map was made on April 1, 2013 and there were approximately 900 sites in Pennsylvania at this time.

1.4.2 Study Objectives

The study objectives are (1) to determine what incidents have happened in Pennsylvania using sources including the Pennsylvania Department of Environmental Protection's Oil and Gas Compliance Report, Considine et al. (2012), and Myers (2012); (2) to seek records of these incidents in online data in the CUAHSI Hydrologic Information System using HydroDesktop; (3) test three water quality sensors to determine their accuracy and accessibility; (4) deploy these sensors in an area potentially impacted by natural gas development.

Chapter 2

Methods

In this project, three different sensors were tested to determine their accuracy and accessibility for future use by citizen-scientists to track contamination around Pennsylvania. Two of the sensors were deployed first in the Shale Hills CZO. Then, after determining where incidents of contamination have occurred due to Marcellus Shale development activities, I deployed them at Blacklick Creek, downstream of the outlet from a flowback water treatment plant (Wilson and VanBriesen, 2012). I also collected and analyzed water samples from the Shale Hills stream and Blacklick Creek during the time I deployed the sensors in order to test the accuracy of the instruments. The third sensor, meant for testing water in a home, was deployed at Karen Reese's residence (from now on referred to as "the private residence") in Grindstone Hollow near an orphaned natural gas well.

2.1 Searching for Incidents of Contamination

As a starting point, I searched public databases and previously published work for incidents of contamination due to Marcellus drilling activities. The sources I used were public databases and websites: *Hydrodesktop* (<http://cuahsi.org/HydroDesktop.aspx>) and the Pennsylvania Department of Environmental Protection's Oil and Gas Compliance Report (www.portal.state.pa.us/portal/server.pt/community/oil_and_gas_compliance_report) databases, as well as a report by Considine et al. (2012), and the website *The Environmental Dangers of Hydro-Fracturing* by Myers (2012). I compiled a list of all incidents mentioned from these sources into a table summarized in Appendix A.

2.2 Description of the Water Sensors

Two of the sensors were built by Carnegie Mellon's CREATE (Community Robotics, Education and Technology Empowerment) Lab and the other is from the Austrian company, S::can Liquid Monitoring Liquid Networks.

2.2.1 The CREATE Lab

The CREATE Lab aims to empower common citizens and scientists with tools they need to collect their own data, share it, and take action based on their gathered evidence. Two of the laboratory's sensors made to help citizens are the CATTfish and WaterBot. Both monitor temperature and electrical conductivity (EC). Both water monitors are easy to use.

For both sensors, temperature is read using an analog temperature sensor (mcp9700) and EC is read by sending an alternating current through the water at a set frequency (CMU's CREATE Lab, 2012). These sensors treat the water as a voltage divider, and measure the voltage when it is half-way through one of the cycles (2012).

Total Dissolved Solids (TDS) is one way to track contamination from Marcellus development. The United States Environmental Protection Agency (US EPA) defines TDS as the combined amount of inorganic and organic substances contained in water in dissolved form. A significant increase in the TDS in water can indicate impact from human activities, such as runoff from gas exploration and well construction activities, mines, a farm, or a salted road. According to 2012 data in the United States Geological Survey's (USGS) National Water Information System (NWIS) for pristine streams in Pennsylvania including Standing Stone Creek and the Black Moshannon, a healthy value for TDS in Pennsylvania is about 100 parts per million (ppm) or lower. For reference, the EPA criteria for drinking water is 500 mg/L (for dilute waters, mg/L equals ppm). If impacted by road runoff, agricultural runoff, or acid mine drainage, TDS generally approaches 1000 ppm (USGS 2012). If impacted by flowback water (water that returns

to the land surface after hydrofracturing a gas well), TDS can increase above 100,000 ppm (Haluszczak et al., 2012).

Although it cannot be directly measured with a sensor, TDS is related to electrical conductivity (EC), a parameter that can be directly measured. To find TDS, EC is measured (in microSiemens per centimeter, $\mu\text{S}/\text{cm}$), and the value can be converted to TDS (in ppm) using a formula from Rhoades (1996):

$$TDS = 0.64 * EC \quad (2)$$

EC can vary depending on the ions in solution but 0.64 is a standard conversion factor for natural waters. Electrical conductivity is explained by the US EPA as a measure of the ability of a material to conduct an electrical current. Therefore, the higher the TDS value, the more ionic solutes are present in the water, resulting in a higher EC. (Note that in some waters, significant dissolved solids can be nonionic, in which case the direct relationship between TDS and EC no longer obtains. Such cases are rare however.) Both the WaterBot and CATTfish measure EC, and from this measurement the amount of total dissolved solids in the water can be calculated.

While the WaterBot and CATTfish have similar intended users, they vary in design. The WaterBot was designed to empower citizen scientists to monitor streams in local watersheds. All data from WaterBots are uploaded to the public website *waterbot.org*, where it is accessible to anyone.

2.2.2 WaterBot

The WaterBot is intended for use in streams. It has three main components: the data-logger, chip, and receiver USB (Figure 2-1).

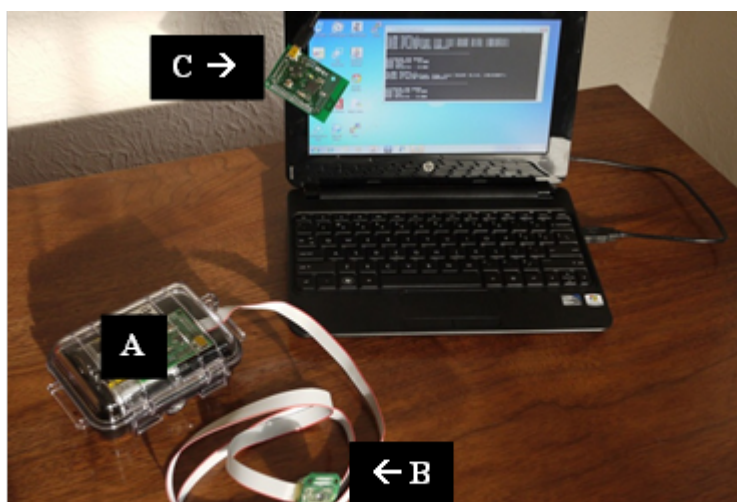


Figure 2-1. A setup of the WaterBot for uploading data. (A) is the data-logger, (B) is the chip and (C) is the receiver USB.

The data-logger contains a circuit board that both stores and transmits the data. The other components of the WaterBot are the sensor chip, which is submerged in the stream to make measurements, and the receiver USB which is maintained far from water and is only used when collecting data from the Bot.

To use the sensor to monitor a stream, the data-logger is mounted to a fence post or other such object to anchor it on the side of the stream. The data-logger must be kept dry and protected since it is not completely waterproof. The chip at the end of the computer wire (B) should be free-floating in the stream.

Data must be recovered from the WaterBot data logger at least every two weeks so as not to exceed its memory limit. If it exceeds the limit, the data is written over previously collected data. To recover data, WaterBot's computer software, WB Uploader, was first set up. The steps for software set up are summarized in Appendix B.

When operating in the field, this software must be open on the computer and the receiver USB attachment connected to the computer, making sure the sensor is within 300 feet line-of-sight. The steps used to collect the data are summarized in Appendix C.

2.2.3 CATTfish

The CATTfish was created to empower homeowners with wells and is intended to be deployed in a toilet tank. As long as no filter is used on the toilet line, a homeowner can use it in this way to analyze the chemistry of their well water directly.

The CATTfish has two main components: a screen read-out with a round silver button and a chip (Figure 2-2).

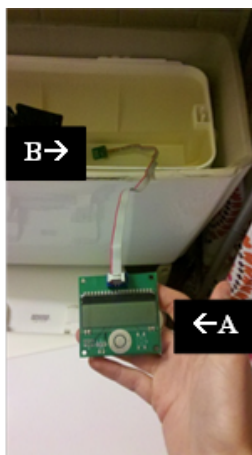


Figure 2-2. Setup of the CATTfish. (A) is the screen readout with the round silver button that hangs out of the toilet tank and (B) is the chip in the tank reservoir.

The chip is placed into the toilet tank with the screen hanging over the outside of the tank, secured in place with the tank cover. To get a CATTfish reading on drinking water that has been filtered, the chip can be placed in a cup of this water. The CATTfish does not store data so it must be recorded by pen or camera. To catch any changes as soon as possible, data should be collected daily. Pressing the round silver button brings up the reading on the screen. The data shown on the screen is four temperature values in degrees Fahrenheit and then four EC values (shown on the screen as “conductance”) in $\mu\text{S}/\text{cm}$ (Figure 2-3).



Figure 2-3. CATTfish screen readout with temperature values followed by conductance values.

The temperature values are read in order as current temperature, temperature minimum (since installation) after the down arrow (↓), temperature maximum after the up arrow (↑), and average temperature after the “A”. The EC values follow the same pattern: current EC, EC minimum (after ↓), EC maximum (after ↑), and average EC (after “A”). Time should be recorded along with the current and maximum conductance values and convert EC to TDS using equation (2). The sensor is designed to help homeowners discover a jump in TDS (such as above 700 $\mu\text{S}/\text{cm}$) that might be a cause for concern.

2.2.4 S::can Spectro::lyser

The company that created the third sensor, S::can, is an 11 year old company based in Vienna that focuses solely on online water quality measurement. They develop and produce measuring instruments for each individual parameter for typical applications in the areas of water, waste water, environmental monitoring, and industrial applications. They focus on optical methods because they believe they are the most reliable, simplest, lowest cost, and most accurate methods. They try to design products by emphasizing simplicity, novelty, and integrity and strive to increase quality monitoring of water in order to reduce the harmful effects to the environmental and human health (S::can Liquid Monitoring Networks, 2013).

The sensor from s::can that was tested was not designed for nonscientists but was designed for deployment by technical personnel: the s::can spectro::lyser. It is significantly more complicated than the previous two sensors because it measures more analytes, has more complex software, and must be periodically cleaned.

2.2.4.1 Methods Used by the S::can Sensor

According to the manual, the s::can spectro::lyser is based on a spectroscopic measurement in the UV and visible of five quantities (total suspended solids – TSS, nitrate as nitrogen – $\text{NO}_3\text{-N}$, dissolved organic carbon – DOC, total organic carbon – TOC, and optical quality). The cell is immersed in the surface water and water flows into the cell within a light beam. The light beam is emitted by a xenon flash lamp, and after the incident light passes through the water, its intensity is measured by a detector over a range of wavelengths. The analyte molecules absorb radiation at known wavelengths. The turbidity calculation is done by estimating the scattering in visible wavelengths. This scattering effect is factored out when the other constituents are calculated. The less light that is transmitted through the water-filled cell, the more the light beam is attenuated, and the higher the calculated concentration of the analyte for a given wavelength. In terms of nitrate, the sensor measures incident versus transmitted light at a wavelength between 200-220 nm and compensates for cross-sensitivities at other wavelengths. DOC is measured at a wavelength between 240-300 nm, and is compensated for turbidity. This sensor has a 35 mm path length and a spectral resolution of 2.5 nm between wavelengths of 200 and 750 nm. Measurements can be collected at up to 2 minute intervals (S::can Liquid Monitoring Networks, 2007). Data can be collected both as spectra and as concentration per analyte. The calculated concentrations are derived from calibration algorithms provided by s::can. Several calibration algorithms are available for waters of different character including municipal water treatment plants, stream waters, polluted waters, etc.

2.2.4.2 Components

In order to operate the s::can spectro::lyser, the following must be deployed: the sensor, a control center for the electronics called the “con::nect”, a computer, and a cleaning system. The spectro::lyser sensor’s components, without the cleaner, are shown in figure 2-4.



Figure 2-4. S::can spectro::lyser device parts. (1) Probe’s housing (emitter side); (2) Measuring section; (3) Probe’s Housing (detector side); (4) Cable gland; (5) Probe cable; (6) Connector.

The sensor, also called a probe, has a measuring section, stainless steel housing on both sides of the measuring section, and a cable that connects to the con::nect. The measuring section is 35 mm wide and when taking a measurement, shoots a light beam across from the xenon light emitter to the detector.

The con::nect provides a power supply for the connected instrument, controls the automatic cleaning via the cleaning valve, and transmits data to the connected computer. The con::nect’s components are shown in figure 2-5.

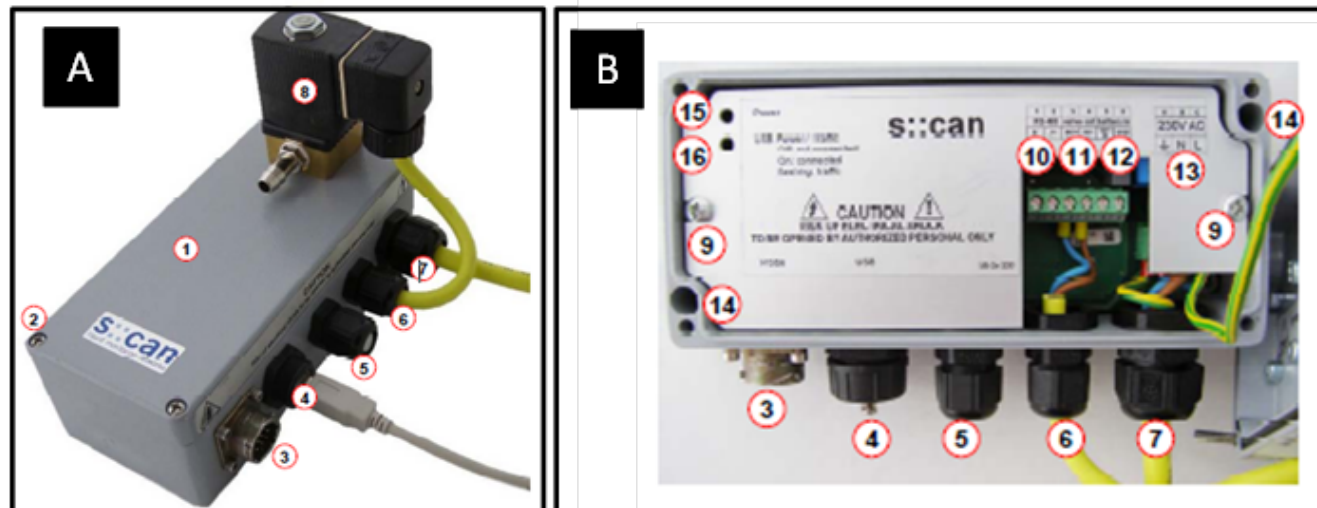


Figure 2-5. S::can connect device parts. (A) is with housing cover on, (B) with housing cover off. (1) Housing, (2) Screw joint to open housing cover, (3) MIL-connector for s::can spectrometer probe, (4) Connector for USB-connection cable to PC, (5) Additional cable bushing, (6) Cable bushing for connection of cleaning valve, (7) Cable bushing for connection of power supply, (8) Cleaning valve, (9) Screw joint to open cover panel, (10) RS 485 terminal, (11) Connection terminal cleaning valve, (12) Connecting terminal 12 VDC power supply for battery operation, (13) Connecting terminal power supply AC, (14) Drillings for mounting of connect, (15) Power supply control LED, (16) USB connection control LED.

There are four main ports for connecting the probe, computer, cleaning valve, and power cord. In figure 2-5, the following locations are shown: (3) where the spectro::lyser cable connects, (4) where the USB cable connects the computer, (6) where the yellow cord for the cleaning valve connect, and (7) where the power cord for AC electricity connects. The probe, USB cable, and power cord plug directly into the connect at (3), (4), and (7) but the cleaning valve requires an extra step. As seen in figure 2-5, part B, there is a small blue and orange wire associated with the plug-in for (6). When plugging in the cleaning valve, these two wires must be fed through (6) and plugged into (11) (the blue wire into the terminal third from the left and orange wire into the terminal directly to the right of that). These terminals provide power to the valve (Figure 2-5A, item 8) which controls the cleaning system.

Since this sensor was designed to be deployed long term in various locations such as water treatment plants or natural waterways, sediment may sometimes obscure the lenses of the measuring section. Therefore, a cleaning system is part of the system. The components that come along with the sensor are a cleaning valve with yellow power cord attached and a 3/8 inch plastic air hose that is UV and ozone resistant (figure 2-6).



Figure 2-6. Cleaning valve and connections to it. (1) Plastic air hose with adapter fitting, (2) Larger connection side of the cleaning valve that connects to the plastic air hose, (3) Yellow tubing that connects to the connection, (4) Thinner connection side of the cleaning valve that connects to the vinyl tubing, (5) Hose clamp, and (6) 3/8 inch vinyl tubing.

The air hose has an adapter fitting at one end shown (figure 2-6 shown as (1)) that attaches to the cleaning valve on the larger connection side (2). The yellow hose (3) and the attachments for the other side of the cleaning valve must be purchased separately from a hardware store. These attachments include four feet of 3/8 inch vinyl tubing (5) and a hose clamp (6) to hold this tubing onto the cleaning valve at the thinner connection side (4).

As part of the cleaning system, compressed air is required to clean the spectrolyser lenses. In this application, I used a 20 pound CO₂ tank with a regulator, which was purchased separately from the spectrolyser. The other end of the vinyl tubing should connect to this as seen in figure 2-7 with a hose clamp.



Figure 2-7. CO₂ tank with regulator and 3/8 inch vinyl tubing connected.

The other end of the air hose screws into the probe on the underside of the measuring section as seen in figure 2-8.



Figure 2-8. Submerged spectro::lyser with 3/8 inch air hose screwed in.

Teflon plumbers tape is used to seal all connections. The cleaning of the spectro::lyser is accomplished by a compressed air blast directly to the measurement section.

2.2.4.3 Field Setup

When choosing a site to install the spectro::lyser, many factors were taken into account. First of all, the water that the sensor is submerged in must be moving but there should be low turbulence. Flow velocity should not exceed three meters per second to avoid cavitation (Scan, 2007). The sensor should be submerged in water with a minimum level of ten centimeters and a temperature between zero and forty-five degrees Celsius (2007).

The required infrastructure for field setup will vary by site but the components used for this study include: (1) a 12 Volt DC battery (e.g. car or lawnmower) + AC/DC Converter (not

needed if AC power is available); (2) a Pelican case/large enclosure for electronics (and cleaning system/CO₂ tank) to guard from weather/animals/people/etc.; (3) a post to mount into ground to attach spectro::lyser and secure place in stream; (4) PVC pipes (one five foot piece and one three foot piece of two inch diameter tube and one 90° elbow to connect the two); (5) pipe clamps + nails; (6) zip ties (various sizes); and (6) plumber's putty.

To set up the sensor, we first assembled and cemented the PVC pipes together and threaded the spectro::lyser's cable through the pipes. We then secured the sensor in place (with the measuring section only slightly out of the tubing and facing up) with plumber's putty. Next, we attached the cleaning system plastic air hose to the sensor and zip-tied the hose up around the piping. We then threaded the sensor's cable and this hose into the enclosure to attach to the connect and cleaning valve. Our enclosure was a large wooden box built into the ground so we mounted the PVC piping directly against it. We mounted the piping with pipe clamps around it screwed into the wooden box, at the correct height so that the spectro::lyser was submerged by approximately ten centimeters. The assembly outside of the enclosure is shown in figure 2-9.



Figure 2-9. Picture of spectro::lyser setup at Shale Hills Critical Zone Observatory.

Inside the enclosure, we attached the cleaning system along with the spectro::lyser cable to the connect, as described earlier. To power the sensor and cleaning system, we used a 12 volt DC lawnmower battery and AC/DC converter. We connected the AC/DC converter to the lawnmower battery with its red and black clamps and plugged the power cord from the connect into the converter.

2.2.4.4 Ana::pro

Ana:pro is the software package distributed by scan to support data collection and analysis from the spectro:lyser. In order to set up the frequency of measurement by the spectro::lyser and cleaning, the connect was attached to a computer and ana::pro was run. The program was entered as a guest with no password. The program searches for and locates the connected spectro::lyser and opens up a new window. To set the measuring interval, recording interval, and cleaning interval, “Program”, “Mode”, “Automatic”, and then “settings” were clicked. We set it to collect one measurement per hour and for cleaning every three measurements. Once set up, the sensor was set to logger mode by clicking “Back” to get to the main screen, then “Mode”, “Logger”, and then “Logger mode”.

To collect data from the spectro::lyser, the computer with ana::pro running was connected to the connect. Once the program identified that the instrument was connected, we clicked “Mode”, “Logger”, “Transfer data”, “Transfer”, and then “Download file”. This downloaded a file to the desktop which could then be opened in Excel as a comma-delimited file.

Raw spectral data collected from the instrument was processed using ana:pro, which applies either a global or a user-defined calibration to the spectral data to recover the concentration-equivalent for each variable. To process the data, we clicked “Mode”, “Offline”, “Measurement”, “Select fp file”, and then selected the file to be processed (named by date and time). At that point, we clicked “Clear display”, and “Start”, and then waited for the data to load on the screen, at which point we clicked “Stop”. Next, we clicked “Back” and then “Save file”

and used the RIVCAL Global Calibration. This calibration, provided by the scan staff, is based on data provided by their user community. It is ideal for natural waters which have a relatively wide range of variability in $\text{NO}_3\text{-N}$ and DOC (compared to treated water) and it reduces the effect of turbidity on other components.

2.3 Testing the Water Sensors

2.3.1 In the Laboratory

Before deploying the sensors at Shale Hills CZO, Blacklick Creek, or the private residence, the WaterBot and spectro::lyser were tested for basic functionality in the laboratory and the CATTfish was tested in a local apartment. The WaterBot was submerged in a sink full of water and run for an hour and then the data were collected onto a computer. The spectro::lyser was submerged in the same sink and using ana::pro, several measurements were taken. The CATTfish was put into a toilet tank for a week and data was recorded daily.

2.3.2 Shale Hills Critical Zone Observatory (CZO)

The Shale Hills CZO is a 7.9-hectare forested catchment in central Pennsylvania where the regolith is developing upon homogeneous shale. This watershed is being monitored in order to learn about the creation, evolution, and structure of regolith as a function of the geochemical, hydrologic, biologic, and geomorphologic processes operating in a moderate, forested terrain (Lin, 2006). The site was chosen as a relatively pristine site close to campus to do initial testing of the WaterBot and spectro::lyser. WaterBot was deployed November 13 - 27, 2012 and the spectro::lyser was deployed January 11 - February 10, 2013.

While the spectro::lyser was deployed, samples were taken two to three times per week to later analyze for DOC and anions (mainly nitrate). Two samples were taken for both parameters each time. The samples for anions were collected in 50 mL HDPE bottles labeled “B” along with their sample name, filtered with a 0.45 micron filter, and stored in a freezer until analysis.

Samples for DOC were collected using a 100 mL HDPE bottle. From there, the water was filtered with a 0.45 micron filter, collected in a 15 mL brown glass bottle, acidified with one drop of 50% hydrochloric acid (HCl), covered with a crimped metal cap, and stored in a freezer until analysis.

2.3.3 Blacklick Creek

Blacklick Creek was chosen because it is within a reasonable distance from Penn State University and because it has been impacted in several ways from Marcellus activities . For example, in October 2012, MTN Gathering LLC released bentonite into and near Blacklick Creek (PA DEP, 2013). In addition to this impact, Blacklick Creek is the receiving stream for the PA Brine Treatment Plant in Josephine, Pennsylvania. The plant is a centralized waste facility and has been described by Wilson and VanBriesen (2012) as accepting produced water from conventional and nonconventional oil and gas wells in PA up until 2011. After 2011, the plant still accepts oil and gas wastewater from conventional oil and gas wells and can discharge it because the plant has TDS discharge limit exemptions. Without an exemption, the TDS discharge standard for water treatment facilities is 500 mg/L in PA. The median TDS level reported in effluent from brine treatment plants with exemptions in southwestern Pennsylvania is 130, 100 mg TDS /L (Wilson and VanBriesen, 2012). Three sites along Blacklick Creek both upstream and downstream of the treatment facility were sampled and tested with the spectro::lyser. A fourth site on the adjacent Two Lick Creek was sampled upstream of its confluence with Blacklick Creek. Note that Blacklick Creek enters Two Lick Creek below the point of wastewater disposal from the Josephine plant. These four sites are shown in figure 2-10.

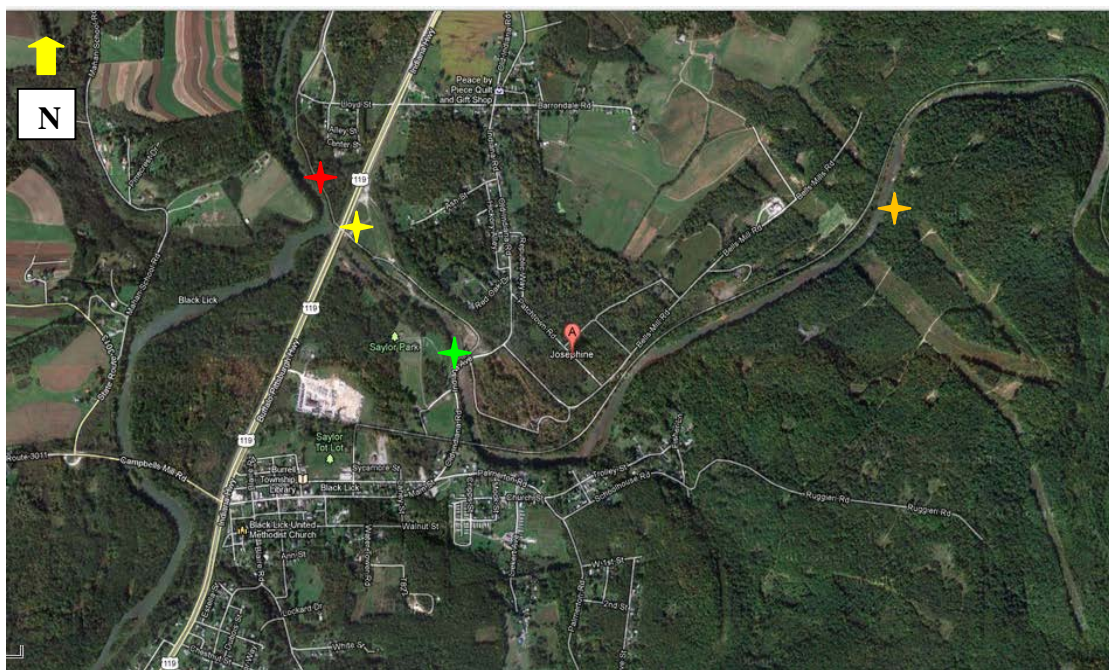


Figure 2-10. Map of Blacklick Creek sampling sites. The four colored stars represent the four places samples were taken from and the spectro::lyser collected data at. The red star is site 1 (on Two Lick Creek, ~30 m upstream of confluence with Blacklick Creek), yellow star: site 2 (on Blacklick Creek around ten meters upstream of where it joins Two Lick, under the bridge for Route 119), green star: site 3 (at the USGS gauge for the NWIS surface water site “03042000 Blacklick Creek at Josephine, PA”, close to the Indiana Avenue bridge in Saylor Park), and orange star: site 4 (on Blacklick Creek approximately 50 meters upstream of the PA Brine Treatment Plant discharge). Blacklick Creek flows west to east and Two Lick Creek south to north.

Sampling Site 1 is located on Two Lick Creek, approximately thirty meters upstream of the confluence with Blacklick Creek and about 200 meters below the point of disposal from the Josephine plant. When we observed the creeks, the discharge for Two Lick Creek was very low at Site 1 compared to the fast-moving Blacklick Creek, and sedimentation was observed to be occurring at the confluence. The spectro::lyser was suspended vertically in order avoid disturbing the fine silty sediment on the stream bank (Figure 2-11). This site was visited and measurements made on March 5, 2013.



Figure 2-11. Picture of vertical deployment at Sampling Site 1, Two Lick Creek.

Site 2 is located on Blacklick Creek around ten meters upstream of where it joins Two Lick, under the bridge for Route 119. It is downstream from the brine treatment facility. This site was visited and measurements made on February 19, 2013.

Site 3 is located at the USGS gauge for the NWIS surface water site “03042000 Blacklick Creek at Josephine, PA” at Latitude 40°28'37" N, Longitude 79°11'13" W, close to the Indiana Avenue bridge in Saylor Park. It is also downstream from the brine treatment facility. This site was visited on February 19 and March 5.

Site 4 is located on Blacklick Creek approximately 50 meters upstream of the PA Brine Treatment Plant discharge. It was accessed via Ghost Town Trail on March 5. While walking to this location, visual observations of the facility discharge were made. There is a discharge pipe which likely drains from the treatment facility directly into the stream as well as two ponds with bright orange sediment, likely caused by acidic conditions, draining to the stream (Figure 2-12).



Figure 2-12. Pictures from around Sampling Site 4. (Left) Bright orange sediment; (Right) discharge pipe, likely from treatment facility.

On February 19, two samples were taken from each site (2 and 3), one for anions (B) and one for DOC. On March 5, four samples were taken from each site (1, 3, and 4), two for anions and two for DOC.

According to information from the Abandoned Mine Reclamation Clearinghouse, Blacklick Creek watershed is significantly polluted by acid mine drainage. Based on water quality sampling from 1973 and 1974, an average net acid load of 335,000 pounds per day were discharging into Blacklick Creek from acid mine drainage. The specific sources of this AMD are predominantly deep mine workings or coal mine refuse banks. Commercial mining at the Bells Mill Mine in Josephine (downhill from the PA Brine plant along the creek) was active from 1905-1937 and other mines have operated into more recent times. Small scale mining dates back to the 1800s (Abandoned Mine Reclamation Clearinghouse, 1978). The Blacklick Creek Watershed

Association lists around 300 AMD sites in the watershed, many of which have received minimal treatment (Blacklick Creek Watershed Association, 2009). In a 1967 study, Blacklick Creek was identified as being one of the most mine-affected streams in the Allegheny River Basin with a stream pH below 3.0; (U.S. Department of Interior, 1967). A USGS study showed a decline in sulfate (the main indicator of AMD based on the dissolution of pyrite under acid conditions) in Blacklick Creek from 1965 to 1995; coal production in the Blacklick Creek Basin, which reached its peak at almost 4 million tons per year in the 1940's, dropped to less than 1 million tons per year by 1995 (USGS, 2000).

2.3.4 Karen Reese Residence

Grindstone Hollow is the site of an orphaned gas well on Chestnut Grove Road in Bellefonte, PA. We deployed the CATTfish at a residence near this well to see if it might be affecting well water in the area. In addition, this area may soon experience drilling and hydrofracturing (Reese, personal interview), so the CATTfish was used to provide the owner with pre-drilling data. Karen Reese's residence is roughly a mile from the orphaned well. The CATTfish sensor was installed in her toilet tank during the months of February and March 2013. This residence obtains water from a nearby spring. It is piped to an outside reservoir where it is held for household use. They do not filter the water in any way. The toilet tank is insulated internally with Styrofoam to help prevent condensation in the summer.

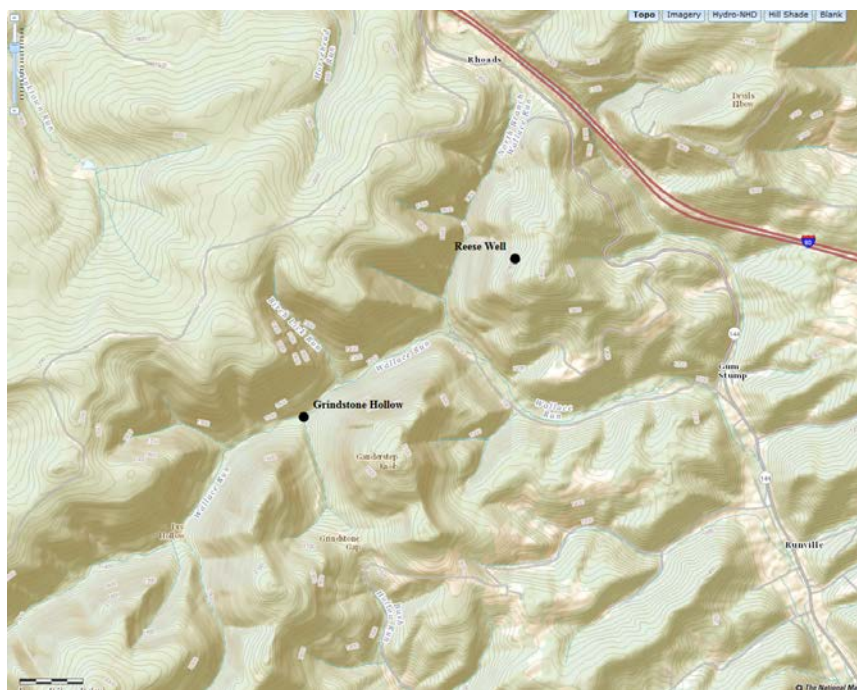


Figure 2-13. Aerial map showing location of Karen Reese's private water well in relation to Grindstone Hollow abandoned natural gas well.

2.4 Analyzing Samples

2.4.1 Nitrate

Anion concentrations in the water samples, including nitrate for comparison with the spectro::lyser, were measured for Shale Hills samples using a Dionex ICS 2500 by Laura Liermann, research assistant in the Department of Geosciences at Penn State University and for Blacklick Creek samples using a Dionex ICS 3000 by Karol Confer, Water Quality Lab manager for the Penn State Institutes of Energy and the Environment. The Ion Chromatograph works by using ion exchange resins packed in a column to separate atomic or molecular ions based on their interaction with their resin. Anions are retained on the column resin and ions in solution are detected by measuring conductivity of the solution as it passes through the detector. Retention time is determined by the affinity of the analyte for the charged group on the resin and the strength of the eluent.

The standards used for the Dionex ICS 2500 Ion Chromatograph were diluted from a stock solution from a company called High Purity Standards. The stock concentrations are 1000 ppm, so they have to be diluted with deionized water to get them down to 10 - 25 ppm in the standards "master mix". The master mix contains 2 ppm each F and Br, 10 ppm each Cl and NO₃, and 25 ppm SO₄. The master mix is not run on the IC; however, dilutions are made of 1:2, 1:5, 1:10 and 1:20 for IC standards. So for example, the concentrations of anions in the 1:2 standard are 25 ppm SO₄, 5 ppm each NO₃ and Cl, and 1 ppm each F and Br. The relative standard deviations for the anions are F = 21.1%, Cl = 3.67%, Br = 12.3%, NO₃ = 15.6%, and SO₄ = 11.3%. The detection limits are F = 0.04 mg/L, Cl = 0.1 mg/L, Br = 0.1 mg/L, NO₃ = 0.5 mg/L, and SO₄ = 0.4 mg/L.

For the Dionex ICS-3000 Ion Chromatograph, chloride was run on a 4.0 - 20.0 mg/L scale and diluted either 1:5 or 1:10. The midscale used for bromide and nitrate was 0.5 - 4.0 mg/L and the low scale used for several of the bromide samples was 0.05 - 0.5 mg/L. Chloride detection limit is 0.02 mg Cl/L. Bromide detection limit is 0.005 mg Br/L and nitrate detection limit is 0.002 mg N/L. Chloride standards were made using a NaCl 1000 mg/L stock solution. The bromide standards were made using a NaBr 1000 mg/L stock, and nitrate standards were made using a NaNO₃ 1000 mg/L stock,. From these stock solutions, a 20 mg/L intermediate standard was made and then from that, four standards for each scale were made.

Prepping the water samples for analysis involved putting 600 µL of sample into a vial using a digital pipette, sealing the vials with filter caps, and putting them into the machine with no blank spaces in the racks. Vials with deionized water and standards were placed before and after the samples to ensure that there was no contamination from the column. The anion samples were taken directly from sample bottles from Shale Hills CZO and Blacklick Creek so they were filtered but not acidified.

Blacklick Creek samples were diluted 1:50 and 1:100 and were also run undiluted. In the cases where concentrations were analyzed after dilution, the concentration of the original sample was computed by: $C1 = C2/D$ where $C2$ is the concentration of the diluted sample and D is the dilution factor which is equal to the final volume divided by the initial volume.

2.4.2 DOC

DOC concentrations in the water samples were measured with the help of Dr. Ephraim Govere using the Shimadzu TOC-500A in 439 ASI Building at Penn State University. Samples were put into glass vials for analysis. Standards were run in the beginning and after every ten samples. Standards with concentrations of 15 and 30 parts per million (ppm) were alternated. To make the DOC standards, we started with 1000 ppm potassium biphthalate stock solution made up according to an EPA method (2.125 grams of potassium biphthalate in 1 liter of deionized water with 1 mL sulfuric acid). Zero ppm standard was made with three drops of ultrapure HCl in 100 mL of deionized water. A five ppm standard was 0.50 mL stock solution plus three drops of ultrapure HCl in 100 mL of deionized water. Fifteen ppm standard is 1.5 mL stock solution plus three drops of ultrapure HCl in 100 mL of deionized water. Thirty ppm standard is three mL stock solution plus three drops of ultrapure HCl in 100 mL of deionized water. The standard vials were filled 1/2 to 3/4 of an inch full after being rinsed seven times with deionized water and once with the standard solution. Standards were simply poured into the vials, not filtered. Around 5 mL of sample were put into each vial after 1/2 mL of the filtered sample was used to wash out the vial.

Two samples from separate sampling dates were selected for duplicate and spiking. These samples were the second one taken on January 29, 2013 and the first one taken on January 31. Nothing was done to the duplicate sample; these two aforementioned samples were simply run a second time. For the spiked samples, each of these two samples was run a third time with 50 microliters (μL) of stock solution (per 5 mL of sample) added. The spike was pipetted into the vial with the sample.

Chapter 3

Results

3.1 Summary of Incidents

Incidents from companies drilling for natural gas from Marcellus Shale were compiled from three sources: (1) Considine et al. (2012); (2) Myers R. (2012); and (3) Pennsylvania Department of Environmental Protection's Oil and Gas Compliance Report, accessed on March 22, 2013. Together, they cover incidents that have occurred from December 8, 2008 until March 22, 2013, all listed and detailed in Appendix A.

Considine et al. (2012) discussed all of the Notices of Violation (NOVs) in the Pennsylvania Department of Environmental Protection's (PA DEP's) Oil and Gas Compliance Report between December 4, 2008 and August 16, 2011 and described only the "major environmental events". The criteria used in that study to define such a major environmental event was that the notice of violation (NOV) on the PA DEP Oil and Gas Compliance Report was not described as an administrative or preventative order but instead was described as an event resulting in major site restoration failure, serious contamination of local water supplies, major land spills, blowouts and venting, or gas migration. To be considered a major environmental event (spill) on land, the spill had to be greater than 400 gallons. From the research over the 44 months indicated, 2,988 violations were issued. Of these, 1,144 were for a violation that involved an environmental event and the other 1,844 violations were administrative violations or citations to prevent pollution. The administrative violations were considered by the authors as unimportant because they had no direct environmental impact but were related only to paperwork. Some common examples of these administrative violations are "Failure to submit well record within 30 days of completion of drilling", "Failure to submit annual production report", and "Failure to

affix, in a permanent manner, a registration number on a well within 60 days of registration” (PA DEP, 2013).

In turn, 25 of these environmental incidents were considered “major environmental events”. The streams that they listed that were impacted from these 25 major events are Pine Creek (Lycoming County, Mar. 15, 2009; discharge of Airfoam), Stevens Creek (Susquehanna County, Sept. 16, 2009; ~8000 gallons of flowback water spilled), Brush Run (Washington County, Oct. 10, 2009; temporary aboveground transfer line released 10,500 gallons of partially recycled flowback water), Little Laurel Creek (Clearfield County, Oct. 12, 2009; cap on a holding tank went bad and spilled ~8000 gallons of flowback water), Dunkle Creek (Hopewell County, Dec. 5, 2009; fracking fluid overflowed a wastewater pit), Towanda Creek (Leroy County, Mar. 19, 2011; blowout caused spill of large amount of flowback water), and an unnamed tributary of Ten Mile Creek (Washington County, July 5, 2011; mud spill).

Robert Myers from Lock Haven University also lists incidents that have occurred between February 2, 2009 and September 1, 2012 (<https://www.lhup.edu/rmyers3/marcellus.htm>). The source overlaps with Considine et al. by 2 years and 6 months so some incidents were found on both sources. His criteria are that any listed incident must represent a significant spill, gas migration, or fire that left the well pad and was not immediately cleaned up. Unlike Considine et al., to list a spill, he imposes no minimum amount of fluid spilled. The streams impacted by Marcellus drilling activities are the same as those mentioned above for the Considine et al. (2012) study, plus a spill into an unnamed tributary of Cross Creek Lake (Washington County, May 5, 2009 where a leaking waste water pipe from a gas well caused a fish kill), Sugar Creek (Bradford County, Feb. 1, 2010; discharge of fracking fluid), an unnamed tributary of Sugar Run (Lycoming County, Nov. 22, 2010; 4,275 gallons of flowback water spilled due to an open valve on an unattended tank), Laurel Lake Creek (Susquehanna County, August 10, 2011; spill of 1500 gallons of drilling mud during attempt to construct pipeline), Larry’s Creek (Lycoming County,

Dec. 26, 2011; two tractor trailers collided on route 287 and spilled fracking fluid), and Loyalsock Creek (Sullivan County, Sept. 1, 2012; discharge of mud, clay, sediment from a company constructing pipeline).

Following the style of the previous two sources, I looked at NOV's from the PA DEP's Oil and Gas Compliance Report for the time period September 2, 2012 to March 22, 2013 and compiled the most significant incidents. I observed 1,253 violations for the almost 5 month period for a total of 154 companies. Many of the companies were repeat offenders and the majority of these NOV's represent either an administrative or preventative order. In my categorization, I defined administrative or preventative as anything having to do with permitting, paperwork, taking measures to minimize pathways for contaminants off the wellpad. Altogether, those in that categorization did not have any environmental impact because it either had to do with paperwork or was an order to do something to prevent contamination before it happened. For wells that had paperwork issues that also resulted in environmental impacts, the database includes information about the NOV related to the actual impact. These preventative orders were dominated by (1) Failure to achieve permanent stabilization of earth disturbance activity (34 cases); (2) Failure to design, implement or maintain Best Management Practices to minimize the potential for accelerated erosion and sedimentation (126 cases); (3) Failure to plug a well upon abandonment (72 cases); and (4) Failure to restore well site within nine months after completion of drilling (21 cases).

Overall, many (~100) companies were cited for not minimizing the amount of sediment they are moving or for not cleaning up after development of the site. My criteria for counting incidents are much less strict than that used by Considine et al. because major incidents with the intensity of those listed in that earlier report are not listed by the PA DEP in the Oil and Gas Compliance Report for this later time period. In other words, no major incidents of the impact level defined by Considine et al. occurred after August 2012. However, there have still been over

one hundred spills of lesser volume on land and into water in the past five months. Many of these included no information on location or details on what happened, or were small, contained to the well pad, and/or cleaned up immediately. I have listed in Appendix A only the spills that left the well pad (22) and therefore could have contaminated water resources. The streams that were impacted in the five month span searched that are likely to have been impacted are Harts Run (Sullivan County, Sept. 4, 2012; around eight inches of bentonite mud in pools on stream ~4000 feet downstream of inadvertent return), Jacob's Creek (Westmoreland County, Sept. 4, 2012; discharge of 100 gallons of drilling mud), Mill Creek (Sullivan County, Sept. 10, 2012; discharge of sediment enough to completely discolor creek), Black Water Run (Sullivan County, Sept. 24, 2012; turbid discharge from dewatering structure), an unnamed tributary of Slack Run (Lycoming County, Oct. 9, 2012; sediment discharge from filter bag), Blacklick Creek (Indiana County, Oct. 15, 2012; release of bentonite), Muncy Creek (Lycoming County, Nov. 21, 2012; sediment discharge from a pipeline), Thorn Creek (Butler County, Dec. 13, 2012; inadvertent return of drilling fluids), Wellman's Creek and Salt Lick Creek (Sullivan County, Dec. 19, 2012; operator caused or allowed unpermitted discharge), Brion Creek (Lycoming County, Dec. 27, 2012; discharge of 232,604 gallons of hydrostatic test water & significant sediment), and Big Bottom Run (Sullivan County, Jan. 31, 2013; sediment-laden water run-off into stream).

In addition to these three sources, I looked for centralized waste treatment facilities that were still permitted to accept produced water under an exemption from TDS discharge limits by the EPA. Wilson and VanBriesen (2012) listed eight facilities still permitted in 2011 in Pennsylvania. These facilities discharged high-TDS waters to Blacklick Creek (Indiana County), Allegheny River (Venango County and Warren County), McKee Run (Indiana County), Conemaugh River, and Susquehanna River (Northumberland County). The facility discharging to the Conemaugh was shut down by the EPA in May 2011 and the facility discharging to the Susquehanna suspended accepting Marcellus produced water in April 2011. Theoretically, all the

other facilities also stopped accepting nonconventional shale-gas production waters sometime in 2011 or by January 2012 at the latest.

Additionally, to get a look at the geography of violations and the companies that are incurring the violations, www.fractracker.org has several helpful maps and tables. One of these maps shows the locations of permits issued, wells drilled, and violations from January 1, 2008 through March 7, 2013, shown here as figure 3-1.

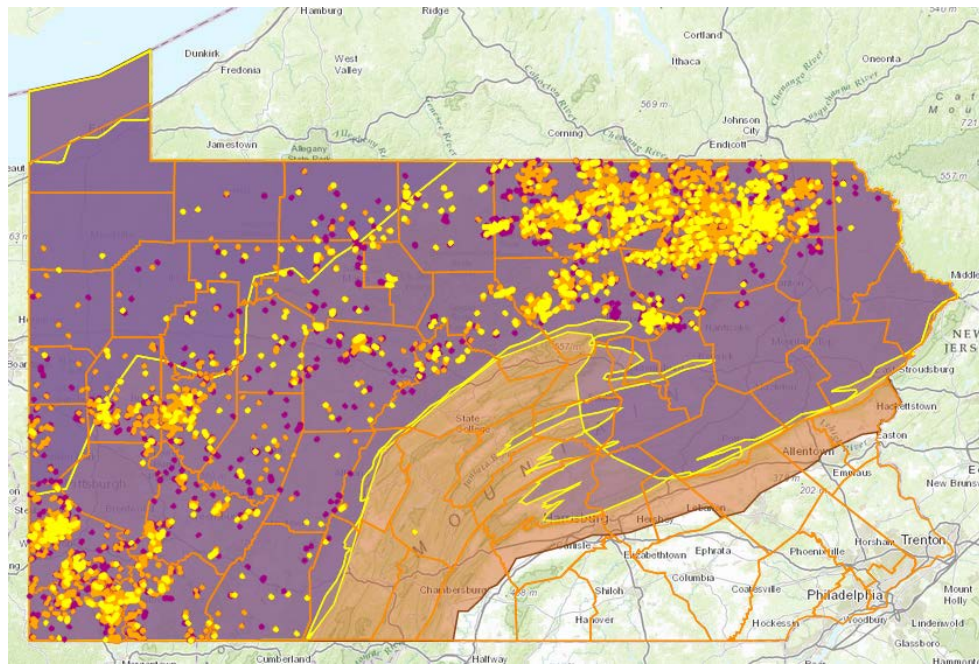


Figure 3-1. Map of Pennsylvania with wells and violations shown. Orange lines show county lines, purple dots show where permits to drill have been issued, orange dots show where wells have been drilled, and yellow dots where violations have occurred, all from January 1, 2008 through March 7, 2013. (from www.fractracker.org).

Development as well as violations have been strongly concentrated in the Northeast and Southwest parts of the state, as expected since this is where the wells are located.

3.2 WaterBot

The WaterBot was relatively simple to deploy and retrieve data from once the software was installed. One problem found was getting the chip to be suspended freely in the water, as seen in figure 3-2.



Figure 3-2. Shale Hills deployment of the WaterBot. A modification was made to allow the chip to be suspended freely in the water (i.e. not floating nor touching the stream bed).

To combat this problem, a board was put across the stream, resting on the two sides of the stream bed. The long cord leading to the chip was wrapped around it, secured with a bungee cord, and the chip was hung down from the board with just enough length to let it be submerged to half the depth of the water. The bigger difficulties with the WaterBot were to get internet access to retrieve the data and that the data had to be retrieved once every two weeks so it would not be written over.

The temperature and electrical conductivity data collected from Shale Hills CZO in November 2012 is shown in figure 3-3.

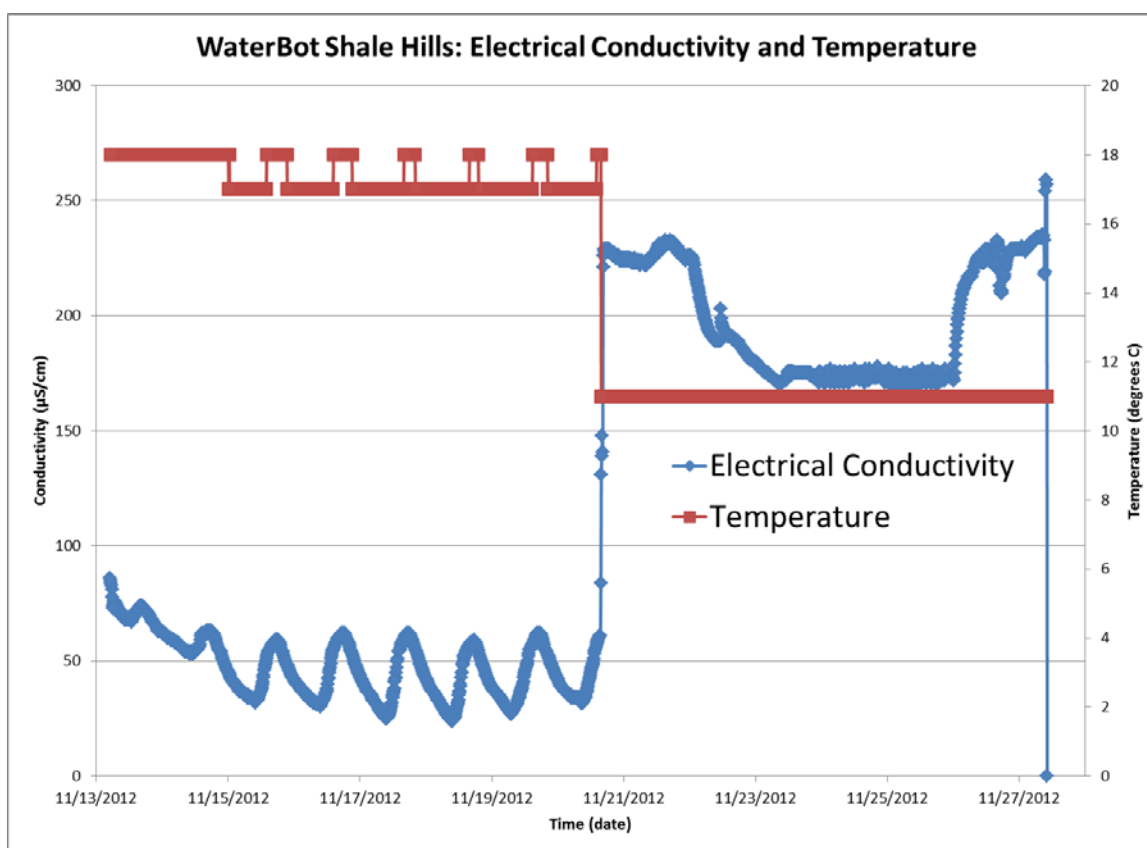


Figure 3-3. WaterBot Shale Hills EC and temperature data, collected November 13–27, 2012. Sensor was placed in the weir of the Shale Hills CZO.

From the date of installation, November 13, until roughly November 15, the WaterBot is likely adjusting to the stream. Then, from November 15 to 20, EC varies daily until 11/21, shown also in table 3-1.

Table 3-1. WaterBot EC Highs and Lows at Shale Hills

Date	EC High ($\mu\text{S}/\text{cm}$)	TDS High (ppm)	Time of High	EC Low ($\mu\text{S}/\text{cm}$)	TDS Low (ppm)	Time of Low
11/20	61	39	4:33pm	32	20	9:23am
11/19	62	40	5:33pm	27	17	8:23am
11/18	59	38	5:43pm	24	11	9:33am
11/17	62	40	5:53pm	26	17	10:43am
11/16	62	40	5:53pm	30	19	9:43am
11/15	59	38	6:33pm	32	21	10:13am

There is a low every day in the morning (8-11am) and a high every late afternoon (4-7pm). Temperature also follows the pattern of a low every day in the morning (17°C) and a high every late afternoon (18°C) during this six day span.

After November 20, the sensor malfunctioned: the temperature read a steady 11°C while the conductivity shot up from 30-60 $\mu\text{S}/\text{cm}$ to 150-250 $\mu\text{S}/\text{cm}$.

Due to this malfunction of the WaterBot in addition to malfunction of the EC and temperature meter brought into the field for comparison, no field comparisons could be made. Therefore, the WaterBot was tested in the laboratory on State College tap water for four days (table 3-2). The EC and temperature meter used was a Mettler Toledo conductivity meter EL3.

Table 3-2. WaterBot Test on Tap Water in the Laboratory

Date	WaterBot		EC &Temp Meter		Error	
	Temp (°C)	EC ($\mu\text{S}/\text{cm}$)	Temp (°C)	EC ($\mu\text{S}/\text{cm}$)	Temp (%)	EC (%)
4/1	40.6	501	42.0	510	3.3	1.8
4/2	39.8	479	41.0	498	2.9	1.8
4/3	42.3	506	43.2	523	2.1	3.3
4/4	36.4	492	38.6	506	5.7	2.8

The average error for the WaterBot based on this laboratory test for temperature is 3.5% and for EC is 2.4%.

3.3 CATTfish

The time series for temperature data from the CATTfish at the private residence near Grindstone Hollow from February 26 to March 15, 2013 is summarized in figure 3-4 and the time series for EC in figure 3-5. As seen in figure 3-4, temperature is higher when the toilet has not been flushed for a while. From figure 3-5, we can see that EC is overall very low, in the 20-35 $\mu\text{S}/\text{cm}$ range, and it does not vary much over time. Although the EC curve follows roughly the

same pattern as temperature, it is not as affected by flushing the toilet and is not always higher or lower due to flushing.

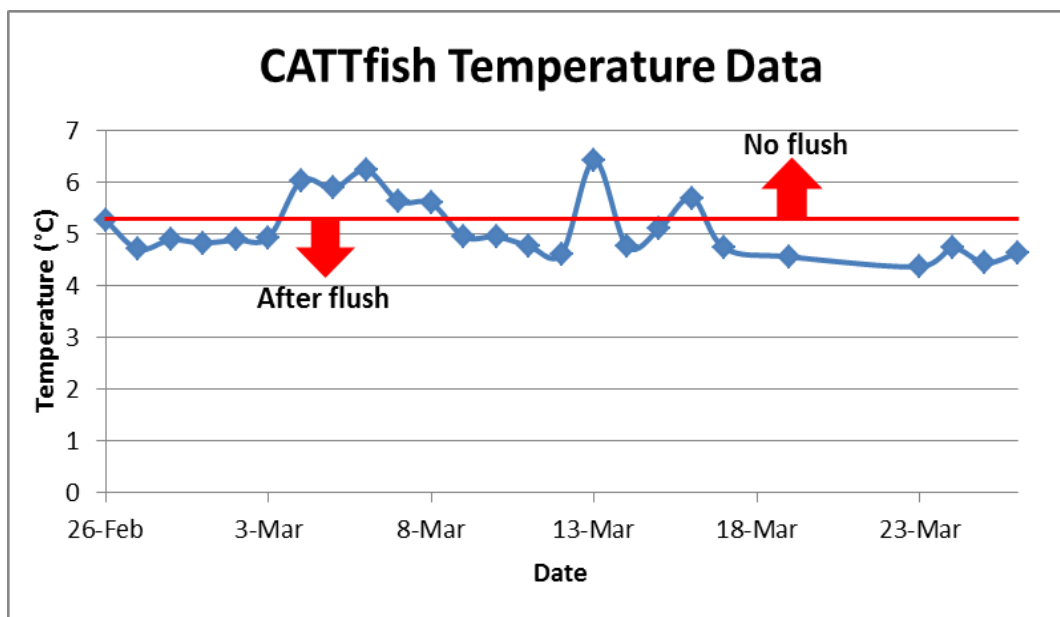


Figure 3-4. CATTfish temperature data, collected from Karen Reese's toilet tank February 26 – March 26, 2013. Below the black line indicates that the measurement was taken soon after flushing and above the line indicates the toilet was not recently flushed. Values taken directly from CATTfish were multiplied by 10 to get them into degrees Celsius.

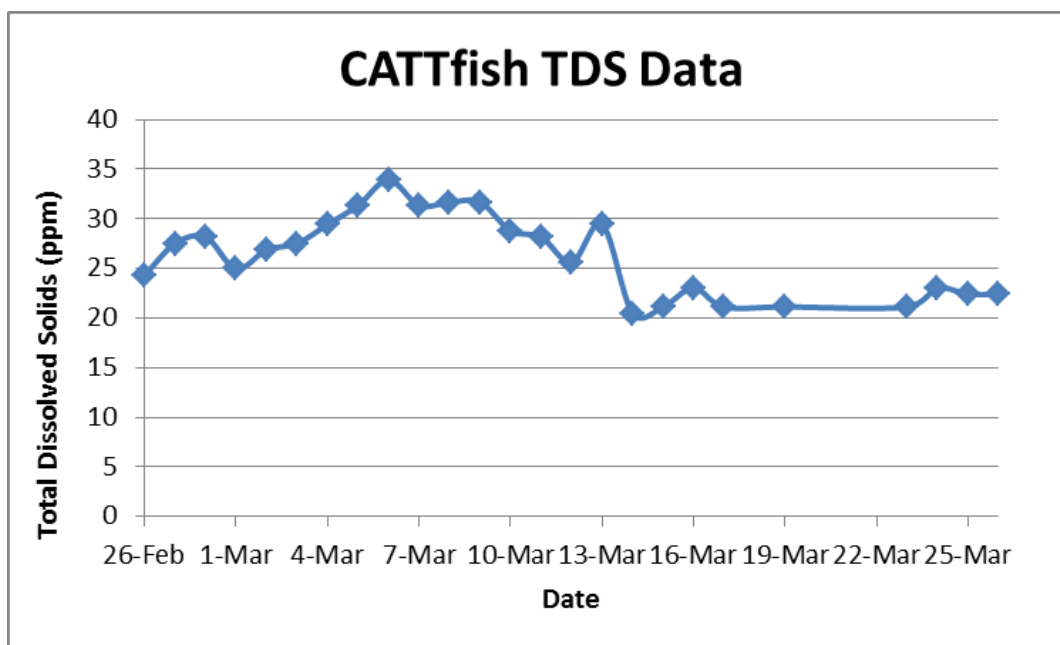


Figure 3-5. CATTfish TDS data, collected from Karen Reese's toilet tank February 26 – March 26, 2013. Electrical conductivity (EC) values taken directly from CATTfish were converted to total dissolved solids (TDS) by equation (2).

Electrical conductivity and temperature data were tested by an EC and temperature meter to judge the accuracy of the CATTfish. The meter was calibrated using an 84 $\mu\text{S}/\text{cm}$ solution and after rinsing thoroughly in DI water, a measurement was taken directly in the toilet tank. This was done on five occasions throughout the month long deployment and the data is summarized in table 3-3. The EC measurements were converted to TDS using equation (1).

Table 3-3. CATTfish Test for Accuracy

Date	CATTfish		EC &Temp Meter		Error	
	Temp ($^{\circ}\text{C}$)	TDS (ppm)	Temp ($^{\circ}\text{C}$)	TDS (ppm)	Temp (%)	EC (%)
2/26	5.2	24.5	5.4	25.0	3.7	2.0
3/3	5.0	27.4	5.2	28.4	3.8	3.5
3/12	4.7	25.8	4.9	25.2	4.1	2.4
3/19	4.6	24.2	4.8	25.1	4.2	3.6
3/26	4.8	23.8	4.9	24.5	2.0	2.9

The average error for the CATTfish based on this laboratory test for temperature is 3.6 % and for EC is 2.9%.

3.4 Spectro::lyser

We had several deployment issues with the spectro::lyser. For example, the cleaning valve leaked so the CO_2 tank ran out halfway through deployment, we had difficulties with the software and this resulted in a gap in data, and the sensor did not respond well at all times in the stream, perhaps due to suspended sediments or the cold temperatures. Figure 3-6 shows the spectro::lyser after two weeks of the cleaning system not running at Shale Hills. Because the cleaning system malfunctioned, the sensor became covered in sediment. In addition, winter conditions resulted in the sensor being submerged under a layer of ice.



Figure 3-6. Spectrolyser photos in bad conditions; freezing temperatures (left) and a lot of sediment (above).

3.4.1 Shale Hills

The results from the scan sensor deployed at the Shale Hills CZO for January – February, 2013 versus the grab samples taken two to three times a week during that time analyzed in the lab are shown in tables 3-4 and 3-5. The two parameters compared were Nitrate and DOC in milligrams per liter. The sensor was underneath several centimeters of ice from January 25 – 29, 2013.

Table 3-4. Spectro::lyser Shale Hills Comparison Data for Nitrate

Date Sample Collected from Field	IC Instrument NO3-Neq Data (mg/L)	S::can NO3-Neq Data (mg/L)	% Difference NO3-Neq
1/15/2013	0.0208	0.031	33
1/15/2013	0.0149	0.031	52
1/17/2013	---	0.025	---
1/17/2013	0.0214	0.025	14
1/25/2013	0.0272	0.034	20
1/25/2013	0.0320	0.034	6
1/27/2013	0.0232	0.033	30
1/29/2013	0.1139	0.087	-31
1/29/2013	0.1113	0.087	-28
1/31/2013	0.0575	0.05	-15
1/31/2013	0.0889	0.05	-78
2/4/2013	0.0224	0.024	7
2/4/2013	0.0190	0.024	21
2/5/2013	0.0217	0.023	6
2/5/2013	0.0227	0.023	1
2/7/2013	0.0238	0	-100
2/7/2013	0.0206	0	---
2/11/2013	0.0595	0.028	-112
2/11/2013	---	0.028	---

The missing data in the table are due to damage of two of the grab samples during transport. The detection limit for NO₃ on the IC is 0.5 mg/L so all of the measurements of the stream are below detection levels. The RIVCAL Global Calibration for the S::can was used for this data. Figure 3-7 shows how well correlated the data from the S::can sensor is with the IC data.

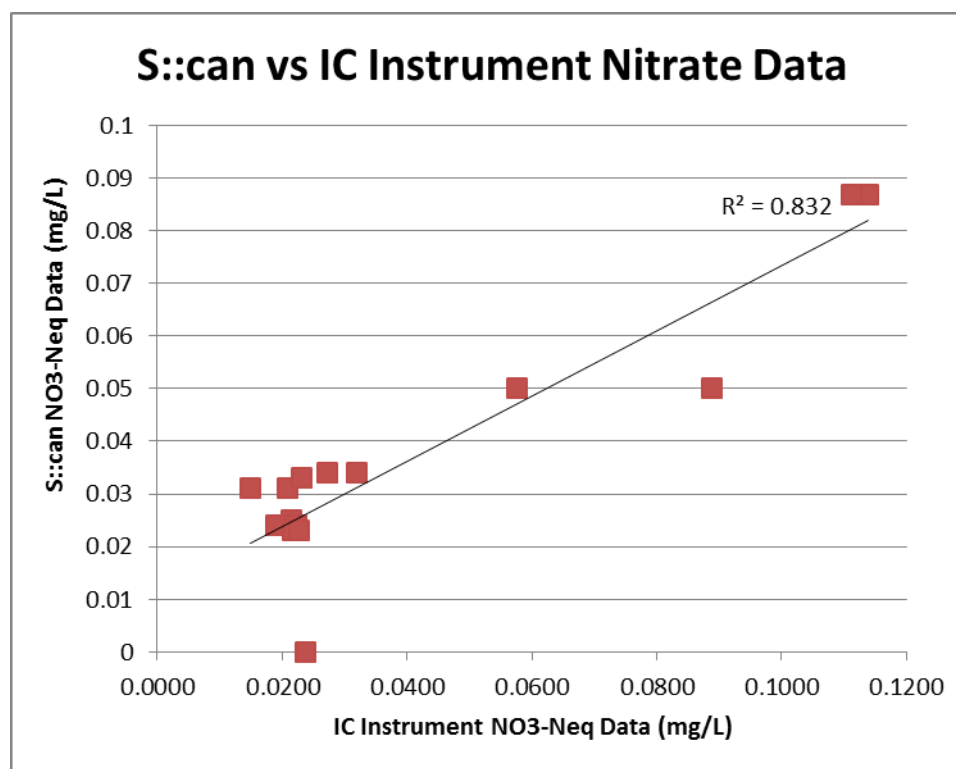


Figure 3-7. Nitrate measurement by the S::can spectro::lyser sensor (y axis) versus the measurement of the grab sample by the IC Instrument (x axis).

The data from the IC instrument and the S::can sensor are fairly well correlated with an R^2 value of 0.832. The detection limit for the S::can sensor for nitrate as nitrogen is 10 mg/L.

Other data collected from the IC Instrument is included in Appendix D. For the Shale Hills CZO, the average concentration for fluoride is 0.092 ± 0.043 mg/L, for chloride is 1.308 ± 0.379 mg/L, for sulfate is 8.983 ± 0.719 mg/L. For Blacklick Creek, the average concentration for chloride is 70.0 ± 27.8 mg/L, and for bromide is 0.318 ± 0.278 mg/L. The concentrations for all three anions in the Shale Hills CZO are relatively low, showing very little contamination. The concentrations for the two anions in Blacklick Creek are relatively high, especially chloride

which has a concentration over fifty times higher than the concentration at Shale Hills, showing contamination possibly from road runoff.

Table 3-5. Spectro::lyser Shale Hills Comparison Data for DOC

Date Sample Collected from Field	DOC Instrument Data (mg C/L)	Spectro::lyser DOC Data (mg C/L)	% Difference DOC
1/15/2013	42.55	1.14	-3632
1/15/2013	33.31	1.14	-2822
1/17/2013	40.9	1.066	-3737
1/17/2013	14.76	1.066	-1285
1/25/2013	19.47	0.691	-2718
1/25/2013	19.34	0.691	-2699
1/27/2013	---	0.675	---
1/29/2013	---	1.158	---
1/29/2013	---	1.158	---
1/31/2013	21.43	2.136	-903
1/31/2013	39.48	2.136	-1748
2/4/2013	18.57	0.899	-1966
2/4/2013	16.56	0.899	-1742
2/5/2013	22.26	0.882	-2424
2/5/2013	28.6	0.882	-3143
2/7/2013	37.1	2.081	-1683
2/7/2013	45.76	2.081	-2099
2/11/2013	2.65	0.763	-247
2/11/2013	1.98	0.763	-160

The missing data in the table is due to three of the grab samples being damaged in transport. The DOC bottles for 1/15-2/7 all broke in the freezer during storage but, upon discovery, were transferred into plastic bottles and allowed to melt while covered with aluminum foil. Again there are very large percent differences, even higher for DOC, for many of the dates. These samples were filtered. These results shown graphically to compare the Spectro::lyser sensor with the Shimadzu TOC-500A are in figure 3-8.

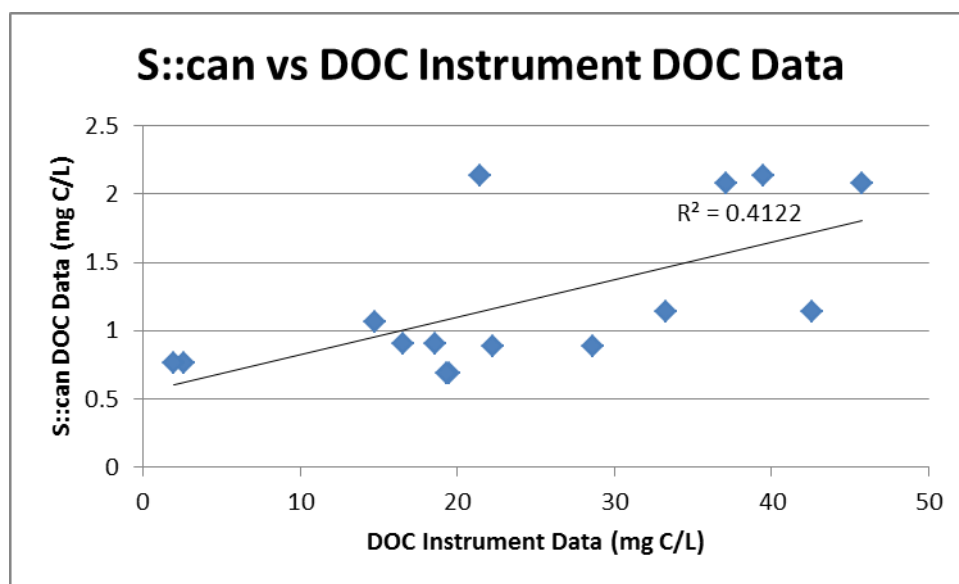


Figure 3-8. DOC measurement by the S::can spectro::lyser sensor (y axis) versus the measurement of the grab sample by the Shimadzu TOC-500A (x axis) for Shale Hills

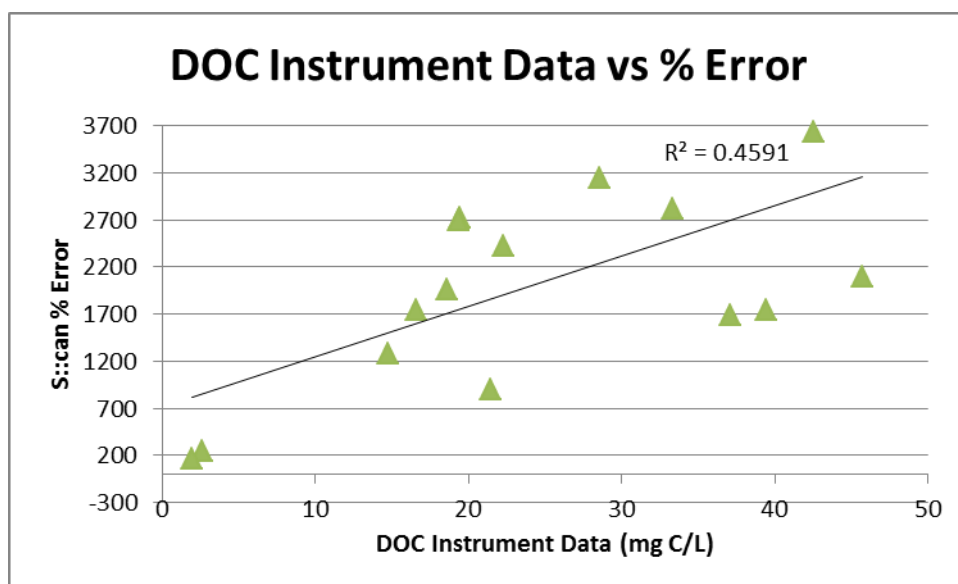


Figure 3-9. % Error for S::can spectro::lyser sensor (y axis) versus the measurement of the grab sample by the Shimadzu TOC-500A (x axis).

Overall, the sensor-measured values for DOC are very low while the values from the Shimadzu TOC-500A in the lab are much higher for all cases besides the two samples from February 11. As seen in figure 3-9, the percent error increases dramatically the higher the concentration of DOC. The RIVCAL Global Calibration was used for this data.

3.4.2 Blacklick Creek

The results from the sensor for the deployment at Blacklick Creek on February 19 and March 5, 2013 versus the grab samples taken on those days analyzed in the lab are shown in tables 3-6 and 3-7. Again, the two parameters compared were Nitrate and DOC in milligrams per liter. Again, the RIVCAL Global Calibration was used for this data.

Table 3-6. Spectro::lyser Blacklick Creek Comparison Data for Nitrate

Location	Month Data Taken	IC Measurement of NO ₃ -Neq (mg/L)	S::can Measurement of NO ₃ -Neq (mg/L)	% Difference
Site 1	March	1.320	1.161	14
Site 2	Feb	0.979	0.837	17
Site 3	March	0.950	0.906	5
Site 3	Feb	0.984	0.837	18
Site 4	March	0.978	0.826	18

There are much lower percent differences for this nitrate as nitrogen data for Blacklick Creek. The highest of these is 18.4% for site 4. The S::can sensor measurement was too low every time. All measurements of nitrate are above the detection limit (0.002 mg N/L). Figure 3-10 shows how well correlated the data from the S::can sensor is with the IC data.

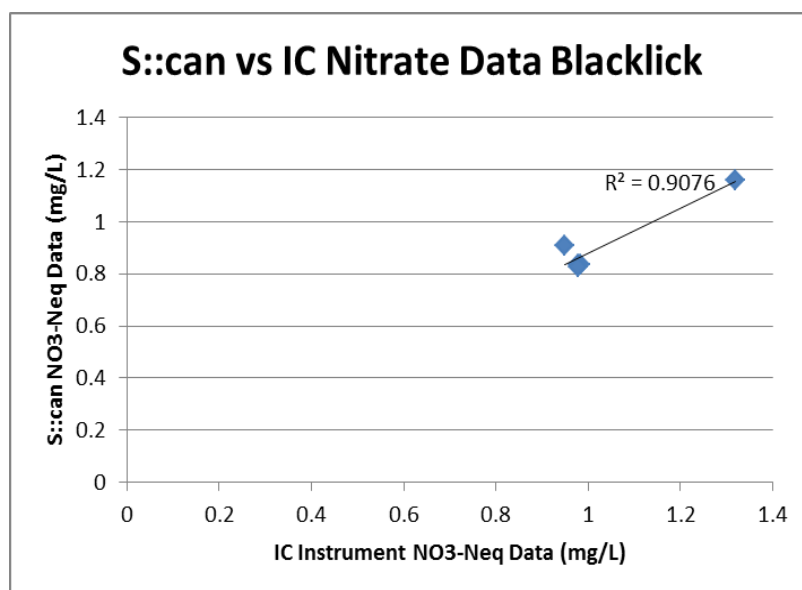


Figure 3-10. Nitrate measurement by the S::can spectro::lyser sensor (y axis) versus the measurement of the grab sample by the IC Instrument (x axis).

The data from the IC instrument and the S::can sensor are fairly well correlated with an R^2 value of 0.9076.

Table 3-7. Spectro::lyser Blacklick Creek Comparison Data for DOC.

Location	Month Data Taken	DOC Analyzer	S::can DOC	% Difference
Site 1	March	BD	0.79	100
Site 1	March	0.25	0.79	69
Site 2	Feb	3.10	0.82	-278
Site 3	March	1.80	0.87	-107
Site 3	March	BD	0.87	100
Site 3	Feb	2.56	0.86	-197
Site 4	March	BD	0.79	100
Site 4	March	BD	0.79	100
BD = Below Detection (<0.1)				

Again, the percent error for DOC measured by the S::can sensor versus analyzed by a Shimadzu TOC-500A in the lab are very large, reaching 278%. The values for DOC as found by the spectro::lyser are all between 0.79 and 0.87 mg/L and those by the Shimadzu TOC-500A are sometimes higher and sometimes lower, even going below the detection limit (0.1 mg C/L). These results are shown graphically for data from the S::can sensor and the Shimadzu TOC-500A in figure 3-11.

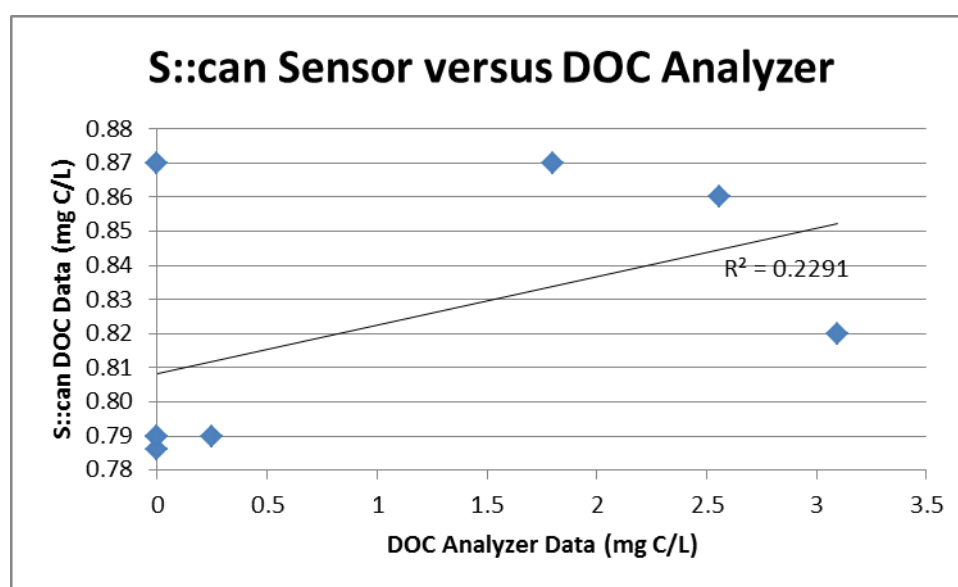


Figure 3-11. DOC measurement by the S::can spectro::lyser sensor (y axis) versus the measurement of the grab sample by the Shimadzu TOC-500A (x axis) for Blacklick

There is close to no correlation between the DOC measurements made by the S::can sensor versus Shimadzu TOC-500A.

To compare to the data found by these two instruments, I also consulted a third source of data, the USGS NWIS. At site 3, data for unfiltered nitrate as nitrogen are reported from 1959 to 1988, listed in table 3-8.

Table 3-8. USGS NWIS Data for Blacklick Creek at Site 3

Sample Date	NO₃-N unfiltered (mg/L)
10/23/1959	1.63
5/3/1960	0.271
1/28/1976	1.36
3/18/1976	1.04
6/18/1976	< 0.40
7/15/1976	0.75
8/12/1976	0.71
11/3/1986	0.44
5/11/1987	0.64
10/19/1987	0.5
5/31/1988	0.56
8/18/1988	0.4

From 1959 to 1988, there is an overall decrease with time for nitrate as nitrogen concentration. All the nitrate data together for Blacklick Creek is shown over time in figure 3-12.

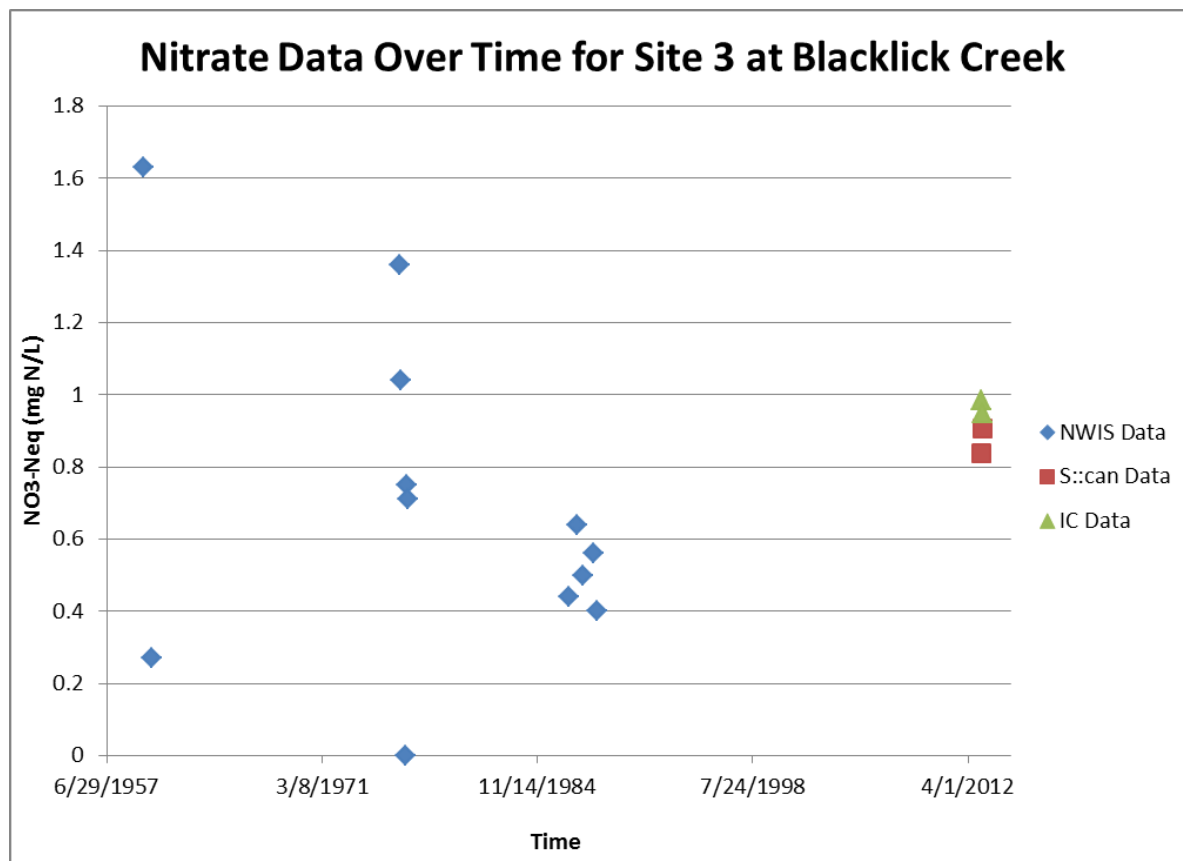


Figure 3-12. Nitrate data over time for Site 3 (the USGS gauge for the NWIS surface water site “03042000 Blacklick Creek at Josephine, PA”, close to the Indiana Avenue bridge in Saylor Park) at Blacklick Creek. Blue diamonds show data from USGS NWIS for October 1959 through August 1988. Red squares show data from the S::can sensor and the green triangles show data from the IC instrument, both for February 19 and March 5, 2013.

The nitrate concentration decreases from 1.63 in 1959 to 0.4 in 1988 and then returns to the middle of those values (0.8 – 1 mg N/L) in 2013.

Additionally, there was DOC and nitrate-as-nitrogen data from the EPA accessed through Hydrodesktop from a nearby stream, Little Yellow Creek. This data is listed in table 3-9 for 2008 through 2012.

Table 3-9. Little Yellow Creek DOC & NO₃-N data

Date & Time	NO3-N (mg/L)	DOC (mg/L)	Date & Time	NO3-N (mg/L)	DOC (mg/L)
8-Apr	0.31	1.1	10-Aug	0.31	0.8
8-May	0.39	1.4	10-Sep	0.46	1.1
8-Jun	0.32	1.1	10-Oct	0.12	1.4
8-Jul	0.31	1.5	10-Nov	0.16	0.7
8-Aug	0.11	1.1	10-Dec	0.64	0.8
8-Sep	0.21	1.7	11-Feb	0.64	0.9
8-Oct	0.05	2	11-Mar	0.53	1
8-Nov	0.11	1.5	11-Apr	0.45	1.3
8-Dec	0.56	1.9	11-May	0.35	1.3
9-Feb	0.51	0.8	11-Jun	0.35	1.3
9-Mar	0.62	0.9	11-Jul	0.4	2.1
9-Apr	0.45	0.9	11-Aug	0.31	1.3
9-May	0.3	2	11-Sep	0.36	1.8
9-Jun	0.29	1.1	11-Oct	0.37	1.7
9-Jul	0.24	1.3	11-Nov	0.44	0.9
9-Aug	0.3	1.5	11-Dec	0.62	0.8
9-Sep	0.36	0.9	12-Jan	0.55	0.8
9-Oct	0.34	2.1	12-Feb	0.53	0.7
9-Nov	0.28	1	12-Mar	0.39	0.9
9-Dec	0.48	0.9	12-Apr	0.31	1.4
10-Mar	0.48	0.9	12-May	0.39	2.9
10-Apr	0.32	0.9	12-Jun	0.44	1.3
10-May	0.32	1.8	12-Jul	0.49	1.2
10-Jun	0.5	1.2	12-Aug	0.47	1
10-Jul	0.34	3.8	12-Sep	0.32	2.7

The nitrate as nitrogen concentrations here for Little Yellow Creek from April 2008 through September 2012 are between 0.11 and 0.64. The range of concentrations from the S::can sensor for Blacklick Creek from February through March 2013 are between 0.826 and 1.161 and

from the IC instrument are between 0.950 and 1.320. Both of these ranges for Blacklick Creek are higher than the range for Little Yellow Creek.

Little Yellow Creek is located north of Blacklick Creek, as seen in figure 3-13. Two Lick Creek flows into Yellow Creek which flows into Little Yellow Creek. Blacklick Creek flows into Two Lick Creek, farther south and upstream.



Figure 3-13. Little Yellow Creek's location (highlighted in yellow) in comparison to Blacklick Creek (highlighted in orange).

Chapter 4

Discussion

Few studies exist to determine water quality impacts of Marcellus shale exploration. Up until now, most studies have investigated the chemistry of shale gas discharge, not the use of sensors to monitor natural water chemistry. These previous studies were used to figure out what to look for to know when an incident has been tracked by the sensors.

My results offer a solution: a way to measure water chemistry at the point of contact for the general public. By sampling water in streams and homes, we gain background concentrations for detection of future incidences of contamination by Marcellus-related discharge. Further development of these sensors, public education about these sensors, subsequent deployment of appropriate sensors around the state in areas being impacted by natural gas development, and collection of data from all of these is needed in PA during this period of rapid Marcellus development.

Future research should include testing out more sensors collecting data that would be indicative of Marcellus impact including electrical conductivity, barium, strontium, to see if they are more accurate and accessible (have affordable cost and are easy to use). Modifications should be made by the manufacturers and by the citizen-scientist users to keep them clean and functioning in very cold and turbid water conditions as well as to collect data for longer and store them in a more user-friendly way.

4.1 Incidents

I present in this thesis a summary of the incidents that have occurred in PA between 2008 and 2013, based on data presented online by the PA DEP (http://www.portal.state.pa.us/portal/server.pt/community/oil_and_gas_compliance_report/20299). In investigating the database, I compiled incidents from Considine et al. (2012), Myers et al. (2012), and the PA DEP Oil and Gas Compliance Report and categorized violations into six categories: (1) blowouts and venting; (2) spills on land; (3) spills into surface water; (4) gas migration, casing, and cementing; (5) site restoration; and (6) fire. Incidents related to erosion problems usually were not listed since they are frequent but not reported as significant; but when they were described as significant, they were categorized under “site restoration” or if the amount of sediment that made it into a stream was quantified, then under “spills into surface water”. By far, the largest categories are spills on land and into surface water. Considine only listed spills larger than 400 gallons but my compilation along with Myers’ lists any spills that were detailed in the PA DEP Oil and Gas Report where the contaminant left the well pad and was not cleaned up immediately.

By analyzing a ten month period that Considine et al. 2012 overlapped with Myers 2012, Considine listed five incidents that Myers did not and Myers listed five that Considine did not. The incidents that only Considine listed were spills that were contained to the well pad and/or were cleaned up immediately or were major site restoration failures. The incidents that only Myers listed were either (1) spills under 400 gallons but which still left the well pad; (2) incidents that occurred away from the well pad. Examples of the latter include (1) a farm where cows were quarantined because they came into contact with flowback water from a leaking containment pond (Tioga County, July 2010); (2) an illegal fracking water transfer station where spilled flowback water covered a 450 square foot area (Canondale, April 2010); and (3) a truck crash where 3400 gallons of flowback water spilled into a private yard (Clinton County, Jan. 11).

Looking at the PA DEP Oil and Gas Compliance Report for this ten month period, one or both Myers and Considine et al. covered all of the incidents with an environmental impact.

Based on my scrutiny of the PA DEP NOV's, there were no incidents during the five month period from September 2012 to March 2013 with as high an impact as the incidents that occurred during the time period of the Considine et al. report (Jan 2008 - Aug 2011). Therefore, it seems that the industry is cleaning itself up, learning from mistakes and the large fines that come with them. At the same time, there is an increase in small violations. There were 445 wells drilled by the end of 2008 and 5674 wells by the middle of 2012. From the research over the 44 months of Considine's report, 2,988 violations were issued (~68 per month); for the five months (Sept 2012 – Mar 2013), 1,253 violations were reported for the almost 5 month period (~250/month). The violations change from violations that include the large incidents listed in the Considine paper to an abundance of preventative orders so incidents will not occur. Despite this improvement, there are still spills occurring into streams, albeit not as large of an amount of fluid (fracking fluid, flowback water, drilling mud, etc.). Regardless, there is still a need to track contamination from Marcellus drilling activities. More so than spills of fluids, it is apparent that many companies are not following the regulations for minimizing accelerated erosion and sedimentation (126 violations from September 2012 through March 2013 for "Failure to design, implement or maintain Best Management Practices to minimize the potential for accelerated erosion and sedimentation"), so increases in turbidity should be monitored near drilling activities.

4.2 WaterBot

Overall, the WaterBot was the better of the two sensors deployed in the stream in terms of accuracy and ease of use. It had the least percent error for all of the sensors, and was slightly better than the CATTfish which measures the same parameters. EC can be a good indicator of impact by Marcellus Shale drilling activities for cases where flowback or production fluids are

spilled. As discussed earlier, flowback water from drilling has TDS levels that are in the hundreds of thousands of milligrams per liter range (Haluszczak et al., 2012) which is drastically different from low natural levels. Furthermore, other common sources of contamination including road salt, agriculture, and acid mine drainage, generally only result in TDS levels as high as 1000 mg/L (Figure 1-1 and Table 1-1). A spike in EC on the WaterBot to levels in the hundreds to low thousands could indicate an impact from road salt, agriculture, or acid mine drainage (which are all worth indicating), and a larger spike could indicate an impact from Marcellus Shale drilling.

Nonetheless, I observed several problems in the WaterBot data collected from Shale Hills. Looking at Figure 3-3, it is unclear why the sensor takes time to adjust and then both EC and temperature data vary in a daily pattern. I expected that the temperature would vary daily with lows right before the sun comes up and highs right before the sun goes down. EC is expected to vary with temperature; the WaterBot is unable to compensate for temperature controlling EC. After observation of the sensor when taking it out of the stream on November 27, it was clear that the measurements toward the end (possibly since November 21) were altered due to the chip being covered in a layer of sediment.

Further looking into the problems with the data that ensued starting on November 21, according to the CREATE Lab, the sensor's range is from 0 to about 1800 $\mu\text{S}/\text{cm}$ and it is most sensitive around the center value of the range of conductivities (150 $\mu\text{S}/\text{cm}$ since the sensor has an exponential response). This most sensitive value corresponds to roughly 100 ppm TDS. At either end, the sensor no longer functions correctly so for EC values below approximately 50 $\mu\text{S}/\text{cm}$, measurements may be invalid. It appears that for the WaterBot's collection of data for November 2012, the conductivity was out of the range that the WaterBot measures that it did not register at all or it shorted out; both are possibilities. Similarly, the lowest temperature that the sensor can detect is 11° Celsius (so the sensor just registers "11" for lower temperatures). Therefore, temperatures below that may have occurred during November. Improvements are

being made by the CREATE Lab but as of now, this sensor should not be used for streams in Pennsylvania to collect accurate temperature or EC measurements during winter months since the temperature and EC may often be lower than the lower detection levels for the WaterBot.

4.3 CATTfish

Looking at the CATTfish data obtained from a homeowners residence in figures 3-4 and 3-5, the temperature was observed to change significantly and frequently, apparently just due to flushing the toilet. The full range of temperature changes (4.2 to 6.3°C) was observed over very short time intervals, for example, over 5 minutes from right before flush to right after. On the other hand, the measured EC was not observed to vary with flushing. As mentioned previously, EC is a good indicator of impact from Marcellus or other contamination. The CATTfish should allow a homeowner to assess easily whether Marcellus brines entered the water supply by spotting a large jump up in the EC reading. The percent error is comparable to the WaterBot's which should be fine for detecting big changes in EC.

The CATTfish worked very well overall for a homeowner who had the time and inclination to record the data by hand. This sensor could be improved if it had memory and some way to upload the data to a computer to allow for better and easier usage of data. In fact however, the fact that it has no software associated with it and the fact that the sensor can be setup in a matter of seconds makes it the easiest sensor to work with. The sensor is ideal for homeowners.

4.4 Spectro::lyser

The spectro::lyser is designed for scientific use and is therefore not a user-friendly instrument that would fare well with non-scientists. Use of this instrument required building the cleaning system and working with the somewhat complicated software. However, it could be an instrument to be used by universities and those inclined to obtain data for a large range of

chemical parameters.

Improvements should be made to make it easier to assemble the cleaning system and to keep it working to preclude sediment covering the instrument. Since the instrument was under several centimeters of ice for about a week and the data collected then does not make sense, the lower temperature range of the instrument should also be extended if possible to allow better use in Pennsylvania streams in the winter.

Looking at the data collected from Shale Hills in tables 3-4 and 3-5, there is a significant amount of error for the spectro::lyser nitrate data and even more for the DOC data. It is possible that in transferring the samples into new bottles when the originals broke in the freezer, the amount of DOC in the samples was altered. Because of this DOC bottle problem, the spectro::lyser's ability to measure DOC should be tested again.

For the data from Blacklick Creek, the DOC and nitrate percent errors are smaller. More care was taken to make sure the bottles did not break. Still, the DOC data is very inaccurate in comparison with the measurements from the Shimadzu TOC-500A. Maybe another calibration from S::can should be used or improvements should be made on the instrument to measure this parameter more accurately. It is unclear why but if you re-scale by a factor of ten, the scan data and lab data fit better together.

4.5 Comparing to Databases

DOC is the concentration of dissolved organic compounds in a water sample reported in units of milligrams of carbon per liter of sample. DOC is often used as a non-specific indicator of water quality: values greater than 1.5 mg C/L are generally representative either of swampy waters or degraded waters (Clescerl et al., 1999). DOC in surface waters comes from decaying natural organic matter and from anthropogenic sources; anthropogenic sources include synthetic compounds such as detergents, pesticides, fertilizers, herbicides, industrial chemicals, and chlorinated organics (US EPA, 2009). Increases in DOC in surface waters can document

impacts from agricultural runoff or industrial discharge, although it is often difficult to identify the specific source (Shih et al., 2010).

Data for Blacklick Creek and nearby Little Yellow Creek were available in the CUAHSI Hydrologic Information System and were accessed through Hydrodesktop. The average nitrate ($\text{NO}_3\text{-N}$) concentration for site 3 at Blacklick Creek for February and March recorded by the spectro::lyser was 0.872 ± 0.024 mg/L and recorded by the IC was 0.967 ± 0.049 mg/L. The DOC data from Hydrodesktop for the same spot from 1967 to 1988 in table 3-8 is lower than this (0.73 ± 0.42 mg/L). Concentration has increased in the past 25 years likely due to Marcellus activities (discharge from the brine treatment facility as well as spills) and other industrial activities that have increased in the area (there is a large power plant in Josephine).

Nitrate levels are lower in Two Lick Creek than in Blacklick Creek, as seen from table 3-6. In this table, site 1 shows concentrations in Two Lick; site 2 concentrations in Blacklick right before it flows into Two Lick; site 3 shows Blacklick further upstream but still downstream of the Brine Treatment Facility; and site 4 shows Blacklick upstream of the facility. Much lower nitrate levels at site 1 in Two Lick compared to levels at sites 2 through 4 in Blacklick could show less impact to Two Lick. This could mean that the area around Blacklick in Josephine, PA generally has pristine waters but Blacklick has been specifically contaminated.

Little Yellow Creek does not have known contamination from Marcellus activities or from any other common source. It is presumably a less impacted creek than Blacklick Creek. Looking at the data in table 3-9, collected from April 2008 to September 2012 and obtained from the EPA using Hydrodesktop, Little Yellow Creek does look like a pristine river with such low DOC concentrations. Since this other clean stream is so close to Blacklick Creek, again this shows that presumably contamination of Blacklick is coming from a point source into the river and not from a contamination source that affects the entire Josephine area. This point source could be the discharge from the PA Brine Treatment Facility or the spill of bentonite into

Blacklick Creek by MTN Gathering LLC natural gas drilling company in October 2012 and discharge from the Pennsylvania Brine Facility into Blacklick.

4.6 Blacklick Creek

Overall, the data collected for Blacklick Creek from the spectro::lyser show significant pollution but it fails to document the specific source. We know from the DEP Oil and Gas Compliance report that Blacklick has been impacted by flowback water spills and discharge from the Josephine Brine Treatment facility. We know from the Abandoned Mine Reclamation Clearinghouse report that Blacklick Creek has also been impacted significantly by AMD. It would be necessary to measure the concentration of other elements to differentiate the AMD pollution from the Marcellus Shale related pollution. As mentioned earlier, sulfate and iron are good indicators of AMD while barium and strontium are good indicators of Marcellus Shale contamination.

Chapter 5

Conclusion

This study has looked at how large of an issue water contamination from Marcellus drilling activities really is and if sensors could be of help. After compiling the most significant incidents of contamination from 2008 to 2013, it is apparent that drilling activities have contaminated at least 25 streams: Pine Creek (Lycoming County), Stevens Creek (Susquehanna County), Brush Run (Washington County), Little Laurel Creek (Clearfield County), Dunkle Creek (Hopewell County), Towanda Creek (Leroy County), an unnamed tributary of Ten Mile Creek (Washington County), an unnamed tributary of Cross Creek Lake (Washington County), Sugar Creek (Bradford County), an unnamed tributary of Sugar Run (Lycoming County), Laurel Lake Creek (Susquehanna County), Larry's Creek (Lycoming County), and Loyalsock Creek (Sullivan County), Harts Run (Sullivan County), Jacob's Creek (Westmoreland County), Mill Creek (Sullivan County), Black Water Run (Sullivan County), an unnamed tributary of Slack Run (Lycoming County), Blacklick Creek (Indiana County), Muncy Creek (Lycoming County), Thorn Creek (Butler County), Wellman's Creek and Salt Lick Creek (Sullivan County), Brion Creek (Lycoming County), and Big Bottom Run (Sullivan County).

Over the past five years, the magnitude of the incidents occurring has decreased from 18 spills of more than 400 gallons between January 2008 and August 2011 to only two spills of that magnitude after that. However, contamination from the natural gas industry in Pennsylvania is still of concern. It is recommended that improvements be made on each of the three sensors tested to see their potential for collecting background data around the state, and more sensors be tested before any further actions are taken. Once the best sensors are found, the simpler sensors should

be given to citizen scientists to measure geochemical parameters around areas of current or future drilling for safety purposes (catching an incident before it impacts water supplies).

If improvements were made to allow the WaterBot to better handle high sediment loads, low temperatures, and low electrical conductivity, it could be an accurate and easy to use sensor to promote for citizen scientists to use in nearby streams even in winter. The CATTfish would be an ideal sensor for a homeowner, especially with improvements made for accuracy and ease of data-recording. The spectro::lyser could be used by dedicated scientists wanting to measure many chemical parameters. In the end, sensors that can measure TDS along with Ba and Sr that can handle heavy sediment loads and a wide range of temperatures, conductivities, and concentrations of elements and are more accurate than these sensors would be ideal. There is hope in the future for public action along with stricter regulation continuing to prevent major incidents!

Marcellus Shale: PA Environmental Incidents

Incident Type	Company	Location	Time	Water affected	Problem	Explanation	Legal Punishment	Remediation	Source of Info	Violation # (DEP)
Blowouts & Venting	Chief Oil & Gas	Bradford County	May-10		Uncontrolled flowback	This flow-back caused more than 1,000 ft of dead vegetation next to the well pad and was found to be major due to this impact on land.			Considine 2012	
	EOG Resources	Clearfield County	Jun-10		Well blowout		Fined \$400,000		Considine 2012 + Myers 2012	589126-31, 589901-02
						A gas well that was being fracked by EOG Resources in Clearfield County experienced a blowout and raged out of control for 16 hours, shooting fracking fluid and gas 75 feet into the air. EOG, whose spokesperson insisted that protecting the environment is of "utmost importance" to the company, waited five hours before contacting the Department of Environmental Protection (Centre Daily Times, "Gas Spews" [6/4/10]). The PA DEP has determined that the accident was caused by "untrained personnel and the failure to use proper well control procedures".				
	Talisman Energy	Tioga County	Jan-11		Blowout	The blowout lasted for several hours and spilled a large amount of fracturing fluids on the well pad located in a state forest. he blowout was caused when blowout preventers failed due to excess pressure.	Fined \$51,478		Considine 2012 + Myers 2012	
	Anadarko Petroleum	Lycoming County	Oct-11		Explosion	Production unit exploded at an Anadarko well site			Myers 2012	
	Chesapeake Energy	Leroy County	Mar-11	Towanda Creek	Blowout	The cause of this incident was equipment failure and resulted in a large amount of produced water flowing into nearby Towanda Creek (Hamill 2011). The impacts of this event are still being monitored, but no aquatic life was harmed, and the water quality of the surrounding wetlands is still normal.			Considine 2012	
Spills on Land	Atlas Resources	Westmoreland County	Oct-09		Diesel spill	790-gallon diesel fuel spill due to the improper connection of a fuel line at its drilling site in Westmoreland County.	Fined \$17,500	Atlas was able to recover 250 gallons of fuel from the spill, but the rest was unaccounted for (PA DEP 2009b). Atlas also placed other collection devices around the spill in hopes of mitigating the impacts further, but was unable to successfully clean up the entire spill.	Considine 2012	
	East Resources	Tioga County	Jul-10		Leaking containment pond	PA Department of Agriculture quarantined 28 cows after they came in contact with drilling wastewater from a leaking containment pond. Tests of the wastewater found that it contained chloride, iron, sulfate, barium, magnesium, manganese, potassium, sodium, strontium and calcium.	Issued a notice of violation by DEP & required to do further sampling and remediation.		Myers 2012	588949-50
	Cabot Oil & Gas	Dimock	Feb-09		Diesel spill	Spilled 100 gallons of diesel fuel.			Myers 2012	575007
	Chief Oil & Gas	Lycoming County	Jan-11		Hydrostatic testing water discharge	Illegally discharged 25,200 gal of hydrostatic testing water at a pipeline project. Chief also allowed an "unknown industrial waste" to mix with the water before it was discharged.	Fined \$34,000		Myers 2012	
	Chief Oil & Gas	Susquehanna County	Jan-11		Fluid spill	150 barrels of production fluid were spilled, but there is no information on whether the environmental impacts had been mitigated. The PA DEP conducted an Act 2 assessment of the site to determine if the polluted land should be considered solid waste and whether it should be removed from the site.		This event was caused by a partially open valve and was the fault of Chief Oil and Gas. The PA DEP has yet to assess a fine for this incident. Chief did follow the proper protocol for reporting the spill.	Considine 2012	
	Anadarko Petroleum	Clinton County	Mar-10		Mud spill	Spilled 8,000-12,000 gal of synthetic-based mud at drilling site in the Sproul State Forest			Considine 2012 + Myers 2012	583988, 584932, 584934
	Anadarko Petroleum	Centre County	Jun-10		Hydraulic fluid spill	Discharged 150 gallons of hydraulic fluid onto the ground at a drilling site.			Myers 2012	589566, 589952
	JW Operating Company	Cameron County	Jul-10		Mud spill	JW Operating Company spilled 1,500 gal of drilling mud; impacts of spill were mitigated. The PA DEP records do not indicate the cause of the event. The JW Operating Company also failed to notify the PA DEP.	Fined \$8000		Considine 2012	
	Cabot Oil & Gas	Susquehanna County	Nov-10		Hose failure	Cabot Oil and Gas reported a spill of 135 barrels, or 5,670 gallons, of drilling mud onto plastic. Cabot was quick to act and was able to vacuum up all of the drilling mud before any major environmental impacts occurred.	NOV		Considine 2012	
	Talisman Energy	Jackson, Tioga County	Jan-11		Production fluid release	~500 barrels (21,000 gallons), of production fluid were spilled into state forestland.	Fined \$24,608	PA DEP & Talisman responded quickly to the spill, avoiding much of the possible impacts. Still serious due to the large amount of fluid spilled & proximity to state forestland.	Considine 2012 + Myers 2012	
	Carrizo	Monroe	Jan-11		Mud spill	Approximately 1,500 gallons of drilling mud and cuttings were spilled when mixing the substance.	None	The spill was completely confined to plastic beneath the rig, so any potential impacts were mitigated. The spill was unavoidable and not the fault of Carrizo because it was following proper procedures. Carrizo also reported this spill to the PA DEP in a timely manner.	Considine 2012	
	Carrizo	Wyoming County	Feb-11		Drilling mud spill	Spilled 500 gal of drilling mud outside of a containment area. Drilling mud is typically made of bentonite clay, water, and other drilling additives.	NOV	Carrizo cleaned up the spill, but did not follow proper procedures for reporting it.	Considine 2012	
	M.R. Dirt	Avis	Jan-10		Drilling wastewater sludge spill	Spilled 7 tons of gas well drilling wastewater sludge. The dump truck driver drove away even though he saw the spill.	Fined \$6000	Fine was paid to Solid Waste Abatement Fund to pay for cleanups across the state.	Myers 2012	
	Stallion Oilfield Services	Canondale	Apr-10		Fracking fluid spill	Operated an illegal fracking water transfer station. Inspectors found 450 square foot area where fracking water had spilled onto the ground.	Fined \$6500	Soil samples showed high levels of chlorides and barium, which are common constituents of fracking water. Stallion subsequently excavated and properly disposed of about seven cubic yards of soil.	Myers 2012	
	Anadarko E&P Onshore LLC	Clinton Conuty, Grugan Twp	Feb-13		Failure to properly store, transport, process or dispose of a residual waste.	200 gallons of triethylene glycol was released to the containment and ground when a union failed on an overhead pipe from the dehydration unit	None	Immediately corrected	DEP	
	Anadarko E&P Onshore LLC	Lycoming County, Cogan House Twp	Dec-12		Failure to properly store, transport, process or dispose of a residual waste.	Pad liner has no berms. wash water leaving liner and infiltrating into the ground	NOV		DEP	632712
	Cabot Oil & Gas	Susquehanna County, Bridgewater Twp	Nov-12		Flowback spill	20 gallons of production fluid spilled due to a hammer union coming apart on the line to the production tank		A total of (20) cubic yards of impacted material has been removed from the site. The impacted material was placed into (2) roll-off containers, each half full.	DEP	656598
							NOV			654812; 654813; 654815

Incident Type	Company	Location	Time	Water affected	Problem	Explanation	Legal Punishment	Remediation	Source of Info	Violation # (DEP)
Spills into Surface Water	Cabot Oil & Gas	Susquehanna County, Brooklyn Twp	Nov-12			Release of 200 gallons of glycol		A total of 21 cubic yards of material were excavated. The excavation was covered with Dura-Skim liner and wooden rig mats were placed over top for safety. The material was staged on site in a roll off container.	DEP	
	Cabot Oil & Gas	Susquehanna County, Jessup Twp	Jan-13			25 gallons of road diesel spilled	None		DEP	655346
	Cabot Oil & Gas	Susquehanna County, Dimock Twp	Feb-13			42 gallons production fluid spilled	None		DEP	657268
	Cabot Oil & Gas	Susquehanna County, Dimock Twp	Feb-13			Water froze and blew out a bull plug from two wells, releasing 20 gallons of production fluid	NOV		DEP	660265-7
	Cabot Oil & Gas	Susquehanna County, Auburn Twp	Mar-13			42 gallons production fluid spilled	None		DEP	661065
	Chevron	Westmoreland County; South Huntingdon Twp	Oct-12			Uncontrolled release of Frack fluids onto the ground while fracking	None		DEP	663106-8
	XTO Energy	Indiana County, Grant Twp	Nov-12		Pit and tanks not constructed with sufficient capacity to contain pollutional substances	Release of 30 barrels of production water from cracked line between two brine tanks. Release not believed to have reached waters of the commonwealth	None		DEP	651551
	Chief Oil & Gas	Somerset County, Jefferson Twp	Jun-11		Hydraulic oil spill		NOV		Myers 2012	653330
	Anadarko Petroleum	Clinton County	Jan-11		Fracking fluid spill		Fined \$180,000		Myers 2012	
	Halliburton	Union County	Aug-12		Hydrochloric acid spill	A truck serving an Anadarko well in Clinton County crashed and spilled 3400 gallons of used fracking fluid into the yard of a private residence			Myers 2012	
	Ultra Resources	Tioga County	Mar-11		Flowback spill	a Halliburton tanker truck leaked 250 gallons of hydrochloric acid, causing a toxic cloud	NOV	Ultra Resources left a valve to a storage tank open and allowed 5,300 gallons of produced fluid to spill. This spill was cleaned up, but did present a high threat to a nearby high-quality water source in Tioga County. Ultra	Considine 2012	
	PA General Energy	Lycoming County	Mar-09	Pine Creek	Creek discharge	Discharged Airfoam into a stream. Airfoam is used to help lift water and drill cuttings to the surface during drilling. The Airfoam escaped when snowmelt and rain washed over the well pad, causing the substance to migrate to a nearby stream.	Fined \$28,960	Operator was able to mitigate the impacts by placing a protective barrier around the stream that had been contaminated by Airfoam.	Considine 2012 + Myers 2012	
	Cabot Oil & Gas	Dimock	Sep-09	Stevens Creek	Fish kill	Approximately 8,000 gallons of produced fracturing fluids spilled into Stevens Creek. The cause of the spill was reportedly linked to the failure of a supply pipe near the creek and resulted in reports of fish swimming erratically in the affected area. Some fish were also found dead in the creek, and the PA DEP reported that the surrounding wetland area was affected as well.	Fined \$56,650	Cabot Oil & Gas eventually cleaned up the impacted area.	Considine 2012 + Myers 2012	572252, 572258
	Range Resources	Washinton County	Oct-09	Brush Run	Stream discharge	A temporary aboveground water transfer line had a connection failure that resulted in the accidental release of 250 barrels, or 10,500 gal, of partially recycled flowback water into Brush Run creek. Approximately 300 minnows were killed by the spill, but other aquatic life in the stream survived.	Fined \$141,175	The site was restored under supervision of the PA DEP, and the environmental impacts have been mitigated.	Considine 2012 + Myers 2012	573283-4, 574350
	EOG Resources	Clearfield County	Oct-09	Little Laurel Creek	Stream discharge	A cap on a holding tank had gone bad and allowed approximately 190 barrels, or 7,980 gallons, of produced fluid to enter creek.	Fined \$99,125	Able to mitigate some of the impacts by flushing the stream.	Considine 2012 + Myers 2012	
	Talisman Energy	Armenia (Bradford County)	Nov-09		Pit overflow	Pit overflow into a small un-named waterway in Bradford County. 4,200-6,300 gallons of fracturing fluid were spilled into the waterway, which is upstream from a fishery. The flowback was caused when a pump failed and sand collected around the valve, causing fluid to flow uncontrolled toward the waterway.	Fined \$93,710		Considine 2012 + Myers 2012	5777167, 577585-87
	Atlas Resources	Hopewell (Washington County)	Mar-10	Dunkle Creek	Pit overflow	Fracking fluid overflowed a waste water pit into a tributary of Dunkle Run, a high quality watershed. Atlas failed to report the spill to the DEP.	Fined \$97, 350		Considine 2012 + Myers 2012	577286-92
	Chief Oil & Gas	Susquehanna County	Jan-11		Fluid spill	Cabot Oil and Gas reported a spill of 135 barrels, or 5,670 gallons, of drilling mud onto plastic.	NOV	Cabot was quick to act and was able to vacuum up all of the drilling mud before any major environmental impacts occurred.	Considine 2012	
	Range Resources	Washington County	May-09	Tributary of Cross Creek Lake	Leaking waste water pipe	A leaking waste water pipe from a gas well polluted the tributary and killed fish, salamanders, crayfish, and aquatic insects.		Flowback of the well was immediately shut down, several check dams were constructed in the tributary, couplings on the pipeline were tightened to eliminate future leaks, remainder of flowback water was trucked away for storage. Flowback water contained by the check dams was pumped out, affected soil was excavated, area of disturbance was seeded and mulched.	Myers 2012	564165
	Fortuna Energy	Bradford County	Feb-10	Sugar Creek	Fracking fluid discharge	Various infractions at a Bradford County site including the discharge of fracking fluid into a tributary of Sugar Creek.	Fined \$3500	Company promptly placed a pump into the sediment basin to pump the fluids back into tanks and hired a consultant to conduct appropriate sampling.	Myers 2012	565284-87, 564580-88, 569257-61
	XTO Energy	Penn Township, Lycoming County	Nov-10	Tributary of Sugar Run	Produced water spill	4,275 gallons spilled due to an open valve on an unattended tank.	NOV		Myers 2012	
	Appalachia Midstream Svcs LLC	Sullivan County, Forks Twp	Sep-12	Harts Run and Mill Creek	Discharge of pollutional mterial to waters of Commonwealth	Thick (around 8") of bentonite mud in pools on Harts Run and Mill Creek up to approximately 4000 feet downstream of the inadvertent return; this porceeded for some time	NOV		DEP	648306; 648307; 648308
	Appalachia Midstream Svcs LLC	Sullivan County, Elkland Twp	Sep-12		Discharge of pollutional mterial to waters of Commonwealth	Erosion and sediment plan not adequate; discharge of sediment into Mill Creek with no apparent attempt to stop it; discharge enough to completely discolor creek; DEP not notified.	NOV		DEP	
	Appalachia Midstream Svcs LLC	Sullivan County	Sep-12	Mill Creek	Discharge of pollutional mterial to waters of Commonwealth	Turbid discharde from dewatering structure entered Black Water Run; DEP not notified.	NOV		DEP	648832-7
	Appalachia Midstream Svcs LLC	Sullivan County	Jan-13	Black Water Run	Discharge of pollutional mterial to waters of Commonwealth	Sediment-laden water into Big Bottom Run; erosion and sediment not minimized.	NOV		DEP	649937-9
				Big Bottom Run	Commonwealth		NOV			659741-4

Incident Type	Company	Location	Time	Water affected	Problem	Explanation	Legal Punishment	Remediation	Source of Info	Violation # (DEP)
	Bluestone Pipeline Co of PA LLC	Susquehanna County; New Milford Twp	Dec-12	Wellmans Creek/Salt Lick Creek	Discharge of pollutional material to waters of Commonwealth	Operator caused or allowed an unpermitted discharge with the potential to pollute the Waters of the Commonwealth; failure to notify DEP	NOV		DEP	656554-61
	Laurel Mtn Midstream OPR LLC	Westmoreland County	Sep-12		Stream discharge	Discharge of 100 gallons of drilling mud onto ground and into unnamed tributary to Jacob's Creek			DEP	
	MTN Gathering LLC	Indiana County	Oct-12	Jacob's Creek	Discharge of pollutional material to waters of Commonwealth		NOV NOV		DEP	648570
	Nisource Midstream Scs LLC	Butler County, Penn Twp	Dec-12	Blacklick Creek	Discharge of pollutional material to waters of Commonwealth	Release of bentonite and diamond seal into and near BlackLick Creek Horizontal Directional Drilling (HDD) on 200A Line located at Route 8 in Penn Township Butler county inadvertent return of drilling fluids to UNT of Thorn creek	NOV		DEP	653324
	PVR Marcellus Gas Gathering LLC	Lycoming County	Dec-12	Thorn Creek	Commonwealth Stream discharge		NOV		DEP	655831
	Anadarko Marcellus Midstream LLC	Lycoming County	Oct-12	Brion Creek Unnamed tributary to Slack Run	Failure to stabilize site until total site restoration ; Discharge of pollutional material to waters of Commonwealth;	Discharge of 232,604 gal. hydrostatic test water & significant sediment (fill) material into Brion Creek Sediment discharge to UNT to Slack Run from pipeline stream crossing and wetland crossing.	NOV		DEP	657370-3
	Chief Gathering LLC	Lycoming County	Mar-13		Discharge of pollutional material to waters of Commonwealth;	Failure to notify DEP of pollution incident.			DEP	651147; 651148; 651149
	Laser Northeast Gathering Company	Susquehanna County	Aug-11	Muncy Creek Laurel Lake Creek	Commonwealth Drilling mud spill	Dewatering HDD bore, pumped water coming out of filter bag with residual sediment, sediment discharge into Muncy Creek Spilled 1500 gallons of drilling mud into Laurel Lake Creek in Susquehanna County as they attempted to construct a natural gas pipeline	None		Myers 2012	663230
	Chesapeake Energy	Potter County	Mar-10		Sediment discharge	Chesapeake failed to implement erosion and sediment controls, resulting in sediment/silt discharges into a tributary of the Galeton Borough Water Authority			Myers 2012	
	Inergy Midstream LP	Sullivan County	Sep-12	Galeton Borough Water Authority Loyalstock Creek	Sediment discharge	Company constructing a natural gas pipeline discharged mud, clay, and sediment in loyalstock creek			Myers 2012	
	Hunlock Creek & Sterling	Lycoming County	Dec-11		Fracking fluid spill	Two tractor trailers collided on Route 287 in Lycoming County, causing one of them to overturn and spill an undetermined amount of fracking fluid into Larry's Creek			Myers 2012	
	CNX Gas Company		Jul-11	Larry's creek Unnamed tributary feeding intoTen Mile Creek	Mud spill	Significant size of spill and area affected	NOV	Not fully mitigated yet	Considine 2012	
Gas Migration, Casing, & Cementing	Cabot Oil & Gas	Dimock	May-09	19 family water wells	Gas migration	Pennsylvania Department of Environmental Protection issued multiple environmental violations to Cabot Oil & Gas because 19 families in Dimock had their water wells contaminated with methane. This contamination arose from gas migration that occurred after Cabot improperly cemented multiple gas wells in the area	Fined more than \$500,000 by the PA DEP. In addition, Cabot later settled for \$4.1 million with the residents who had their water affected.	The three wells that were found to be the source of the migrating gas were plugged, and since then there has been a noticeable improvement in the water quality of the affected water wells.	Considine 2012 + Myers 2012	
	Chesapeake Energy	Bradford County	May-11	16 family water wells	Gas migration	Largest fine issued by the PA DEP to date & was issued due to the severity of the gas migration. At various times throughout 2010, the PA DEP investigated private water well complaints from residents of Bradford County's Tuscarora, Terry, Monroe, Towanda, & Wilmot townships near Chesapeake's drilling operations. Gas was observed to have been bubbling up from the Susquehanna River during the initial investigation.	Fined \$900,000	The PA DEP determined that due to improper well casing & cementing in shallow zones, natural gas from non-shale shallow gas formations had experienced localized migration into groundwater & contaminated 16 families' drinking water supplies. Chesapeake took corrective action to mitigate the impacts of this migration and restore water supplies.	Considine 2012 + Myers 2012	
Site Restoration	Atlas Resources		Dec-08		Major site restoration failure	Atlas allowed 15 acres of land to remain disturbed after drilling was completed.	Fined \$9,641	After receiving the NOV, Atlas did eventually clean up the site and mitigate the impacts that the drilling had in the area.	Considine 2012	
	Ultra Resources		Aug-11		Major site restoration failure	Failed to restore 21 acres of land affected by drilling activity in Tioga County. This was the largest amount of land not restored after drilling activities.	Fined \$58,000	Site restoration is important because it allows the local ecosystem to return to its natural condition, and if it is not completed, major erosion can take place and damage more land than was originally affected by drilling. Ultra did eventually clean the site.	Considine 2012	
Fire	Chesapeake Energy	Washinton County	Feb-11		Condensate fire	While testing and collecting fluid from wells on a drill site in Washington County, three condensate separators caught fire, injuring three subcontractors working on the site	Fined \$188,000	The PA DEP determined that the cause was improper handling of condensate, which is a wet gas found only in certain geological areas. To ensure the fire was contained, approximately 20 acres of land was cleared and will need to be restored . The men who were injured in the fire were wearing flame-resistant clothing at the time the fire erupted, and it was stated that none of their injuries were life threatening.	Considine 2012 + Myers 2012	
	Chief Oil & Gas	Susquehanna County	Aug-12		Valve fire	Well Site shut down because of a well fire			Myers 2012	
12/4/2008 - 8/16/2011 2/2/2009 - 9/1/2012 9/2/2012-3/21/2013	Considine T. etal (2012) Environmental Impacts During Marcellus Shale Gas Drilling: Causes, Impacts, and Remedies. <i>Shale Resources and Society Institute</i> . Myers R. (2012) The Environmental Dangers of Hydro-Fracturing. Lock Haven University. https://www.lhup.edu/rmyers3/marcellus.htm Pennsylvania Department of Environmental Protection's Oil and Gas Compliance Report,									

*Note: Dates given by Considine are the date of the incident while dates given by Myers is the date of the DEP response action.

Appendix B

WaterBot Software Setup

1. To first install the USB firmware,
 - b. Connect laptop or netbook to the internet
 - c. Plug in the USB receiver
 - d. Permit Windows to auto-install the driver by choosing “Locate and install driver software”
2. Navigate to www.waterbot.org/howto.html to download the “WaterBot Uploader Necessary Files.”
 - a. Right-click on the file link and choose “Save”
 - b. Do not download the 2nd file called “WB_Uploader” yet
3. Choose the icon labeled “Install_first_python-2.7.2” to install “Python” (Python is open-source software, used to package executable programs like the WB_Uploader)
 - a. Use default options to install
4. Single-click to select the second file called “Install_second_pyserial-2.6” and choose the option to “Extract All” either in the toolbar or by double-clicking to extract/unzip
 - a. Choose to save the file on your Desktop
 - b. Open the *unzipped* file folder and choose the executable file “INSTALL_SERIAL”
 - c. A command-line window will pop up and then auto-close (black window with scrolling white text)
 - d. On some machines, it is necessary to double-click on the file, which will prompt Windows to extract all. Choose “Extract All,” and from the new window, open the file folder (not the compressed file) called “Waterbot_uploader_necessary_files” and choose “INSTALL_SERIAL”
5. Return to the website www.waterbot.org/howto.html
 - a. Right to download the “WB Uploader” by choosing “Save target as...” to the Desktop
 - b. If machine is set to save to the downloads folder, drag the “WB Uploader” icon from the downloads window to the desktop
 - c. You can now delete the other installation files from your downloads folder
6. Connect the receiver and confirm that the computer is connected to the Internet.
7. Double click the “WB Uploader” to open the program.
8. A green light on the receiver means it is powered and active. A blinking red light on the receiver means it “hears” a Waterbot

Appendix C

WaterBot Data Collection

1. Confirm that *www.waterbot.org* is ready to receive data
2. Execute the “WB Uploader” and confirm that the receiver recognizes the Bot. A blinking red light will indicate such
3. The Python window will read:
 “LISTENING FOR NODES
 NODE DETECTED: [ID:00##, POINTS: ##]
 Node 00xx,” (indicating the WaterBot’s I.D. number)
 Download page [1/#]”
 - a. The code will automatically scroll and indicate a number of data points, automatically download pages and show a “Data saved” message
 - b. It will then automatically try to “connect” to the Internet. If the laptop is not 3G, it will scroll a series of “Not connected, retrying” messages until the device is connected to the Internet
 - i. Your data will be saved in a folder that is created on your desktop as .csv files
 - c. Note that all you need to do is open the program!
4. Once connected to the internet, upload the data by again opening the “WB Uploader”
 - a. The text will confirm that the data is uploading with a series of “+” signs
 - b. Confirm that it is showing accurately on WaterBot.org

Appendix D

Additional IC Data

Sample Collection Time	Fluoride (mg/L)	Chloride (mg/L)	Sulfate (mg/L)	Bromide (mg/L)
1/15/13 1:30PM	0.0701	0.9538	8.7557	n.a.
1/15/13 1:30PM	0.2024	1.124	8.8006	n.a.
1/17/13 1:55PM	0.0549	0.9715	8.9403	n.a.
1/17/13 1:55PM	0.0635	1.1594	8.9545	n.a.
1/25/13 10:00AM	0.06	1.0068	8.8726	n.a.
1/25/13 10:00AM	0.0611	1.073	9.4262	n.a.
1/27/13 11:40AM	0.1088	1.1387	6.2991	n.a.
1/29/13 2:05PM	0.1613	1.5805	8.9093	n.a.
1/29/13 2:05PM	0.1279	1.4393	9.0602	n.a.
1/31/13 1:20PM	0.0974	2.0193	8.6517	n.a.
1/31/13 1:20PM	0.1031	1.9977	8.7263	n.a.
2/4/13 11:25AM	0.0509	0.9948	9.7147	n.a.
2/4/13 11:25AM	0.061	1.034	9.2638	n.a.
2/5/13 1:45PM	0.0671	1.0595	9.3609	n.a.
2/5/13 1:45PM	0.05	1.0959	9.3208	n.a.
2/7/13 10:00AM	0.0589	1.2895	9.4283	n.a.
2/7/13 10:00AM	0.0822	1.3136	9.3924	n.a.
2/11/13 10:40AM	0.1286	1.441	9.5427	n.a.

Figure D-1. Fluoride, chloride, sulfate, and bromide data for Shale Hills CZO grab samples from January 15 to February 11, 2013. Measured by Dionex ICS 2500 Ion Chromatograph. Detection limits are F = 0.04 mg/L, Cl = 0.1 mg/L, Br = 0.1 mg/L, and SO₄ = 0.4 mg/L.

Sample Site	Sample Collection Date	Cl (mg Cl/L)	Br (mg Br/L)
Site 3	2/19/2013	72	0.428
Site 2	2/19/2013	91	0.504
Site 3	3/5/2013	115	0.785
Site 3	3/5/2013	91	0.600
Site 4	3/5/2013	31	0.053
Site 4	3/5/2013	34	0.048
Site 1	3/5/2013	75	0.047
Site 1	3/5/2013	49	0.080

Figure D-2. Chloride and bromide data for Blacklick Creek grab samples from February 19 and March 5, 2013. Measured by Dionex ICS 3000 Ion Chromatograph. Detection limits are Cl = 0.02 mg Cl/L, and Br = 0.005 mg Br/L.

Additional S::can Spectro::lyser Data

S::can Shale Hills Turbidity and TOCeq Data Jan-Feb 2013						
Date/Time	Turbidity [FTUeq]	TOCeq [mg/l]		Date/Time	Turbidity [FTUeq]	TOCeq [mg/l]
2013.01.11 12:19:06	2.696	2.154		2013.01.13 16:19:06	3.455	2.945
2013.01.11 13:19:06	2.727	2.17		2013.01.13 17:19:06	3.35	2.947
2013.01.11 14:19:06	5.787	2.977		2013.01.13 18:19:06	3.263	2.904
2013.01.11 15:19:06	19.38	7.127		2013.01.13 19:19:06	3.099	2.858
2013.01.11 16:19:06	18.216	8.927		2013.01.13 20:19:06	3.269	2.858
2013.01.11 17:19:06	14.374	8.505		2013.01.13 21:19:06	3.13	2.797
2013.01.11 18:19:06	11.878	7.992		2013.01.13 22:19:06	3.054	2.778
2013.01.11 19:19:06	9.828	7.431		2013.01.13 23:19:06	3.184	2.738
2013.01.11 20:19:06	8.201	6.693		2013.01.14 00:19:06	2.89	2.693
2013.01.11 21:19:06	6.854	5.96		2013.01.14 01:19:06	6.445	3.51
2013.01.11 22:19:06	6.49	5.51		2013.01.14 02:19:06	7.524	4.81
2013.01.11 23:19:06	6.523	5.132		2013.01.14 03:19:06	5.322	4.549
2013.01.12 00:19:06	6.264	4.914		2013.01.14 04:19:06	4.489	4.062
2013.01.12 01:19:06	6.316	4.733		2013.01.14 05:19:06	4.397	3.903
2013.01.12 02:19:06	6.092	4.517		2013.01.14 06:19:06	4.414	3.751
2013.01.12 03:19:06	6.048	4.364		2013.01.14 07:19:06	3.753	3.467
2013.01.12 04:19:06	5.515	4.193		2013.01.14 08:19:06	3.661	3.299
2013.01.12 05:19:06	5.698	4.123		2013.01.14 09:19:06	3.793	3.188
2013.01.12 06:19:06	5.62	4.201		2013.01.14 10:19:06	3.358	3.045
2013.01.12 07:19:06	5.406	4.115		2013.01.14 11:19:06	3.196	2.942
2013.01.12 08:19:06	5.065	3.988		2013.01.14 12:19:06	3.324	2.921
2013.01.12 09:19:06	4.722	3.856		2013.01.14 13:19:06	3.293	2.868
2013.01.12 10:19:06	4.415	3.748		2013.01.14 14:19:06	3.446	2.831
2013.01.12 11:19:06	4.517	3.688		2013.01.14 15:19:06	3.31	2.789
2013.01.12 12:19:06	4.535	3.676		2013.01.14 16:19:06	3.106	2.701
2013.01.12 13:19:06	4.589	3.698		2013.01.14 17:19:06	3.182	2.701
2013.01.12 14:19:06	4.506	3.718		2013.01.14 18:19:06	3.175	2.651
2013.01.12 15:19:06	4.542	3.759		2013.01.14 19:19:06	3.297	2.636
2013.01.12 16:19:06	4.524	3.8		2013.01.14 20:19:06	2.94	2.553
2013.01.12 17:19:06	4.626	3.831		2013.01.14 21:19:06	3.022	2.518
2013.01.12 18:19:06	4.559	3.775		2013.01.14 22:19:06	3.065	2.527
2013.01.12 19:19:06	4.234	3.698		2013.01.14 23:19:06	2.728	2.453
2013.01.12 20:19:06	4.074	3.552		2013.01.15 00:19:06	2.991	2.474
2013.01.12 21:19:06	3.898	3.45		2013.01.15 01:19:06	2.849	2.439
2013.01.12 22:19:06	4.116	3.411		2013.01.15 02:19:06	2.985	2.469
2013.01.12 23:19:06	4.488	3.422		2013.01.15 03:19:06	2.686	2.411
2013.01.13 00:19:06	4.217	3.403		2013.01.15 04:19:06	2.894	2.4
2013.01.13 01:19:06	4.23	3.368		2013.01.15 05:19:06	2.632	2.358
2013.01.13 02:19:06	4.637	3.412		2013.01.15 06:19:06	2.728	2.363
2013.01.13 03:19:06	4.299	3.326		2013.01.15 07:19:06	2.684	2.343
2013.01.13 04:19:06	4.631	3.324		2013.01.15 08:19:06	2.76	2.322
2013.01.13 05:19:06	4.4	3.213		2013.01.15 09:19:06	2.516	2.273
2013.01.13 06:19:06	3.897	3.081		2013.01.15 10:19:06	2.667	2.274
2013.01.13 07:19:06	3.948	3.053		2013.01.15 11:19:06	2.801	2.302
2013.01.13 08:19:06	3.728	2.971		2013.01.15 12:19:06	2.783	2.313
2013.01.13 09:19:06	3.331	2.871		2013.01.15 13:19:06	2.915	2.33
2013.01.13 10:19:06	3.369	2.837		2013.01.15 14:19:06	2.806	2.318
2013.01.13 11:19:06	3.389	2.839		2013.01.15 15:19:06	3.162	2.366
2013.01.13 12:19:06	3.361	2.849		2013.01.15 16:19:06	2.97	2.335
2013.01.13 13:19:06	3.23	2.845		2013.01.15 17:19:06	3.024	2.358
2013.01.13 14:19:06	3.444	2.887		2013.01.15 18:19:06	3.067	2.326
2013.01.13 15:19:06	3.244	2.901		2013.01.15 19:19:06	3.053	2.313

Date/Time	Turbidity [FTUeq]	TOCeq [mg/l]
2013.01.15 20:19:06	2.889	2.291
2013.01.15 21:19:06	2.922	2.286
2013.01.15 22:19:06	2.832	2.253
2013.01.15 23:19:06	3.034	2.277
2013.01.16 00:19:06	2.927	2.263
2013.01.16 01:19:06	2.81	2.244
2013.01.16 02:19:06	2.541	2.196
2013.01.16 03:19:06	2.544	2.189
2013.01.16 04:19:06	2.603	2.2
2013.01.16 05:19:06	2.586	2.193
2013.01.16 06:19:06	2.522	2.188
2013.01.16 07:19:06	2.445	2.194
2013.01.16 08:19:06	2.482	2.198
2013.01.16 09:19:06	2.377	2.196
2013.01.16 10:19:06	2.349	2.198
2013.01.16 11:19:06	2.424	2.206
2013.01.16 12:19:06	2.525	2.218
2013.01.16 13:19:06	2.56	2.236
2013.01.16 14:19:06	2.534	2.247
2013.01.16 15:19:06	2.767	2.299
2013.01.16 16:19:06	2.939	2.326
2013.01.16 17:19:06	3.083	2.363
2013.01.16 18:19:06	2.905	2.361
2013.01.16 19:19:06	2.827	2.33
2013.01.16 20:19:06	2.879	2.34
2013.01.16 21:19:06	2.73	2.311
2013.01.16 22:19:06	2.746	2.283
2013.01.16 23:19:06	2.55	2.259
2013.01.17 00:19:06	2.53	2.235
2013.01.17 01:19:06	2.357	2.206
2013.01.17 02:19:06	2.253	2.175
2013.01.17 03:19:06	2.593	2.194
2013.01.17 04:19:06	2.448	2.16
2013.01.17 05:19:06	2.415	2.145
2013.01.17 06:19:06	2.4	2.133
2013.01.17 07:19:06	2.32	2.132
2013.01.17 08:19:06	2.335	2.131
2013.01.17 09:19:06	2.384	2.128
2013.01.17 10:19:06	2.347	2.122
2013.01.17 11:19:06	2.299	2.126
2013.01.17 12:19:06	2.495	2.145
2013.01.17 13:19:06	2.681	2.208
2013.01.25 10:29:47	4.572	1.986
2013.01.25 11:29:47	4.511	1.992
2013.01.25 12:29:47	4.634	2.003
2013.01.25 13:29:47	4.809	2.031
2013.01.25 14:29:47	4.809	2.03
2013.01.25 15:29:47	4.773	2.028
2013.01.25 16:29:47	4.817	2.043
2013.01.25 17:29:47	4.653	2.022
2013.01.25 18:29:47	4.826	2.017

Date/Time	Turbidity [FTUeq]	TOCeq [mg/l]
2013.01.25 19:29:47	4.741	2.022
2013.01.25 20:29:47	4.611	2.01
2013.01.25 21:29:47	4.589	1.99
2013.01.25 22:29:47	4.531	1.992
2013.01.25 23:29:47	4.579	1.984
2013.01.26 00:29:47	4.447	1.973
2013.01.26 01:29:47	4.578	1.986
2013.01.26 02:29:47	4.567	1.956
2013.01.26 03:29:47	4.565	1.961
2013.01.26 04:29:47	4.469	1.952
2013.01.26 05:29:47	4.61	1.974
2013.01.26 06:29:47	4.596	1.98
2013.01.26 07:29:47	4.516	1.971
2013.01.26 08:29:47	4.502	1.97
2013.01.26 09:29:47	4.513	1.968
2013.01.26 10:29:47	4.561	1.967
2013.01.26 11:29:47	4.613	1.984
2013.01.26 12:29:47	4.493	1.98
2013.01.26 13:29:47	4.562	1.995
2013.01.26 14:29:47	4.504	2.007
2013.01.26 15:29:47	4.705	2.031
2013.01.26 16:29:47	4.716	2.045
2013.01.26 17:29:47	4.805	2.054
2013.01.26 18:29:47	4.627	2.063
2013.01.26 19:29:47	4.905	2.082
2013.01.26 20:29:47	4.795	2.093
2013.01.26 21:29:47	4.851	2.079
2013.01.26 22:29:47	4.723	2.078
2013.01.26 23:29:47	4.869	2.062
2013.01.27 00:29:47	4.66	2.041
2013.01.27 01:29:47	4.663	2.053
2013.01.27 02:29:47	4.563	2.032
2013.01.27 03:29:47	4.691	2.029
2013.01.27 04:29:47	4.531	2.023
2013.01.27 05:29:47	4.533	2.013
2013.01.27 06:29:47	4.706	2.01
2013.01.27 07:29:47	4.418	1.971
2013.01.27 08:29:47	4.648	1.984
2013.01.27 09:29:47	4.56	1.972
2013.01.27 10:29:47	4.569	1.959
2013.01.27 11:29:47	4.628	1.962
2013.01.27 12:29:47	4.445	1.96
2013.01.27 13:29:47	4.358	1.951
2013.01.27 14:29:47	4.531	1.973
2013.01.27 15:29:47	4.551	1.994
2013.01.27 16:29:47	4.562	1.996
2013.01.27 17:29:47	4.655	2.022
2013.01.27 18:29:47	4.807	2.038
2013.01.27 19:29:47	4.838	2.052
2013.01.27 20:29:47	4.675	2.043
2013.01.27 21:29:47	4.735	2.057

Date/Time	Turbidity [FTUeq]	TOCeq [mg/l]		Date/Time	Turbidity [FTUeq]	TOCeq [mg/l]
2013.01.27 22:29:47	4.717	2.034		2013.01.30 02:26:26	3.133	2.444
2013.01.27 23:29:47	4.734	2.034		2013.01.30 03:26:26	3.31	2.407
2013.01.28 00:29:47	4.741	2.048		2013.01.30 04:26:26	3.11	2.354
2013.01.28 01:29:47	4.722	2.024		2013.01.30 05:26:26	3.1	2.301
2013.01.28 02:29:47	4.851	2.041		2013.01.30 06:26:26	2.92	2.273
2013.01.28 03:29:47	5.017	2.06		2013.01.30 07:26:26	2.871	2.22
2013.01.28 04:29:47	4.64	2.029		2013.01.30 08:26:26	3.101	2.231
2013.01.28 05:29:47	4.857	2.071		2013.01.30 09:26:26	2.967	2.203
2013.01.28 06:29:47	5.136	2.093		2013.01.30 10:26:26	2.977	2.213
2013.01.28 07:29:47	5.083	2.076		2013.01.30 11:26:26	3.13	2.276
2013.01.28 08:29:47	5.036	2.075		2013.01.30 12:26:26	3.389	2.429
2013.01.28 09:29:47	4.908	2.042		2013.01.30 13:26:26	4.365	2.88
2013.01.28 10:29:47	4.758	2.051		2013.01.30 14:26:26	5.585	3.496
2013.01.28 11:29:47	4.947	2.074		2013.01.30 15:26:26	7.695	4.574
2013.01.28 12:29:47	4.992	2.091		2013.01.30 16:26:26	10.029	5.906
2013.01.28 13:29:47	4.986	2.118		2013.01.30 17:26:26	10.946	6.878
2013.01.28 14:29:47	5.116	2.148		2013.01.30 18:26:26	14.839	8.308
2013.01.28 15:29:47	5.459	2.226		2013.01.30 19:26:26	26.487	12.509
2013.01.28 16:29:47	5.451	2.284		2013.01.30 20:26:26	33.439	16.343
2013.01.28 17:29:47	5.664	2.342		2013.01.30 21:26:26	30.151	16.149
2013.01.28 18:29:47	5.501	2.348		2013.01.30 22:26:26	30.612	16.142
2013.01.28 19:29:47	5.799	2.409		2013.01.30 23:26:26	41.081	17.089
2013.01.28 20:29:47	5.85	2.442		2013.01.31 00:26:26	47.154	18.467
2013.01.28 21:29:47	6.04	2.479		2013.01.31 01:26:26	59.275	19.467
2013.01.28 22:29:47	6.013	2.489		2013.01.31 02:26:26	51.018	17.124
2013.01.28 23:29:47	5.769	2.491		2013.01.31 03:26:26	60.68	17.231
2013.01.29 00:29:47	5.996	2.533		2013.01.31 04:26:26	33.872	11.716
2013.01.29 01:29:47	6.063	2.578		2013.01.31 05:26:26	24.051	9.29
2013.01.29 02:29:47	6.306	2.64		2013.01.31 06:26:26	16.252	7.423
2013.01.29 03:29:47	6.639	2.733		2013.01.31 07:26:26	12.559	6.473
2013.01.29 04:29:47	6.734	2.82		2013.01.31 08:26:26	9.57	5.69
2013.01.29 05:29:47	7.206	2.973		2013.01.31 09:26:26	8.696	5.383
2013.01.29 06:29:47	7.276	3.103		2013.01.31 10:26:26	7.833	5.067
2013.01.29 07:29:47	7.363	3.179		2013.01.31 11:26:26	8.639	5.167
2013.01.29 08:29:47	7.318	3.218		2013.01.31 12:26:26	7.206	4.8
2013.01.29 09:29:47	7.082	3.196		2013.01.31 13:26:26	8.648	5.014
2013.01.29 10:29:47	6.911	3.162		2013.01.31 14:26:26	6.403	4.456
2013.01.29 11:29:47	6.891	3.144		2013.01.31 15:26:26	5.808	4.257
2013.01.29 12:29:47	6.564	3.083		2013.01.31 16:26:26	6.374	4.328
2013.01.29 13:29:47	6.452	3.044		2013.01.31 17:26:26	6.005	4.151
2013.01.29 14:26:26	3.093	2.522		2013.01.31 18:26:26	5.435	3.941
2013.01.29 15:26:26	3.237	2.496		2013.01.31 19:26:26	4.932	3.771
2013.01.29 16:26:26	3.321	2.586		2013.01.31 20:26:26	5.234	3.724
2013.01.29 17:26:26	3.469	2.674		2013.01.31 21:26:26	5.132	3.631
2013.01.29 18:26:26	3.526	2.716		2013.01.31 22:26:26	5.076	3.538
2013.01.29 19:26:26	3.447	2.706		2013.01.31 23:26:26	4.991	3.492
2013.01.29 20:26:26	3.928	2.794		2013.02.01 00:26:26	5.147	3.415
2013.01.29 21:26:26	4.139	2.848		2013.02.01 01:26:26	4.969	3.392
2013.01.29 22:26:26	3.766	2.756		2013.02.01 02:26:26	5.137	3.349
2013.01.29 23:26:26	3.686	2.664		2013.02.01 03:26:26	5.181	3.293
2013.01.30 00:26:26	3.42	2.559		2013.02.01 04:26:26	4.974	3.229
2013.01.30 01:26:26	3.472	2.501		2013.02.01 05:26:26	5.045	3.213

Date/Time	Turbidity [FTUeq]	TOCeq [mg/l]		Date/Time	Turbidity [FTUeq]	TOCeq [mg/l]
2013.02.03 08:26:26	6.569	2.543		2013.02.05 13:26:26	6.323	2.352
2013.02.03 09:26:26	6.448	2.523		2013.02.05 14:25:05	6.759	2.407
2013.02.03 10:26:26	6.391	2.513		2013.02.05 14:26:43	6.465	2.365
2013.02.03 11:26:26	6.498	2.512		2013.02.05 15:26:42	6.512	2.395
2013.02.03 12:26:26	6.265	2.499		2013.02.05 16:26:42	6.203	2.354
2013.02.03 13:26:26	6.342	2.512		2013.02.05 17:26:42	6.551	2.398
2013.02.03 14:26:26	6.545	2.541		2013.02.05 18:26:42	6.498	2.414
2013.02.03 15:26:26	6.435	2.537		2013.02.05 19:26:42	6.862	2.436
2013.02.03 16:26:26	6.648	2.578		2013.02.05 20:26:42	6.438	2.403
2013.02.03 17:26:26	6.793	2.583		2013.02.05 21:26:42	6.208	2.374
2013.02.03 18:26:26	6.77	2.578		2013.02.05 22:26:42	6.939	2.485
2013.02.03 19:26:26	6.83	2.582		2013.02.05 23:26:42	6.684	2.421
2013.02.03 20:26:26	6.65	2.555		2013.02.06 00:26:42	6.352	2.388
2013.02.03 21:26:26	6.555	2.548		2013.02.06 01:26:42	6.58	2.391
2013.02.03 22:26:26	6.469	2.526		2013.02.06 02:26:42	6.379	2.372
2013.02.03 23:26:26	6.374	2.502		2013.02.06 03:26:42	6.67	2.399
2013.02.04 00:26:26	6.364	2.476		2013.02.06 04:26:42	6.23	2.343
2013.02.04 01:26:26	6.155	2.439		2013.02.06 05:26:42	6.356	2.354
2013.02.04 02:26:26	6.1	2.415		2013.02.06 06:26:42	6.504	2.377
2013.02.04 03:26:26	6.175	2.426		2013.02.06 07:26:42	6.26	2.35
2013.02.04 04:26:26	6.123	2.386		2013.02.06 08:26:42	6.627	2.373
2013.02.04 05:26:26	5.887	2.364		2013.02.06 09:26:42	6.528	2.362
2013.02.04 06:26:26	6.03	2.365		2013.02.06 10:26:42	6.614	2.384
2013.02.04 07:26:26	5.917	2.362		2013.02.06 11:26:42	6.519	2.377
2013.02.04 08:26:26	6.071	2.377		2013.02.06 12:26:42	6.533	2.381
2013.02.04 09:26:26	6.128	2.376		2013.02.06 13:26:42	6.675	2.403
2013.02.04 10:26:26	6.117	2.353		2013.02.06 14:26:42	6.881	2.484
2013.02.04 11:26:26	5.931	2.322		2013.02.06 15:26:42	8.13	3.56
2013.02.04 12:26:26	5.883	2.324		2013.02.06 16:26:42	13.518	7.535
2013.02.04 13:26:26	6.071	2.319		2013.02.06 17:26:42	17.55	10.695
2013.02.04 14:26:26	6.134	2.363		2013.02.06 18:26:42	22.57	14.239
2013.02.04 15:26:26	6.014	2.354		2013.02.06 19:26:42	35.971	21.918
2013.02.04 16:26:26	6.768	2.428		2013.02.06 20:26:42	52.758	NaN
2013.02.04 17:26:26	6.77	2.454		2013.02.06 21:26:42	60.468	NaN
2013.02.04 18:26:26	6.599	2.403		2013.02.06 22:26:42	58.257	NaN
2013.02.04 19:26:26	6.491	2.432		2013.02.06 23:26:42	51.29	NaN
2013.02.04 20:26:26	6.588	2.421		2013.02.07 00:26:42	43.552	NaN
2013.02.04 21:26:26	6.478	2.427		2013.02.07 01:26:42	36.262	NaN
2013.02.04 22:26:26	6.492	2.421		2013.02.07 02:26:42	30.777	19.933
2013.02.04 23:26:26	6.493	2.412		2013.02.07 03:26:42	25.604	16.839
2013.02.05 00:26:26	6.944	2.418		2013.02.07 04:26:42	23.489	14.527
2013.02.05 01:26:26	6.814	2.435		2013.02.07 05:26:42	20.103	12.186
2013.02.05 02:26:26	6.923	2.422		2013.02.07 06:26:42	16.941	9.905
2013.02.05 03:26:26	6.559	2.394		2013.02.07 07:26:42	15.422	8.623
2013.02.05 04:26:26	7.071	2.441		2013.02.07 08:26:42	13.906	7.423
2013.02.05 05:26:26	6.864	2.407		2013.02.07 09:26:42	12.852	6.582
2013.02.05 06:26:26	6.545	2.384		2013.02.07 10:26:42	12.152	5.932
2013.02.05 07:26:26	6.588	2.376		2013.02.07 11:26:42	11.553	5.376
2013.02.05 08:26:26	6.86	2.408		2013.02.07 12:26:42	10.932	4.891
2013.02.05 09:26:26	6.387	2.347		2013.02.07 13:26:42	11.095	4.925
2013.02.05 10:26:26	6.42	2.339		2013.02.07 14:26:42	14.053	6.479
2013.02.05 11:26:26	6.468	2.341		2013.02.07 15:26:42	23.877	12.203
2013.02.05 12:26:26	6.457	2.351		2013.02.07 16:26:42	29.423	15.894

Date/Time	Turbidity [FTUeq]	TOCeq [mg/l]		Date/Time	Turbidity [FTUeq]	TOCeq [mg/l]
2013.02.07 17:26:42	29.313	16.157		2013.02.09 22:26:42	13.641	3.41
2013.02.07 18:26:42	26.489	14.882		2013.02.09 23:26:42	13.807	3.382
2013.02.07 19:26:42	23.917	13.253		2013.02.10 00:26:42	13.611	3.351
2013.02.07 20:26:42	20.804	11.451		2013.02.10 01:26:42	13.829	3.332
2013.02.07 21:26:42	19.905	10.031		2013.02.10 02:26:42	15.694	3.76
2013.02.07 22:26:42	28.586	10.699		2013.02.10 03:26:42	15.635	3.838
2013.02.07 23:26:42	32.601	11.279		2013.02.10 04:26:42	15.59	3.911
2013.02.08 00:26:42	49.495	14.201		2013.02.10 05:26:42	15.128	3.736
2013.02.08 01:26:42	40.674	12.388		2013.02.10 06:26:42	14.582	3.604
2013.02.08 02:26:42	35.591	11.445		2013.02.10 07:26:42	14.332	3.518
2013.02.08 03:26:42	37.465	11.346		2013.02.10 08:26:42	14.26	3.461
2013.02.08 04:26:42	57.02	14.859		2013.02.10 09:26:42	14.085	3.415
2013.02.08 05:26:42	50.361	14.22		2013.02.10 10:26:42	13.948	3.359
2013.02.08 06:26:42	36.734	10.82		2013.02.10 11:26:42	14.003	3.34
2013.02.08 07:26:42	27.339	8.158		2013.02.10 12:26:42	13.976	3.338
2013.02.08 08:26:42	22.824	6.828		2013.02.10 13:26:42	13.845	3.331
2013.02.08 09:26:42	19.949	5.907		2013.02.10 14:26:42	13.84	3.361
2013.02.08 10:26:42	18.043	5.239		2013.02.10 15:26:42	13.88	3.381
2013.02.08 11:26:42	16.788	4.857				
2013.02.08 12:26:42	15.559	4.422				
2013.02.08 13:26:42	15.051	4.224				
2013.02.08 14:26:42	15.039	4.191				
2013.02.08 15:26:42	15.018	4.161				
2013.02.08 16:26:42	15.136	4.146				
2013.02.08 17:26:42	15.583	4.244				
2013.02.08 18:26:42	16.154	4.364				
2013.02.08 19:26:42	16.455	4.468				
2013.02.08 20:26:42	16.218	4.461				
2013.02.08 21:26:42	15.689	4.267				
2013.02.08 22:26:42	15.127	4.183				
2013.02.08 23:26:42	14.698	4.011				
2013.02.09 00:26:42	14.513	3.917				
2013.02.09 01:26:42	14.721	3.896				
2013.02.09 02:26:42	14.218	3.796				
2013.02.09 03:26:42	14.948	3.898				
2013.02.09 04:26:42	16.775	4.254				
2013.02.09 05:26:42	16.719	4.336				
2013.02.09 06:26:42	16.66	4.412				
2013.02.09 07:26:42	16.172	4.271				
2013.02.09 08:26:42	15.518	4.056				
2013.02.09 09:26:42	15.043	3.929				
2013.02.09 10:26:42	14.795	3.813				
2013.02.09 11:26:42	14.73	3.762				
2013.02.09 12:26:42	14.389	3.685				
2013.02.09 13:26:42	14.212	3.636				
2013.02.09 14:26:42	13.865	3.568				
2013.02.09 15:26:42	14.091	3.562				
2013.02.09 16:26:42	14.292	3.572				
2013.02.09 17:26:42	14.053	3.537				
2013.02.09 18:26:42	13.921	3.518				
2013.02.09 19:26:42	13.96	3.488				
2013.02.09 20:26:42	13.946	3.449				
2013.02.09 21:26:42	13.879	3.448				

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ACADEMIC VITA

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Education

B.S., Geosciences, Hydrogeology Option, 2013, Penn State University, University Park, PA

Honors and Awards

- Schreyer Honors Scholar
- Dean's List every semester at Penn State
- Phi Kappa Phi National Honor Society
- Winner of Grundy Haven Student Writing Competition, PCPG Student Essay Contest, and The Water is Rising Paper Competition
- Awarded many scholarships for excellence in academics, hydrogeology, and service

Association Memberships/Activities

In this section, list all memberships in:

- Pennsylvania Council of Professional Geologists, Student Member
- American Geophysical Union, Student Member
- Global Water Brigades, Volunteer in Ghana Winter 2012-13
- Penn State International Dance Ensemble (PSIDE), Member
- Penn State Dance Marathon, PSIDE Overall Chair

Professional Experience

- **Excel Environmental Resources, Inc. Intern, N. Brunswick, NJ** (Jun-Aug 2012)
 - Edited and wrote portions of reports
 - Conducted field work (groundwater sampling and oversight of oil extraction)
 - Interpreted sites hydrogeologically
 - Completed & submitted paperwork for NJDEP & EPA
 - Tabulated & evaluated contaminant and groundwater & soil data
- **Renewable Energy & Sustainability Collaborator, Costa Rica** (June 2011)
 - Attended GREEN program: <https://thegreenprogram.com/#page=#students-page-hash>
 - Enhanced knowledge on sustainability & renewable energy via plant visits and community involvement
 - Collaborated with fellow attendees and local college students on a project which we presented to local experts
- **Hydrogeophysics Field Worker/ Researcher** (May-June 2011)
 - Attended Dr. Kamini Singha's field camp where I learned how to use borehole & surface instrumentation in a controlled watershed and use computer programs to analyze our data
 - Presented research: "A Stream's Connection with Its Aquifer Using ER: Implications to Climate Change"
- **Soils and Climate Change Researcher** (January-December 2010)
 - Worked with Dr. Jason Kaye to analyze how climate change will affect soil carbon dynamics, <http://cropsoil.psu.edu/research/kaye-lab/carbon-cycling>

Research Interests

My broad interest is in the engineering of solutions to environmental problems, especially in the realms of surface and ground water quality.