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SURFACE AND GROUND WATER QUALITY WITHIN THE CROSS CREEK WATERSHED, MAY 2015-2016

A Thesis

Submitted to Bayer School of Natural and Environmental Sciences

Duquesne University

In partial fulfillment of the requirements for

the degree of Master of Science

By

Tyler Umstead

August 2016

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Tyler Umstead

SURFACE AND GROUND WATER QUALITY WITHIN THE CROSS CREEK WATERSHED, MAY 2015-2016

By

Tyler Umstead

Approved July 18, 2016

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ABSTRACT

SURFACE AND GROUND WATER QUALITY WITHIN THE CROSS CREEK WATERSHED, MAY 2015-2016

By

Tyler Umstead August 2016

Thesis supervised by John Stolz, Ph.D.

Unconventional shale gas extraction in the Marcellus has expanded throughout Pennsylvania since 2005, and poses potential risks to water resources. This study investigated water quality in Cross Creek County Park (CCCP), Washington County, Pennsylvania, surface waters and nearby residential water wells. Twenty-five wells have been drilled within CCCP over the past 8 years. Six sites were monitored bi-monthly for temperature, pH, dissolved oxygen, and conductivity, as well as selected anions, cations, and light hydrocarbons. Detection of methane and ethane, surfactants, and other water chemistry parameters (e.g., mass ratios) suggest water quality has been impacted for sites Cross Creek 1, Streams A and C, and some well water samples. Spatial patterns were analyzed to evaluate drilling, mining, agriculture, and hydrology of the Cross Creek Watershed. File review of oil and gas documents revealed that drilling wastes were buried within the park, suggesting a possible source of contamination for the impacted streams.

DEDICATION

I would like to dedicate this paper to my parents, Daniel & Jill, to my sister Erica, to my girlfriend Nicole, and also to all my friends and family for their continuous love, support, and encouragement, as I pursued my master's degree here at Duquesne University.

ACKNOWLEDGEMENT

I would like to thank Dr. Stolz for including me as one of his graduate research assistants, and for his guidance and mentorship throughout my time in the program. I would like to thank the entire Stolz lab group; Colleen Nolan, Linnea Manley, and Daniel Robinson for their constant help and participation in this study. Without their continuous energy, drive, and dedication towards this research, this study would not have been possible.

A special thanks to Dr. Tetiana Kondratyuk, who devoted numerous hours of her time to perform the laboratory analyses needed to keep this project afloat, and for guiding me through the data analysis. Thank you Dr. Partha Basu and Dr. Dan Bain for all your help and contribution, and for guiding me through focusing on the bigger picture of this research. Lastly, thank you Dr. Dan Bain for allowing us to test our water chemistry with your ICP/MS at the University of Pittsburgh, and thank you to Dr. F.L. Dorman and P. Piotrowski at the Pennsylvania State University for testing our foam water samples.

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LIST OF ABBREVIATIONS

ACHD – Allegheny County Health Department

AMD – Abandoned Mine Drainage

AML – Abandoned Mine Lands

API – American Petroleum Institute

Bdl – Below Detection Limit

CCCP – Cross Creek County Park

CCW – Cross Creek Watershed

DBP – Disinfection Byproduct

GCxGC/TOFMS – (2D Gas Chromatography / Time of Flight Mass Spectrometry

HAA - Haloacetic Acid

HAP – Hazardous Air Pollutant

HFFF – Hydraulic Fracturing Flowback Fluids

HQ – High Quality Water

HVHF – High Volume Hydraulic Fracturing

IC – Ion Chromatography

ICP/MS – Inductively Coupled Plasma / Mass Spectrometry

Mcf – Million cubic feet

MCL – Maximum Contaminant Level

N/A – Not Available

NORM – Naturally Occurring Radioactive Material

NPDWS – National Primary Drinking Water Standard

NSDWS – National Secondary Drinking Water Standard

PA DCNR – Pennsylvania Department of Conservation and Natural Resources

PA DEP – Pennsylvania Department of Environmental Protection

RCRA – Resource Conservation and Recovery Act

SDWA – Safe Drinking Water Act

SMCL – Secondary Maximum Contaminant Level

SPUD – To begin to drill a well

TCF – Trillion cubic feet

TDS – Total Dissolved Solids

THM - Trihalomethane

US EIA - United States Energy Information Administration

US EPA – United States Department of Environmental Protection

USGO – Unconventional Shale Gas Operations

USGS – United States Geological Survey

WWF – Warm Water Fish

CHAPTER 1 – INTRODUCTION

1.1 Unconventional Gas Extraction from Marcellus Shale

1.1.1 Natural Gas Boom

Fossil fuel resources such as coal, petroleum, and natural gas provide for most of the energy requirements in the U.S., and these energy sources are expected to provide for 76% of electricity generation by 2040 (US EIA, 2015). Advances in technology have allowed a recent boom in natural gas extraction by a process known as high-volume hydraulic fracturing (HVHF). The importance of shale oil and gas to global energy demand is revealed in the U.S. Energy Information Administration's (US EIA) 2013 oil and gas assessment, which estimated about 7299 trillion cubic feet (TCF) of gas and 345 billion barrels of oil could be recovered from shale deposits in the U.S. and 40 other countries (Brittingham et al., 2014). There are 20 plays that account for a majority of all shale gas deposits in the continental U.S., and one of the largest gas deposits lies in the Marcellus Shale formation that stretches across Ohio, West Virginia, Pennsylvania, Maryland, and New York. Figure 1 shows the major oil and gas plays currently within Pennsylvania.

Exploitation of natural gas in the Marcellus Shale began in 2004 with the completion of the Renz No. 1 well; a vertical well in Mount Pleasant Township, Washington County, Pennsylvania (Carter et al., 2011). The Renz well was originally drilled into the middle Rochester Shale (8470 ft) and large quantities of gas were detected when once the gas company drilled through the Middle Devonian shales. In 2004 the well was hydraulically fractured and stimulated the organic-rich zones of the Marcellus and Skaneateles formations. The Renz No. 1 well began producing natural gas in 2005 with an average of 300 million cubic feet (mcf)/day. Several other wells were subsequently developed in Washington County using both

unconventional drilling and HVHF techniques used in the Barnett Shale play to extract natural gas from the Marcellus Shale formation. After the success of the Renz well, several other operators began their own operations to extract natural gas from this organic-rich formation (Carter et al., 2011). While the shale gas deposits in the U.S. are projected to provide 38% of the entire U.S. hydrocarbon use by 2040, a large portion of this energy (33%) will come from the Marcellus and Utica formations in the Appalachian region (Figure 1) (Cluff et al., 2014).



Figure 1. Varying oil and gas resource locations in Pennsylvania. Map generated from O&G fields, PA Geologic Survey and EIA Marcellus Shale Play data.

Thanks to gas extraction in shale deposits (i.e. Marcellus, Bakken, Utica, Barnett, etc.), the portion of electricity generated from natural gas has increased from $\sim 20\%$ (2000) to $\sim 30\%$ (2012) and is projected to increase to $\sim 50\%$ by 2040 (Warner et al., 2014). Horizontal-drilling hydraulic fracturing has been used in many forms for decades, but it is the combination of HVHF and the technology of horizontal drilling that has brought about hydrocarbon extraction from resources that were previously uneconomically attainable (Brittingham et al., 2014). Pennsylvania already has a history with oil and gas extraction (i.e. coalbed methane, shallow oil and gas), and the use of horizontal drilling and hydraulic fracturing techniques have been used to further exploit fossil fuel extraction in the state (Figure 1).

1.1.2 The Marcellus Shale Formation

A Devonian age formation, the Marcellus shale has common characteristics of sedimentary rock formations that include black, organic-rich shale (Brantley et al., 2014; Kargbo et al., 2010). This black shale is a mudrock that contains silt, organic matter, and clay-sized mineral grains (Tourtelot, 1979). A majority of black shales are of marine origin and can cover areas exceeding thousands of square kilometers. Such formations can contain increased concentrations of metals like Mo, Ag, Zn, Cu, Cr, Ni, V, and in some black shales Co, Se, and U (Tourtelot, 1979). The clay-sized grains typically lie flat during black shale accumulation, and a thin layered formation of shale rock is formed after pressurized compaction (Kargbo et al., 2010). As organic materials in the deposits undergo anaerobic degradation, natural gas is formed. Most of the Marcellus shale gas is thermogenic and dry natural gas is primarily produced thanks to high heat and pressure (Kargbo et al., 2010).

1.1.3 Natural Gas

Formed from fossilized organic matter and millions of years of heat and pressure, natural gas is a mixture of methane (dry gas) and heavier hydrocarbons such as ethane, propane, and butane (wet gas) (Schumann and Vossoughi, 2012). Wet gases are a vital resource because they can be converted relatively easily into other fuels and materials. For example, the use of petrochemical plants, or "cracker plants", would enable the conversion of extracted ethane into ethylene, which is used extensively in the production of plastics (Chaudhuri, 2016).

1.1.4 Conventional and Unconventional Drilling

In terms of obtaining oil and gas from underground rock formations, the two types of drilling include vertical (conventional) and horizontal (unconventional) drilling. Conventional drilling, which includes drilling straight into the target formation, is relatively simpler as the trapped and accumulated gas can flow to the surface once the boring provides the connection. In contrast, shale's fine granular structure has a low permeability to water and gas. Gas molecules trapped within the shale either occupy natural fractures in the shale or they are tightly bound to clay surfaces (Schumann and Vossoughi, 2012). This distribution of gas necessitates the more complex unconventional drilling process. Both horizontal drilling and HVHF techniques are used to break apart shale formations so that enough gas can escape to the surface. Unconventional drilling is used to extract resources like methane hydrates, shale gas, deep gas, tight gas, and coal-bed methane (Schumann and Vossoughi, 2012). Unconventional shale gas operations (USGO) and conventional exploration in Pennsylvania lie primarily to the north and west of the Appalachian Mountains (Figure 2).

1.1.5 Exploration and Gas Extraction

In Pennsylvania, after leasing the mineral rights and determining the best location for a well pad, the drilling company must obtain a drilling permit from the Pennsylvania Department of Environmental Protection (PA DEP), Bureau of Oil and Gas Management (Flaherty and Flaherty, 2014). This step is a major challenge for the well pad location has the potential to impact habitat or sensitive ecosystems (Kargbo et al., 2010).



Figure 2. Conventional and Unconventional Oil and Gas Wells in Pennsylvania. Map generated from PASDA data and EIA Marcellus Shale Play data.

Because of this, well pad locations can be adjusted to account for environmentally sensitive regions, such as wetlands, streams, or protected and endangered wildlife (Flaherty and Flaherty, 2014). Well pad locations are also based on the distance from other producing wells and the placement of entrance roads and gas pipelines. Careful planning can minimize impacts on citizens and the land. Plans to minimize natural erosion and sedimentation processes must also be developed (Flaherty and Flaherty, 2014).

Before drilling can begin, geologists need to understand the underground rock formations and potential gas reservoirs. Studies are made on surface rocks as well as rock cutting samples acquired from other nearby drilling operations (Flaherty and Flaherty, 2014). In addition, seismic surveys are made to create 3-dimensional images of the subsurface and natural gas reservoirs (Kargbo et al., 2010). This process, known as seismic reflection, uses surface sensors and either "thumper trucks" or in-ground explosives to produce sound waves in all directions (Flaherty and Flaherty, 2014). These sound waves are reflected off the varying rock formations and return to the surface to be detected by the sensors. With this information, geologists can map out the formation types, fault locations, and their depths. This allows geologists find the most prospective target for oil or gas, which may be where the rock reservoir is most porous, permeable, or thickest.

After all permits are acquired, the suitable area of land determined for the well pad is cleared and access roads and pipelines are constructed. Wellpads are constructed to accommodate multiple wells at once, which can be as little as 15 ft apart (Flaherty and Flaherty, 2014). A drilling rig (Figure 3a) is then used to drill vertically to approximately 1000 ft above the target gas reservoir. Modern drilling equipment usually entails a rotary bit or an air hammer (pneumatic) bit. Next, the specialized drill starts to angle the well hole to direct it horizontally into the shale formation of interest (e.g. Marcellus Shale). The well is then drilled several thousand feet into the target formation. Air, as well as water- and synthetic-based fluids, are pumped down the well hole to ensure a faster and easier drilling process (Flaherty and Flaherty, 2014).



Figure 3. (a) The drilling stage at the Christman Unit 9H, 11-14H wellpad just outside of CCCP on 9/19/2014 (photo courtesy of Robert M. Donnan), (b) Well bore casings used in unconventional gas extraction (Flaherty and Flaherty, 2014).

Air returning to the surface is vented, and the drilling mud is pumped into large containers or a waste pit. Drill cuttings, or any rock fragments or soil excavated by the drill bit to the surface, are stored on site until being transported to disposal sites (Brantley et al., 2014; ODNR, 2012). Drill pipe is then added to the well until the "casing point" is reached. The casing point depth indicates when the drill is removed and a steel and cement casing is installed. Several layers of steel and cement are used to prevent well cave-ins and to protect underground aquifers (Figure 3b). The cement is circulated down the bottom of the hollow casing and back up the outside casing of the well. Once the cement is dry and the casing layers are complete, further vertical and subsequent horizontal drilling into the target formation is completed (Flaherty and Flaherty, 2014). On a well pad, six or more horizontal wells can be drilled exceeding 2000 m laterally, with a network of fractures exceeding 500 m or more into the target rock layer (Cluff et al., 2014).

Once the well is drilled and casing is established, geologists will "log" the well (Flaherty and Flaherty, 2014). This process records depths and characteristics of the rock formations penetrated by the drill. In addition, sensors that constantly record characteristics such as rock type, porosity, electrical resistivity, hole diameter, and temperature are used to record continuous characteristics. The geophysical logging data are used by geologists to determine drilling accuracy and whether the formation permeability is acceptable for oil or gas extraction.

Before hydraulic fracturing and hydrocarbon capture, a final casing is extended along the well to the farthest extent of the drilling (Flaherty and Flaherty, 2014). The casing seals off the entire extent of the well before HVHF. Explosive charges are inserted into the well and placed in locations along the horizontal portion of the well where fracturing is set to occur. The explosives are detonated and this creates perforations, or holes, in the casing along the horizontal portion of

the well. The perforations allow sand (proppant) and fracturing fluids to fracture the target formation. The next step involves high volume hydraulic fracturing, a process that entails the highly pressurized injection of 8-40 million liters of fracturing fluids into the wellbore to ensure the target resource formation is fractured and remains open for oil and gas hydrocarbons to escape to the surface (Figure 4a) (Brittingham et al., 2014; Cluff et al., 2014; Sang et al., 2014; Warner et al., 2014). HVHF starts with the farthest end of the horizontal portion of the wellbore. Each stage of perforations made by the previous detonations is fractured with fluids and proppant. A plug is inserted into the well to isolate each stage from the rest during HVHF. When each perforation stage is fractured, the plug is removed. Once the well is opened, fluids, debris, and hydrocarbons are allowed to flow back to the surface (Flaherty and Flaherty, 2014).



Figure 4. (a) An example of the hydraulic fracturing at the Gillett Ann Unit 1H-5H wellpad in Buffalo Twp, Washington County, PA (photo courtesy of Robert M. Donnan) and (b) an example of proppant used to keep fractures in the shale formation open for hydrocarbon release (Flaherty and Flaherty, 2014).

1.1.6 Chemical Use in HVHF

The fracturing fluids used in the unconventional drilling process entail a mixture of water, proppant, and other chemical additives (accounting for < 1% total volume) that include polymers, acids, alcohols, biocides, organic solvents, friction reducers, and lubricants (Cluff et al., 2014; Sang et al., 2014; Thurman et al., 2014). These additives are used to protect the well from corrosion and fouling, increase shale porosity, and transport proppant to the fractures (Figure 4b) (Cluff et al., 2014). While these chemicals are injected deep underground and aid in hydrocarbon extraction, their fate and transport over extended time periods is not certain. In 2011, the United States House of Representatives Committee on Energy and Commerce generated an overview of 652 hydraulic fracturing products containing 29 chemical compounds (Table 1) that are Hazardous Air Pollutants (HAPs) under the Clean Air Act, known or potential carcinogens, or chemicals subject to the Safe Drinking Water Act (SDWA) (Waxman et al., 2011).

Table 1. Overview of hydraulic fracturing products with major environmental and human health risks (Waxman et al., 2011). Hazardous Air Pollutants are those substances that cause or may potentially cause cancer or additional harmful health effects that can include birth defects, reproductive effects, or adverse ecological and environmental effects.

Chemical Additive	Chemical Risk Category	Number of Products
Methanol (Methyl alcohol)	HAP	332
Ethylene glycol (1,2-ethanediol)	HAP	119
Diesel	Carcinogen, SDWA, HAP	51
Naphthalene	Carcinogen, HAP	44
Xylene	SDWA, HAP	44
Hydrogen chloride (Hydrochloric acid)	HAP	42
Toluene	SDWA, HAP	29
Ethylbenzene	SDWA, HAP	28
Diethanolamine (2,2-iminodiethanol)	HAP	14
Formaldehyde	Carcinogen, HAP	12
Sulfuric acid	Carcinogen	9
Thiourea	Carcinogen	9
Benzyl chloride	Carcinogen, HAP	8
Cumene	HAP	6
Nitrilotriacetic acid	Carcinogen	6
Dimethyl formamide	HAP	5
Phenol	HAP	5
Benzene	Carcinogen, SDWA, HAP	3
Di (2-ethylhexyl) phthalate	Carcinogen, SDWA, HAP	3
Acrylamide	Carcinogen, SDWA, HAP	2
Hydrogen fluoride (Hydrofluoric acid)	HAP	2
Phthalic anhydride	HAP	2
Acetaldehyde	Carcinogen, HAP	1
Copper	SDWA	1
Ethylene oxide	Carcinogen, HAP	1
Lead	Carcinogen, SDWA, HAP	1
Propylene oxide	Carcinogen, HAP	1
p-Xylene	HAP	1
Number of Products Containing a Component of Concern		

1.1.7 Hydrocarbon Collection and Transportation

After unconventional drilling and HVHF, the well is ready to produce hydrocarbons for capture (Flaherty and Flaherty, 2014). There have been cases of wells producing both oil and natural gas, but usually the well will produce either oil or gas. Wet gases (ethane, propane, butane, etc.) are separated from dry gas (methane, CH₄) after drilling and subsequent dehydration (Flaherty and Flaherty, 2014; Schumann and Vossoughi, 2012). The wet gases can then be sold as separate products or used as chemical additives (Chaudhuri, 2016). Produced gas from the well is transported through gathering pipelines to processing plants, where dry and wet gases are separated (Flaherty and Flaherty, 2014). The dry gas is sent through transmission pipelines to directly to electrical generating units or to liquidation plants for export. Compressor stations are constructed along the pipeline network to keep the gas moving and maintain pressure.

1.1.8 Plugging the Well

If an operator must abandon a well, several rules apply under 025 Pa. Code § 78.91 for plugging the well. This can occur for various reasons, such as economic viability or the loss of a radioactive logging source. The well is disconnected from all pipelines and casing inside the well is scrapped for value. If the casing cannot be retrieved, the operator must follow 025 Pa. Code § 78.91(d) to plug strata bearing gas, oil, or water. Cement is pumped down the borehole to seal off the well, and a vent pipe is then installed on the surface to ensure a build-up in pressure does not occur (Flaherty and Flaherty, 2014). Other requirements under 025 Pa. Code § 78.91 describe procedures for plugging a well from the attainable bottom, when the well is located in a coal area, and developing plugging schedules that do not interfere with the environment or public health.

1.1.9 Waste Generation

1.1.9.1 Flowback Fluids and Produced Fluids

Within two weeks, rock deformation and release of pressure resulting from HVHF drives the release of hydraulic fracturing flowback fluids (HFFF), which consists of 10-70% of the original injected fluids during HVHF, to return to the surface along with the escaping hydrocarbons (Cluff et al., 2014; Haluszczak et al., 2013; Mohan et al., 2013). The fluids and chemical additives used during the HVHF process causes the dissolution of shale constituents, such as organic matter, salts, heavy metals, and NORMs, into the original injected solution. Because of this, flowback fluids return to the surface as a mixture of chemical additives and the naturally occurring dissolved substances (Balaba and Smart, 2012; Cluff et al., 2014; Haluszczak et al., 2013; Kahrilas et al., 2015; Murray, 2013; Osborn et al., 2011; Sang et al., 2014; Vengosh et al., 2014). As the shale formation water continues to mix with injected fluids, the flowback fluids returning to the surface typically continue to rise in salinity (Vengosh et al., 2014).

After the initial two week surge of HFFF, additional fluids known as produced fluids continue to migrate to the surface of the borehole throughout the life of the well (Brittingham et al., 2014; Cluff et al., 2014). Produced fluid is the native groundwater present in the target formation that has been fractured during natural gas extraction (Thurman et al., 2014; Veil et al., 2004). Hydrocarbons are extracted to the surface as a mixture of produced waters, gaseous or liquid hydrocarbons, chemical additives, and dissolved or suspended solids (Veil et al., 2004). During the production process, the gas is separated from the produced water. Produced fluids from this process contain low-molecular weight aromatic hydrocarbons such as xylene, benzene, toluene, and ethylbenzene from both the target formation chemistry and chemical additives used during the extraction (Veil et al., 2004). Depending on the shale formation, produced fluids also have a high total dissolved solids (TDS) content that can range in salinity from below to over 7 times that of seawater (Vengosh et al., 2014). For example, the produced fluids from Marcellus Shale have been recorded to vary in TDS up to 180,000 ppm (Vengosh et al., 2014). Some of the most concentrated inorganic constituents of flowback/produced waste fluids from the Appalachian Basin are Na, Cl, Mg, and Ca (Brantley et al., 2014). At lower concentrations, Ba (2000 to 8000 mg/L), Sr (1000 to 7000 mg/L), and SO₄ are also present in brines from hydraulically fractured wells.

1.1.9.2 Drilling Fluids

The process of drilling itself requires water and chemical additives to lubricate and cool the drilling equipment and clear drill cuttings, which generates "drilling fluid" waste (Lutz et al., 2013). This drilling fluid often contains high suspended and total dissolved solids. As drilling and the technology associated with the gas extraction process continues to develop, the amount of drilling fluids used and waste generated are expected to continue (Lutz et al., 2013).

1.1.9.3 Dill Cuttings and Flowback Fracturing Sand

Drill cuttings include any rock fragments or soil excavated by the drill bit to the surface before HVHF (Brantley et al., 2014; ODNR, 2012). Because drill cuttings are extracted before HVHF, they contain chemical additives used in drilling fluids. The rock fragments or soil can contain components of the black shale such as pyrite, high salt content, heavy metals, and naturally occurring radioactive material (Brantley et al., 2014). In addition to liquid wastes and chemical fluids used in the hydraulic fracturing process, these naturally occurring components within drill cuttings also pose a danger to human health and environmental integrity. Pyrite, or iron disulfide (FeS₂), in particular is problematic because it can oxidize to form sulfuric acid (H₂SO₄) and impact surface and groundwater with decreased pH and the release of metals from the soil (Brantley et al., 2014).

1.1.9.4 Disposal and Storage of Waste

Both HFFF and produced waters are typically stored temporarily on site in closed tanks or open impoundments (Barbot et al., 2013; Mohan et al., 2013; Vengosh et al., 2014). Impoundment storage can last weeks or several months before any treatment or reuse for further hydraulic fracturing. These wastewater impoundments are large artificially created ponds designed to evaporate the water via solar radiation as well as prevent downward migration of wastewater or subsurface infiltration into groundwater (Figure 5) (Bahadori, 2013). Because municipal waste treatment facilities are generally not equipped for treating such high TDS concentrations in hydraulic fracturing wastewater, a mandate by the PA DEP in 2010 limited the amount of wastewater being sent to these facilities by Marcellus drilling.



Figure 5. Wastewater impoundment pond from the Baker Carol Unit in Washington County, PA (photo courtesy of Robert M. Donnan).

Industrial treatment facilities flocculate suspended solids and/or precipitate metals in Marcellus wastewater, but few can remove many of the ions associated with the high TDS loads of the wastewater. As a result of prior waste disposal via industrial treatment facilities and subsequent discharging into local waterways like the Monongahela River, new effluent standards based on limiting TDS more strictly [Pa. Code § 95.10., 2010] were implemented by Pennsylvanian legislature (Lutz et al., 2013). With unconventional wastewater volumes increasing annually and limitations on the use of municipal and industrial waste treatment facilities, the focus for disposal switched to deep well injection sites in 2011. Class II injection disposal wells are designed to inject waste fluids from oil and natural gas operations deep underground (Cluff et al., 2014; Murray, 2013). Such disposal wells are used most commonly to prevent contamination of surface water and soils (US EPA, 2015).

While most of the wastewater (>95%) associated with gas drilling in the U.S. is disposed of via Class II injection wells, strong public opposition and natural geology in Pennsylvania made this disposal method unsuitable in the Marcellus Shale region (Lutz et al., 2013; Murray, 2013). Because of this, other methods of waste management have been used, such as (1) partial wastewater treatment and recycling for further use in hydraulic fracturing, (2) the use of private industrial wastewater facilities to treat and reuse effluent or discharge treated materials into waterways, (3) utilizing municipal wastewater treatment facilities and subsequent discharge into local waterways, (4) and transporting wastewater to areas where the capacity for Class II injection disposal sites exist (Lutz et al., 2013).

1.1.9.5 Alternative Waste Management Practices

In addition to primary disposal waste methods like Class II injection wells, oil and natural gas drilling companies may request PA DEP approval of Alternative Waste Management Practices (OG-071). Such practices can include; (1) construction of temporary containment (pits and tanks) for wastes and fluids produced from constructing oil and gas wells [Pa. Code § 78.56, 2010]; (2) alternative waste disposal practices for drill cuttings generated from above the surface

casing [Pa. Code § 78.61, 2010]; (3) alternative waste disposal practices for drill cuttings and residual waste below surface casing [Pa. Code § 78.62 or § 78.63, 2010]; and (4) the development of on-site treatment systems designed to treat flowback fluids for potential reuse/recycling [Pa. Code § 78.56, 78.61, 78.62, & 78.63 2010].

1.2 Area of Study

Located in Washington County, PA, the Cross Creek County Park (CCCP) was originally constructed in 1984 as part of a larger project for the Cross Creek Watershed (CCW) by the U.S. Department of Agriculture's Soil Conservation Service (Grant, 1973). With local organizational support (i.e. Washington County Conservation District, Washington County Commissioners, Cross Creek Township Supervisors, Independence Township Municipal Authority) and aid from the federal government, the project included flood prevention and watershed protection for 142 km² of the Cross Creek Watershed. Four dams were constructed to reduce stream sedimentation, control erosion on 59.9 km², and to provide 100-year frequency storm protection. As one of those dams, the Cross Creek Watershed Multiple Purpose Dam (PA-661) also established a 258-acre recreational lake (i.e. Cross Creek Lake). The Cross Creek Lake was then used as the nucleus for the establishment of the 3,500-acre county park that exists today. Overall, the project was implemented to improve the hydrologic condition of the watershed, improve habitat, retard runoff, and establish 0.99 km² of warm water fisheries (Grant, 1973). Today the Cross Creek Lake is stocked annually with fish that can include bluegill, bass, perch, crappie, and saugeye (Grant, 1973; Ventorini, 2007).

According to 025 Pa. Code § 93.9w (Drainage List W) issued under sections 5 and 402 of The Clean Streams Law (35 P. S. § § 691.5 and 691.402), the Cross Creek Basin qualifies as having High Quality Water (HQ) and water uses include Warm Water Fish (WWF). A WWF

protected water use requires the "maintenance and propagation of fish species and additional flora and fauna which are indigenous to a warm water habitat" (025 Pa. Code § 93.3. Protected water uses). To qualify as a High Quality Waters, the Cross Creek Basin must meet one or more of the conditions below (025 Pa. Code § 93.4b. Qualifying as High Quality or Exceptional Value Waters):

(1) Chemistry.

(i) The water has long-term water quality, based on at least 1 year of data which exceeds levels necessary to support the propagation of fish, shellfish and wildlife and recreation in and on the water by being better than the water quality criteria in § 93.7, Table 3 (relating to specific water quality criteria) or otherwise authorized by § 93.8a(b) (relating to toxic substances), at least 99% of the time for the following parameters: (1) temperature; (2) pH; (3) ammonia nitrogen; (4) aluminum; (5) iron; and (6) dissolved oxygen, nickel, copper, cadmium, arsenic, lead, and zinc.

(ii) The Department may consider additional chemical and toxicity information, which characterizes or indicates the quality of a water, in making its determination.

(2) Biology. One or more of the following shall exist:

(i) Biological assessment qualifier.

(A) The surface water supports a high quality aquatic community based upon information gathered using peer-reviewed biological assessment procedures that consider physical habitat, benthic macroinvertebrates or fishes based on Rapid Bioassessment Protocols for Use in Streams and Rivers: Benthic Macroinvertebrates and Fish, (Plafkin et al., 1989), (EPA/444/4-89-001), as updated and amended. The surface water is compared to a reference stream or watershed, and an integrated

benthic macroinvertebrate score of at least 83% shall be attained by the referenced stream or watershed.

(B) The surface water supports a high quality aquatic community based upon information gathered using other widely accepted and published peer-reviewed biological assessment procedures that the Department may approve to determine the condition of the aquatic community of a surface water.

(C) The Department may consider additional biological information which characterizes or indicates the quality of a water in making its determination.

(ii) Class A wild trout stream qualifier. The surface water has been designated a Class A wild trout stream by the Fish and Boat Commission following public notice and comment.

1.3 Surface and Ground Water

Groundwater is an essential part of the hydrologic cycle, or the continuous planetary movement of water through evaporation and transpiration, precipitation, runoff, and subsurface groundwater (Botkin and Keller, 2010; Chapman, 1996). Groundwater typically refers to water below the water table in saturated conditions, and it is the largest source of fresh water globally (Botkin and Keller, 2010; Cunningham and Cunningham, 2012). Because approximately 2.4% of all water on Earth is freshwater and only 12% of that is groundwater, it's vitally important to maintaining terrestrial life (Cunningham and Cunningham, 2012). Groundwater originates ("recharges") from precipitation that leaches into the layers of rock and soil. The shallower soil containing both air and water, or zone of aeration/unsaturated zone, provides moisture to plants while the zone of saturation, or deeper soil layers that contain pockets of filled water, provide water for drinking wells. The percolating water from precipitation eventually reaches the aquifer,
a saturated geologic layer containing porous layers of sand, rock, and gravel (Botkin and Keller, 2010; Clemens et al., 2009; Cunningham and Cunningham, 2012). Aquifer depth varies greatly but most aquifers are below 100 feet in Pennsylvania (Clemens et al., 2009).

Ground water moves horizontally underground from upland to nearby lowland areas, and eventually flows to meet the point where the water table meets the surface. This point is known as a discharge zone and it can include springs, low-lying wetlands, streams, and lakes (Botkin and Keller, 2010; Clemens et al., 2009; Cunningham and Cunningham, 2012). Streams have watersheds, or areas of land where surface and groundwater drain into a stream (Clemens et al., 2009). Aguifers vary greatly and there are four major types in Pennsylvania that include (1) unconsolidated sand and gravel, (2) sandstone and shale, (3) carbonate rock, and (4) crystalline rock aquifers. In the case of Cross Creek County Park in Washington, PA, the aquifer is sandstone and shale at depths of 80-200 ft, but sometimes exceeding 400 ft (Clemens et al., 2009). Pennsylvania has more than 1 million private drinking water wells supplying drinking water to nearly 3 million residents, making groundwater a critical resource (Clemens et al., 2009). Because groundwater feeds PA's rivers and lakes and provides for our drinking water needs, it is very important to monitor the water quality of both surface water and groundwater near human activities. High volume hydraulic fracturing is an industrial process that uses and generates large wastewater volumes that, if handled incorrectly, have the potential to seriously impact groundwater resources (Waxman et al., 2011).

The term watershed is used to describe the area in terms of a high-elevation landscape (e.g. mountain peak or ridge top) that causes water to flow into different rivers, lakes, or seas. (Conners, 2013). A drainage basin refers to the area that contributes runoff to a stream or waterbody. These terms are often used synonymously with each other, but the drainage basin is

the correct term to describe the water runoff into Cross Creek, a tributary of the Ohio River. For consistency, this water runoff area for Cross Creek was designated as a watershed to coincide with the hydrology terminology used by the U.S. Geological Survey (USGS).

1.3.1 Drinking Water Standards

Under the Safe Drinking Water Act (SDWA) of 1974 and subsequent amendments, the U.S. Environmental Protection Agency (US EPA) is authorized by Congress to set National Primary and Secondary Drinking Water Regulations (NPDWRs or primary standards and NSDWRs or secondary standards) to ensure quality drinking water to all Americans. (Background on Drinking Water Standards in the Safe Drinking Water Act (SDWA), n.d.) The standards set by the US EPA are characterized by Maximum Contaminant Levels (MCLs) and Secondary Maximum Contaminant Levels (SMCLs). These maximum contaminant levels are the maximum allowable quantity of a given contaminant in drinking water that reaches the consumer (US EPA, 2016a). Primary and Secondary MCLs include inorganic contaminants, such as metals, salts, and minerals, that are shown in Table 2. Primary standards are legally enforceable by federal law to ensure the protection of public health (US EPA, 2016b). Secondary standards are not enforceable by law and are considered for aesthetic (color, taste, odor), cosmetic (nondamaging, undesirable body effects), and technical (equipment damage) effects. According the US EPA, at the SMCL, contaminants are not considered a risk to human health (US EPA, 2016a).

With regard to hydraulic fracturing for natural gas, nearly all underground chemical injections are subject to SDWA protection, but in 2005 Congress modified the SDWA to exclude from the Act's protections "the underground injection fluids or propping agents (other than diesel fuels) pursuant to hydraulic fracturing operations related to oil, gas, or geothermal

production activities" (Waxman et al., 2011). Only if oil and gas companies use diesel products

in the fracturing process will they be regulated by the US EPA.

Analyte	EPA MCL (mg/L)				
pH*	6.5-8.5				
Silver (Ag)**	0.1				
Aluminum (AI)**	0.2				
Arsenic (As)*	0.01				
Barium (Ba)**	2				
Cadmium (Cd)*	0.01				
Chloride (CI)**	250				
Chromium (Cr)	0.1				
Copper (Cu)**	1.3				
Iron (Fe)**	0.3				
Fluoride (F)**	2				
Mercury (Hg)	0.002				
Manganese (Mn)**	0.05				
Nitrite (NO ₂)*	3.3				
Nitrate (NO ₃)*	44.3				
Lead (Pb)*	0.02				
Antimony (Sb)*	0.01				
Selenium (Se)*	0.05				
Sulfate (SO ₄)**	250				
Total Dissolved Solids (TDS)**	500				
Uranium (U)*	0.03				
Zinc (Zn)**	5				

Table 2. National Primary* and Secondary** Maximum Contaminant Levels (MCLs) set by the US EPA and tested for in this research (US EPA, 2016b).

1.4 Significance of Research

Since the year 2000, the production of natural gas from underground reservoirs has greatly expanded. Between 1/1/2000 and 3/3/2015, a total of 46,969 wells were drilled (38,034 conventional and 8,935 unconventional) and 18,964 unconventional permits were issued in Pennsylvania. In that time, 664 conventional and 1,238 unconventional wells were drilled and 2,157 permits were issued in Washington County alone (PA DEP, 2016a). Despite a 30%

increase in gas production in the last decade, the industrial process of natural gas extraction from Marcellus Shale formations via hydraulic fracturing generates a number of potential risks and hazards to human health and the environment (Brantley et al., 2014; Brittingham et al., 2014; Kahrilas et al., 2015; Kiviat, 2013; Lutz et al., 2013; Osborn et al., 2011; US EPA, 2012; Vengosh et al., 2014; Warner et al., 2012, 2014). This study focused on the analysis of surface and groundwater quality near unconventional shale gas operations around Cross Creek County Park in Washington, PA. The research is in response to the concerns posed by unconventional shale gas development near the county park, such as (1) the magnitude of drilling operations, (2) the wastewater volumes generated from existing and future drilling operations, (3) the methods of storing, transporting, and disposing of waste, and (4) potential routes of discharge or leaks from these operations.

Unlike other methods of fossil fuel extraction, hydraulic fracturing is poorly regulated by the federal government. Well fracturing processes are not regulated by the Safe Drinking Water Act (SDWA), wastewaters from hydraulic fracturing are not regulated by the Resource Conservation and Recovery Act (RCRA), and only the recent Emergency Planning and Community Right-to-Known Act has allowed the U.S. Environmental Protection Agency (US EPA) to request drilling firms to voluntarily report some of the chemical constituents in their fracturing fluids (Kargbo et al., 2010; Osborn et al., 2011). The United States House of Representatives Committee on Energy and Commerce requested that oil and gas companies release proprietary information concerning chemical additives used for hydraulic fracturing (Waxman et al., 2011). In most cases, these companies stated they had no access to proprietary information about the products they purchased. This means that many oil and gas companies are injecting chemical fluids underground with some chemicals they cannot identify themselves

(Waxman et al., 2011). With little regulation under the SDWA and minimal disclosure of fluids used in hydraulic fracturing, there exists a void of information concerning hydraulic fracturing and the ability to which regulators and the public can assess the risks this process may have human health and the environment. Because of this, it is critical that coordinated, long-term sampling and water monitoring is conducted near USGO to promote an increase in knowledge and stewardship of natural gas extraction (Osborn et al., 2011).

CHAPTER 2 – HYPOTHESES AND SPECIFIC AIMS

2.1 Hypotheses

There were two main hypotheses for this work.

- (1) The analysis of surface and ground water quality parameters, such as temperature, dissolved oxygen, pH, specific conductivity, anions, cations, dissolved gases, and surfactants can be used to determine whether or not water resources are being impacted near Cross Creek County Park, an area with extensive unconventional shale gas drilling.
- (2) Chemical ratios (e.g. Cl/Br, Na/Cl, Mg/Cl, Ca/Cl, Sr/Cl, Br/SO₄, SO₄/Cl, Ba/Cl, Sr/Ca, Ba/Ca, and Mg/Ca) can be used to distinguish the source of water impact, if any, between unconventional shale drilling and other activities, such as mining and agriculture.

2.2 Specific Aims

The specific aim of this research was to assess the state of water quality (surface) within Cross Creek County Park and the surrounding area (groundwater). The area has a history of agriculture, mining, and, since 2007, oil and natural gas extraction activity. The initial water quality study in southwestern Pennsylvania was begun by Alawattegama et al., 2015, and this research extended that study. This research will clarify water quality conditions for a county park that is located in a watershed with designated High Quality (HQ) Waters and Warm Water Fish (WWF) 025 Pa. Code § 93.9w. Drainage List W. Assessments were made on waste generation from hydraulic fracturing and its toxicity, mapping the extent of gas exploration in the area surrounding the park, the vital importance of surface and groundwater to human health and the environment, and the poor extent of regulation on chemicals and waste disposal from unconventional shale gas drilling. These issues stimulated the need for a coordinated monitoring of water resources in the CCCP and the surrounding area. Numerous studies have investigated wastewaters to produce methods for identifying these solutions in the case of pollution (Balaba and Smart, 2012; Barbot et al., 2013; Chapman et al., 2012; Dresel and Rose, 2010; Haluszczak et al., 2013; Osborn et al., 2011; Warner et al., 2014; Zhang et al., 2015). However, little research has used these methods for studying the impact of gas drilling on water quality in county parks. The specific aims include: the following:

- Analyze the spatial extent of unconventional gas extraction, mining, land use, and hydrology of Cross Creek County Park and the Cross Creek Watershed;
- (2) Synthesize data on solid and liquid waste generation, gas and oil production, and water use for unconventional gas extraction using the PA DEP oil and gas reporting applications and well completion reports, respectively;
- (3) Sample surface waters from streams draining to and from the Cross Creek Lake;
- (4) Sample groundwater from residential wells in the area surrounding the park;
- (5) Survey residents when acquiring well water samples to obtain information about the wells and drinking water issues;
- (6) Perform in-field tests (i.e. YSI-Multimeter for temperature, pH, dissolved oxygen, pressure, conductivity, and specific conductivity) and instrumental analysis (i.e. anions, cations, dissolved gases, and organics in all water samples via ion chromatography (IC), inductively coupled plasma/mass spectrometry (ICP/MS), and gas chromatography (GC), and two-dimensional gas chromatography coupled to time of flight mass spectrometry (GCxGC/TOFMS) respectively) for water samples;
- (7) Generate a repository of data and information acquired from resident surveys and instrumental analysis.

(8) Utilize ArcGIS software to show water sample locations in proximity to unconventional shale gas operations.

CHAPTER 3 – MATERIALS AND METHODS

This study collected surface and well water samples, analyzed those samples for various chemical constituents, and established a repository of the obtained data to assess water quality in proximity to natural gas extraction activities near Cross Creek County Park. The information and data included in this repository were resident's answers to survey questions, information on water sample acquisition, chemical analysis data, and sample locations. In addition, spatial patterns in topography, hydrology, land use, and all fossil fuel extraction operations within and around the park were analyzed. Finally, data on water use, waste generation, and natural gas production were also evaluated. Sources for all GIS files are shown in

Appendix A: GIS Sources by Layer.

3.1 Geospatial Analysis

The geographical information system ArcMap 10.3.1(Esri, Redlands, CA) was used to organize geospatial data and generate maps in order to better understand the watershed for which Cross Creek County Park is a part, i.e. the Cross Creek Watershed. ArcMap was utilized to investigate not only the hydrology of the area but other factors such as oil and gas operations, mining, and land use. Such areas of interest were investigated for CCW and not just CCCP because water flows into the park from other areas of the watershed, and there are other activities within the watershed that may impact water resources than just USGO.

3.1.1 Determining the Cross Creek County Park Boundary

Geospatial data on county parks within Pennsylvania could not be found, so the park area was determined via the georeferencing tool in ArcMAP 10.3.1 and a public map of Cross Creek County Park provided by the Washington County Department of Parks and Recreation (Washington County).

3.1.2 Analyzing the Extent of Unconventional Gas Extraction within CCW

Public SPUD data from the PA DEP Office of Oil and Gas website were collected to obtain GPS coordinates of all unconventional wells in the area. The PA DEP's Oil and Gas Public Reporting Application was used to determine which wells are currently producing natural gas or oil. PA DEP completion reports and well location plats were acquired from the Pennsylvania Department of Conservation and Natural Resources (PA DCNR). GPS data for proposed top hole, landing point, and bottom hole, along with other distance data from well location plats, were used to in conjunction with the editor tool in ArcMAP 10.3.1 to construct a

2D representation of drilled, underground well laterals for each unconventional gas well in the Cross Creek Watershed (Appendix H: Well Location Plat Example). Land use areas for unconventional gas extraction activities within Cross Creek County Park were determined via manually drawn polygon shapefiles in ArcMap 10.3.1 over georeferenced aerial photographs from the USGS Map Viewer and Google Earth.

3.1.3 Analyzing the Hydrology of CCW

Surface water flow direction within the Cross Creek basin was determined from digital elevation model (DEM) data that were obtained from the USGS National Map Viewer (<u>http://viewer.nationalmap.gov/viewer/</u>). Elevation data (i.e. DEM) and hydrology spatial analyst tools (i.e. Fill, Flow Direction, Flow Accumulation, Pour Point, Watershed, etc.) on ArcMAP 10.3.1 were used to determine hydrology features and the direction of surface water flow. Such information was instrumental in determining the best locations for surface water sampling in streams and lakes within Cross Creek County Park.

3.2 Residential Survey Questions

A survey was given to each resident upon collecting well water samples and it was used to determine whether or not homeowners have experienced changes in water quality. Six survey questions were reviewed and approved by Duquesne University's Institutional Review Board (IRB) and they are as follows:

- 1. Do you have well water and where is your well located?
- 2. What kind of well is it (e.g. artesian, rotary, cable tool)?
- 3. Do you know how deep the well is and have you noticed a change in your well depth?
- 4. Have you noticed any change in water quality (taste, smell, color) and if so when?
- 5. Have you noticed any change in water flow or quantity?
- 6. Have you had the water tested and would you be willing to share those results?

Lastly, a Duquesne University approved consent form was signed by the researcher and homeowner, which detailed the scope of the project, sources of funding, and confidentiality of information about the homeowner (Appendix B: Letter of Consent Form).

3.3 Sample Acquisition

3.3.1 Acquiring water samples

Well water samples were obtained prior to water softeners or filtration systems, and any line, pipe, or hose used to collect the water was purged for ten minutes to prevent interference of the actual water quality before sample collection. If the homeowner was experiencing water shortages, the purge method was not utilized. For both well water and surface water, samples were collected in a 1 L French square glass bottle (VWR International, Bridgeport, NJ) and a pre-acidified (10 M HNO₃) 60 mL pulp/vinyl interior French square bottle (VWR International, Bridgeport, NJ). Water samples for dissolved gas analysis were collected with no head space in 40 mL USP Type I Class A or B amber borosilicate vials with PTFE faced 14B rubber lined caps (Ace Glass Incorporated, Vineland, NJ). All samples were stored in the dark at 4 °C until chemical analysis. A hand-held GPS unit (Earthmate PN-20 by DeLorme) was used to log GPS coordinates for every well water sample collected.

3.3.2 Surface Water Locations

Surface waters within the park involved both stream and lake waters. Starting on 5/22/15, six streams were sampled every two weeks within the park and included: (1) Cross Creek 1 (CC1); (2) Cross Creek 2 (CC2); (3) Stream A (SA); (4) Stream B (SB); (5) Stream C (SC); and (6) Stream D (SD) (Figure 6). One other stream (i.e. Stream E) was only sampled once. It was observed that Stream E did not have consistent flow and was deemed unsuitable for a long term study. Streams F-I were actually surface waters taken from Cross Creek Lake. The samples were

labeled as streams because they flowed into bay areas of the lake and were sampled where the streams mixed with the lake water. The streams themselves were too difficult to reach because of the terrain and vegetation. In addition, limited access to kayaks resulted in acquiring only two replicate water samples from Streams F-I. Figure 7 shows each of the six streams sampled over the 1-year study.



Figure 6. Water sampling locations in proximity to USGO in Cross Creek County Park (See Appendix E: Water Sampling Locations in Cross Creek County Park for larger image). Map created from USDA hydrology, USGS DEM, PA DEP SPUD, and USGS national map viewer data.



Figure 7. Streams sampled within Cross Creek County Park. Cross Creek 1 (a), Cross Creek 2 (b), Stream A (c), Stream B (d), Stream C (e), and Stream D (f).

3.4 Chemical Analysis

3.4.1 Field Analysis via YSI-Pro Plus Multimeter

Upon collecting water samples, a YSI-Pro Plus Multimeter (YSI Incorporated, Yellow Springs, OH) was used on-site to record preliminary measurements on temperature, dissolved oxygen (DO% and DO mg/L), pH, pressure (mmHg), conductivity (μ S), and specific conductivity (μ S\cm). The YSI probe was placed into the water and allowed to stabilize before reading. For well water, two replicate measurements were taken, i.e. (1) before water line purge; and (2) after 10-minute purge. Only one measurement was logged for each surface water sample.

3.4.2 Laboratory Anion Analysis via Ion Chromatography

Fluoride (F), chloride (Cl), bromide (Br), nitrate (NO₃), nitrite (NO₂), phosphate (PO₄), and sulfate (SO₄) were analyzed with ion chromatography (IC) according to EPA Method 300.0 (Pfaff, 1993).

3.4.2.1 Sample Preparation

Before anion analysis, suspended solids were removed from the sample. The water samples were prepared by filtering through a 0.45 μ m PES filter (VWR International, Bridgeport, NJ) and a Dionex OnGuard II M filter (Dionex, Sunyvale, CA, USA). Samples were only diluted if specific conductance was higher than the ion chromatograph's detection range (0-1500 μ S/cm³). Dionex polyvials (Dionex, Sunyvale, CA, USA) were filled with 5 mL of the filtered sample before anion analysis.

3.4.2.2 Standard Solutions and Chemical Reagents

IC standards and eluents were prepared with deionized H_2O , Type I reagent grade (18 M Ω -cm specific resistance). Standard solutions were prepared and stored at 4 °C with standard stock solutions (Fluka Analytical) of anions (chloride, fluoride, bromide, nitrate, nitrite,

phosphate, sulfate, and multi-element IC anion standards) with 1000 mg/L certified molar concentrations. Eluent was prepared using an AS14A Eluent Concentrate (100x) from Fluka Analytical. Standard stock solutions (1000 mg/L) were diluted by mass in volumetric flasks with deionized water to prepare working standard solutions. A five-point calibration was run on the IC to determine chloride, fluoride, bromide, nitrate, nitrite, phosphate, and sulfate anion concentrations.

3.4.2.2 Instrumentation

A Thermo Scientific Dionex AS-DV auto-sampler was used to deliver water samples to a Dionex ICS-1100 Ion Chromatography System (equipped with a conductivity cell and UV/VIS detector). For collecting and processing data and instrument control, a Thermo Scientific Dionex Chromeleon 7 Chromatography Data System was used. An IonPac AS22A Carbonate Eluent Anion-Exchange Column (2×250 , $6.5 \mu m$ particle diameter) with a IonPac AG22 Guard Column ($2 \times 50 mm$), coupled with a Dionex ASRS-300 anion self-regenerating suppressor, was used to separate target analyte anions. The Minimum Detection Limits (MDLs) for each target anion are listed in Table 3.

Anion	Minimum Detection Limit (ppm)
Fluoride (F)	0.035
Chloride (Cl)	0.01
Nitrite (NO ₂)	0.02
Bromide (Br)	0.05
Nitrate (NO ₃)	0.045
Phosphate (PO ₄)	0.05
Sulfate (SO ₄)	0.05

Table 3. Minimum detection limits (MDLs) for target anions analyzed with ion chromatography.

3.4.3 Laboratory Cation Analysis via ICP-MS

By following EPA Method 200.8, Revision 5.4, a suite of 31 metals were analyzed using an Inductively Coupled Plasma Mass Spectrometry (ICP/MS) system. Water samples (1 mL) were filtered with a 0.45 μ m PES filter (VWR, Bridgeport, NJ) and followed by dilution with 2% HNO₃. Calibration solutions and standards were prepared with deionized H₂O, Type I reagent grade (18 MΩ-cm specific resistance). Calibration standard solutions were prepared from highpurity single and mulit-element standard stock solutions and stabilized in 2% HNO₃ (trace metal grade). Beryllium, germanium, and thallium internal standards were added to check instrument performance during sample analysis. Cationic element concentrations were measured on a Perkin-Elmer NexION 300x (Waltham, MA, USA) ICP/MS system at the University of Pittsburgh, with a NexION 300x ICP-MS software and Perkin Elmer S10 auto sampler, The MDLs for each target cation in this research are listed in Table 4.

Target Cation	Minimum Detection Limit (ppb)				
Lithium (Li)	0.088				
Boron (B)	2.533				
Sodium (Na)	0.527				
Magnesium (Mg)	3.504				
Aluminum (Al)	2.571				
Silicon (Si)	29.5				
Phosphorus (P)	2.098				
Potassium (K)	2.051				
Calcium (Ca)	2.464				
Titanium (Ti)	0.171				
Vanadium (V)	2.182				
Chromium (Cr)	0.097				
Manganese (Mn)	0.897				
Iron (Fe)	1.509				
Cobalt (Co)	0.133				
Nickel (Ni)	0.140				
Copper (Cu)	2.272				
Zinc (Zn)	1.202				
Arsenic (As)	0.239				
Selenium (Se)	0.566				
Rubidium (Rb)	0.002				
Strontium (Sr)	0.100				
Molybdenum (Mo)	0.096				
Silver (Ag)	7.996				
Cadmium (Cd)	0.021				
Tin (Sn)	0.243				
Antimony (Sb)	0.024				
Barium (Ba)	0.521				
Tungsten (W)	0.004				
Mercury (Hg)	0.066				
Uranium (U)	0.030				
Lead (Pb)	0.028				

Table 4. Minimum detection limits (MDLs) for target cations analyzed with ICP/MS.

3.4.4 Laboratory Dissolved Gas Analysis via Gas Chromatography

Water samples were taken to VaporTech Industries, Inc. (Valencia, PA) for analysis of dissolved gases. Analysis included methane, ethane, ethene, propylene, propane, and butane, and the Lower Detection Limits (LDLs) were 0.1 µg/L, 0.01 µg/L, 0.01 µg/L, 0.02 µg/L, 0.01 µg/L, and 0.03 µg/L, respectively. VaporTech Services, Inc. is authorized by the PA DEP Bureau of Laboratories to perform Analytical Method WA1 (Analysis of Dissolved Light Hydrocarbons in Water) and RSKSOP-175 using gas chromatography equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). Water samples were logged, tracked, and placed under 4 °C conditions until final analysis (within 7 days of collection), and a chain of custody was used to ensure quality assurance and quality control (QA/QC).

3.4.5 Analysis of Foam in Surface Water

Foam found in surface waters within the park was collected and analyzed by Dr. F.L. Dorman and P. Piotrowski at Pennsylvania State University using two-dimensional gas chromatography coupled to time of flight mass spectrometry (GCxGC/TOFMS).

3.5 Data Management

Data collected by the YSI- Multimeter were recorded on an electronic template in the field (Appendix C: YSI Field Data Sheet & Well Water Survey). After collecting water sample GPS coordinates, residential surveys, and performing instrumental analysis, a repository of information was created (Microsoft Excel) to ensure optimal organization of data and perform accurate calculations and data trend analyses. Organization of data in this manner also lowered the possibility error and multiple versions of data. A mail merge template of Microsoft Word was used to generate a letter of water quality results from data repository in Microsoft Excel to send to all residents participating in the well water sampling. Letters were peer reviewed before

mailing to ensure the data was correct and homeowners received the correct information about their water.

3.6 Chemical Ratios

Figures of chemical ratios from literature were digitized using OriginLab 2015 software (Northampton, MA). OriginLab 2015 was then used to plot data alongside results from previous studies on the indicative trends of chemical ratios for varying saline sources.

CHAPTER 4 – RESULTS

4.1 Environmental Observations

While the primary purpose of this study was to investigate water chemistry in proximity to unconventional gas extraction, there were also multiple observations regarding other environmental issues within the park. This included potential abandoned mine drainage, fish kills, foam in surface waters, and garbage piles that were observed in the park during the period of sampling water for analysis. These issues can occur anywhere, but they were still important in discerning the causation of well water results in an area that also has high density USGO.

4.1.1 Fish Kill

The deaths of several hundred fish were personally observed on the eastern shorelines of Cross Creek Lake on the first day of sampling water for this study (5/22/15) (Figure 8). Due to the timing of initial sampling for this study and, at the time, inadequate knowledge of the park and water flow, no water samples were taken from the lake to investigate any potential cause of impact. On 6/11/2015, biologists and a PA DEP water quality specialist from Pittsburgh analyzed the lake with a YSI-556 multimeter, and the characteristics, such as temperature, pH, conductivity, and dissolved oxygen, were determined at ten sites on the Cross Creek Lake (Figure 9). Results of the DEP analysis are shown in Table 5. While initial observations of the dead fish only accounted for one species (i.e. bluegill), subsequent investigation by the PA DEP indicated that other species (i.e. crappie) were also found dead at sites 1-4 (Figure 9). Water conditions, which were provided by the office of Pennsylvania Senator Daylin Leach, observed by the PA DEP analysis were normal, except for a pH exceeding 9 at sites 8-10. In addition, dissolved oxygen levels were low in deeper sections of the lake (i.e. sites 7-8). The PA DEP

concluded the observed fish kill was due to spawning stress because most of the dead fish were found in shallow waters.



Figure 8. Over 200 dead fish observed in the Cross Creek Lake on 5/22/2015; (a-d) dead fish found at four locations along the short of the Cross Creek Lake seen in Figure 9.

			Surface Site		Bottom Site				
Sample	Temp. (ºC)	Cond.	DO	рН	Temp. (°C)	Cond.	DO	pН	Depth (ft)
1	21.52	345	10.85	8.6	15.4	371	11.61	7.95	16
2	21.39	346	10.94	8.27	20.91	350	9.65	8.02	10
3	21.07	347	10.78	8.18		S	Surface Onl	у	
4	21.66	341	10.81	7.68	21.56	342	10.47	8.11	10
5	21.67	337	10.88	8.02	21.58	338	10.58	8.2	N/A
6	22.03	335	10.76	8.04	21.76	335	11.12	7.97	N/A
7	21.93	334	10.78	8.07	5.87	412	2.11	7.41	N/A
8	21.89	340	10.43	9.3	8.65	401	1.27	7.6	N/A
9	22.02	339	10.54	9.59	19.61	348	12.29	9.14	N/A
10	22.11	338	10.64	9.11	22.13	314	11.33	9.38	N/A

Table 5. PA DEP water quality analysis results for the Cross Creek Lake.



Figure 9. Locations where dead fish were observed (a-d) as well as PA DEP sampling sites (1-10).

4.1.2 Abandoned Mine Drainage

Potential abandoned mine drainage was observed several times within the park during the time of sample acquisition. Iron and manganese precipitation was observed in Stream A and in low-lying wet areas nearby (Figure 10). This led to further investigation of mining history and abandoned mines in the area using documents acquired from the file review with Washington County. This information was analyzed using ArcGIS software to determine mining locations in proximity to water sample sites and oil and gas operations. All current mining operations within the Cross Creek Watershed are downstream of CCCP. There is a flooded abandoned surface coal strip mine in the southern region of the park. In addition, the file review documents acquired from Washington County indicate a mine dump, as well as another strip mine located just outside the northern boundary of the park. Both Streams A and C begin very close to where the mine dump and strip mine are located just north of the park. With a large of amount of unconventional drilling in close proximity to these legacy mining sites, the observed AMD conditions within the park could suggest these sites have been disturbed to the point of impacting subsurface or surface waters.



Figure 10. Potential abandoned mine drainage (AMD) observed within Cross Creek County Park. Lowlying areas in the park showed signs of Fe and Mn laden water seeping out of the ground (a-d).

4.1.3 Foam in Surface Waters

While acquiring surface water samples from Stream A on 2/24/16, foam was observed on the surface (Figure 11) and extra samples were taken for analysis with GCxGC/TOFMS. Small amounts of foam like the example in Figure 11a were found in multiple places upstream and downstream of the usual sampling location for Stream A.



Figure 11. Collections of foam (a) and more diffuse (b) examples of foam found on the surface of several parts of Stream A 2/24/16.

4.1.4 Buried Garbage Pits

Upon further investigation of the potential AMD site (Figure 10a-c), evidence of an abandoned garbage pit was also observed. A number of items including metal fencing, electrical boxes, old bottles, and tires were discovered in an area no larger than 50 ft² (Figure 12). In addition, evidence of a plastic liner, which may have been used to cover the garbage, was found on site (Figure 12d).



Figure 12. Garbage pit within CCCP that included (a) metal sign posts, (b) tires, (c) metal electrical boxes, and (d) an old plastic liner.

4.1.5 Weather Conditions

The weather around CCCP strongly influenced observed water concentrations over the course of the year. Precipitation frequency was much higher during May, June, and July, 2015 compared to the precipitation during the remainder of the 1-year study (Figure 13). Most of August had very little precipitation and September had a few, isolated precipitation events.



Figure 13. Precipitation recorded in Washington, PA since May, 2015 as recorded by Accuweather.com.



Figure 14. Air temperature as recorded in Washington, PA since May, 2015 by Accuweather.com (accessed 5/11/16).

4.2 Geospatial Analysis of the Cross Creek Watershed

4.2.2 Hydrogeology

As designated by the U.S. Water Resources Council, the Cross Creek Watershed is within the Pittsburgh-Wheeling-Beaver Sub region (05 03) in the Ohio Region (05) (see Appendix E: Water Sampling Locations in Cross Creek County Park). (Cross Creek Watershed Project Final Environmental Statement, 1973) Figure 15 shows the geospatial arrangement of the Cross Creek and its watershed as a tributary to the Ohio River. The CCW drains approximately 230 square kilometers (51,000 acres) of land in Pennsylvania (Canton, Cross Creek, Hopewell, Independence, Jefferson, Mt. Pleasant, and Smith Townships) and West Virginia (Follansbee, Weirton, and Wellsburg Townships).

The drainage divide, or the boundary between neighboring drainage basins, for the Cross Creek Watershed is represented in Figure 16 by the dashed line connecting the hills and ridges, and thus surrounding or outlining the drainage basin or the (Conners, 2013). This drainage divide can also be used to approximate regional groundwater flow. The drainage divide indicates the separation between the flow of surface water runoff into the CCW streams and adjacent drainage basins (indicated by arrows along the drainage divide) (Conners, 2013).

SPUD unconventional well locations, obtained from the PA DEP and the West Virginia Department of Environmental Protection (WV DEP), are also shown in topographic context in Figure 17. Most unconventional well pads are located on hilltops or higher elevations compared to nearby streams in the surrounding valleys.



Figure 15. Hydrology of the Upper Ohio Watershed with regards to the Cross Creek Watershed and Cross Creek County Park. Map created from USDA Geospatial Gateway hydrology data.



Figure 16. The Cross Creek basin and its drainage divide. Map created from USDA Geospatial Gateway hydrology data.



Figure 17. Cross Creek Watershed elevation and unconventional wells with regards to CCCP. Map created from USDA Geospatial Gateway hydrology data, PA DEP SPUD data, and USGS DEM data.

4.2.3 Land Use & Land Cover

The land cover for the Cross Creek Watershed was obtained from the U.S. Geological Survey's NLCD 2006 Land Cover (2011 Edition, amended 2014) – National Geospatial Data Asset (NGDA). Area calculations were made from pixel count per feature. The patterns of land cover and land uses are shown in Figure 18. A large majority of the "developed, medium-high intensity" areas are west and down river from CCCP. Closer to the park, "open, developed" areas represent a very small percentage of land use and consist mainly of roads. Transportation routes could contribute to increased salt content and total dissolved solid concentration in nearby streams or waterbodies after road salting. The only other large land use surrounding the park itself is agriculture, which can contribute animal waste, sediment, pesticide, and fertilizer runoff into nearby streams and waterbodies in the park.

Developed land, which according to the USGS, is categorized as high intensity (0.119 km², 0.05%), medium intensity (0.548 km², 0.2%), and low intensity (3.49 km², 1.5%) areas account for approximately 4.2 km² (1.8%) of the Cross Creek Watershed. In addition, developed open land, which may include roads and parking lots, accounts for approximately 13.7 km² (6.0%) of the watershed. Land dedicated to agriculture, such as cultivated crops (26.6 km², 11.6%) and pasture/hay (38.6 km², 16.8%), account for approximately 65.2 km² (28.4%) of the Cross Creek Watershed. Vegetation in the Cross Creek Watershed, such as deciduous forest (137 km², 60%), grassland/herbaceous areas (5.81 km², 2.5%), evergreen forest (0.732 km², 0.3%), mixed forest (0.025 km², 0.0108%), and shrub areas (0.023 km², 0.0100%) account for approximately 143 km² (62.5%). Vegetation and regrowth in forests, grasslands, and shrub areas still represent a significant portion of the land in this watershed, despite development, drilling, mining, and agriculture. Open water in the CCW includes all lakes, ponds, reservoirs, and streams, and accounts for approximately 1.67 km² (0.7%) of the watershed. Wetlands account for

the smallest land area in the Cross Creek Watershed and include approximately 0.016 km^2 (0.007%) of the land. Barren lands, which can include rock, sand, and clay deposits, can be attributed to mining or construction projects and account for approximately 1.23 km² (0.54%) of the land in the CCW.



Figure 18. Land use and land cover for Cross Creek Watershed and CCCP. Map created from USGS land cover data.

Since 2007, development for unconventional gas extraction within the park has made portions of the park inaccessible. This includes clearing land for wellpads, water or chemical storage, pipelines, and access roads (Figure 19). The calculated area for these activities accounts for approximately 0.27 km² (2.4%) of the total park lands. Once operations for unconventional drilling and HVHF are complete and the wells are producing natural gas, the actual footprint of each wellpad is smaller.



Figure 19. Known unconventional shale gas operations (USGO) within CCCP. Map created from manually tracing unconventional shale gas operations from aerial photographs from Google Earth and USGS National Map Viewer.

Table 6. The seven unconventional wellpads within CCCP (seen in Figure 19) and their respective wells.

Unconventional Gas Wells	Wellpad Designation #
CCCP 5	1
CCCP 6H, 8H	2
CCCP 7H, 9H-A, 25H	3
CCCP 14H- 16H	4
CCCP 17H-19H, 45H-47H	5
CCCP 41H-44H	6
CCCP 48H-53H	7

4.2.3 Fossil Fuel Extraction

Cross Creek County Park lies over the Marcellus Shale Basin, which has seen extensive oil and gas exploration in this area over the last ten years (see Appendix G: Marcellus Formation Geology). Current extraction of fossil fuels beneath the CCW includes oil and natural gas, but a history of coal mining exists as well.

4.2.3.1 Unconventional Oil and Gas Activities

Data PA DEP well completion reports and well location plats, such as well location, well status, well type, and the path of drilling, were used to map all horizontal laterals drilled for unconventional wells in the Pennsylvania portion of the Cross Creek Watershed (Figure 20). As of May, 2015, approximately 212 unconventional oil and gas wells have been SPUD in the Cross Creek Watershed since 2007. Additionally, there are other oil and gas well pads located outside of the watershed that have been drilled and hydraulically fractured under the watershed. Of the 212 wells, horizontal wells account for 179 and the other 33 wells are of a vertical configuration. From the total 179 horizontal wells, only two are currently plugged. In addition, several unconventional wells to the west of CCCP have drilled through or beneath abandoned or currently operating coal mining areas.

Seven wellpads have been developed within Cross Creek County Park (Figure 19) and each wellpad was designated with a number for easier interpretation (Table 6). The Cross Creek County Park Well No. 5 (Wellpad No.1 in Table 6) was a vertical, unconventional well and it was SPUD in 2007, produced natural gas until the July-December 2013 reporting period, and was subsequently plugged. The remaining six wellpads within CCCP contain horizontal unconventional wells and are still producing natural gas. Three of those producing wellpads (i.e. CCCP Nos. 3, 4, and 7 wellpads as designated by Table 6) have had at least one violation since

2007. As of the last reporting period in 2015, 107 of the 200 (53.5%) wells in the portion of CCW within Pennsylvania were producing natural gas or oil. Those wells that are or have been producing both oil and natural gas lie mostly to the northeast of CCCP. While the lease for Cross Creek County Park only permits the development of seven wellpads within the park, other wellpads have been constructed just outside of the park boundary and gas wells were subsequently drilled and hydraulically fractured underneath the park (Figure 21). This includes the Avella Land Ventures Unit Nos. 2H-6H, the Christman Unit Nos. 9H, 11H-13H, and the Krajacic Unit Nos. 3H, 7H, 8H.


Figure 20. USGO in the Cross Creek Watershed. Horizontal laterals were created from PA DEP Well Location Plats obtained from the PA DCNR.



Figure 21. Designated wellpads 1-7 of CCCP and other wellpads with gas wells under Cross Creek County Park.

3.2.3.2 Coal Mining Activities

Coal has been mined in the Cross Creek Watershed since at least 1920, primarily from the Pittsburgh Coal Seam. There are abandoned mining areas within the watershed and include dry and flooded strip mines, spoil piles, refuse piles, and subsidence prone areas. Pennsylvania has a long history of coal mining and the harmful environmental impact of abandoned mine drainage. Nearly all mining areas are downstream and to the north and west of Cross Creek County Park. There is one coal surface strip mine south of Cross Creek Lake and within the park limits. Currently, it is unknown whether or not this mine has issues with abandoned mine drainage leaking into the surrounding environment. Another strip mine and mine dump are located just north of the park.



Figure 22. Areas of mining and abandoned mine lands (AML), as reported by the PA DEP in the Cross Creek Watershed. Map created from PASDA data on mining.

4.3 Data Analysis and File Review

To better evaluate the unconventional drilling for natural gas in Cross Creek County Park and its watershed, data obtained from the PA DEP on oil and gas production and waste generation for the portion of the Cross Creek Watershed within Pennsylvania only were evaluated. Well completion reports obtained from the PA DCNR were evaluated for total water use for hydraulic fracturing within the park. Finally, other files such as lease agreements and Request for Approval of Alternative Waste Management Practices forms were also evaluated.

4.3.1 Generated Waste

Storage and transportation of solid and liquid wastes from production sites may increase the potential for leaks and spills, which can impact the surrounding land and surface and ground waters (US EPA, 2012). Some potential routes for waste release and subsequent hazards include: (1) insufficient shale gas wastewater treatment and discharge, which can include utilizing treatment plants with inadequate halogen, heavy metal, or radionuclide removal designs; (2) shale gas flowback and produced water spills or surface leaks from onsite spills, breaching of surface pits, or poor pit lining; and (3) illegal or unauthorized direct disposal of untreated shale gas wastewater (Vengosh et al., 2014). Surface leaks or spills involving shale gas flowback or produced wastewaters can pollute surface water, soil, and groundwater with salts, metals, organics, and a wide variety of other substances that are either anthropogenic or naturally resulting from shale gas drilling (Vengosh et al., 2014).

Data on generated waste from unconventional gas extraction in the Cross Creek Watershed were acquired from the PA Department of Environmental Protection's (PA DEP) Oil and Gas Public Reporting Application (PA DEP, 2016b). Waste data were collected from 2009-2015 in 6-month reporting periods. The sum of solid and liquid wastes generated by oil and gas

operations in CCW was calculated. For liquid wastes the largest generated volume in barrels (Bbl) by type was produced fluids, followed by fracking fluid and drilling fluid waste (Figure 23). For solid waste the largest quantity (tons) generated by type was drill cuttings, followed by a considerably smaller amount of flowback fracturing sand (Figure 24).



Figure 23. Total liquid waste generated in the Cross Creek Watershed as of the 2015b period.



Drill Cuttings
Flowback Fracturing Sand



Even though unconventional OG operations started in Washington County, PA as early as 2005, public-access reporting from the PA DEP only accounts for wastes generated in the

Cross Creek Watershed since the July 2009 – June 2010 reporting period. Unlike the yearly analysis of oil and natural gas production, waste generation was reported in the six-month reporting period format adopted by the PA DEP. This was conducted only because early waste reports from the PA DEP generalized all liquid wastes as "Brine", which made it impossible to differentiate liquid waste types. This resulted in an inconsistent categorization of waste types per report on the PA DEP's six-month reporting periods. Reports for the total amount of drill cuttings generated (tons) in the Cross Creek Watershed started in the January – June 2012 reporting period (Figure 25). Drill cuttings generally increased until a large drop in 2015 that could most likely be attributed to low gas prices and lower demand among gas operators to drill. Along with flowback fluid wastes, sand also returns to the surface after high volume hydraulic fracturing operations. Like drill cuttings, flowback fracturing sand quantities (tons) were not reported by the PA DEP until the January – June 2012 reporting period (Figure 26). Flowback fracturing sand wastes volume generated in the CCW has continued to increase despite the apparent decrease in drilling. Flowback fracturing fluid waste (Bbl) has increased since the first PA DEP reporting period (July 2009 – June 2010). No waste data were reported from July 2010 - June 2011 for OG activities in the CCW. Like drill cuttings, drilling fluid waste has decreased dramatically in 2015 (Figure 27). Fracturing fluid waste volumes increased since 2009 (Figure 28). No data were provided for the July-December 2010 reporting period, and only a small amount of fracturing fluid waste was generated for the January-June 2011 reporting period. More waste was generated in the first half of 2014 than any other reporting period thus far. Generation of fracturing fluid waste continues despite a decrease in OG drilling activity. Reported data on produced fluid waste (Bbl) indicates a strong positive trend in the CCW since 2009 (Figure 29). Overall, produced fluids have accounted for much larger volumes than the other any other liquid

wastes associated with OG activity. While the amount of drilling and hydraulic fracturing activity may change due to economic reasons, the quantity of total produced fluid waste will continue as a by-product of unconventional oil and gas operations. In addition to CCW, the quantity of solid (Figure 30) and liquid waste (Figure 31) generated only within CCCP was evaluated. For solid waste, the quantity (tons) of drill cuttings was exceedingly larger than flowback fracturing sand. Comparing solid and liquid indicates that only solid waste data are available for three of the seven wellpads within CCCP.



Figure 25. Drill cuttings generated from OG activities in the Cross Creek Watershed. (a) January-June (b) July-December.



Figure 26. Flowback fracturing sands generated from OG activities in the Cross Creek Watershed. (a) January-June (b) July-December.



Figure 27. Drilling fluid wastes generated from OG activities in the Cross Creek Watershed. (a) January-June (b) July-December.



Figure 28. Fracturing fluid wastes generated from OG activities in the Cross Creek Watershed. (a) January-June (b) July-December.



Figure 29. Produced fluid waste generated from OG activities in the Cross Creek Watershed. (a) January-June (b) July-December.



Figure 30. Solid waste generated for three of the seven unconventional wellpads within CCCP. The (#) represents the wellpad number indicated in Table 6.



Figure 31. Liquid waste types and their respective quantities generated per wellpad in CCCP. The (#) represents the wellpad number indicated in Table 6.

4.3.2 Natural Gas Production

The first unconventional wells in the Cross Creek Watershed were SPUD in 2006 and production of both oil (Bbl) and natural gas (Mcf) began in 2007, as reported by the PA DEP (Figure 32). Production from unconventional wells within the Cross Creek Watershed has included both oil and natural since 2007, with the exception of no reported oil production in 2015. No production data were available from the PA DEP for 2008.

The first unconventional well in CCCP, Cross Creek County Park 5, was SPUD on 5/24/2007 and generated a small quantity of oil and gas by the end of the year (Figure 33). In 2008, six additional wells were SPUD (CCCP 6-8H, 9H-A, 14-15H) and no production data were reported by the PA DEP for 2008. In 2009, two additional wells were SPUD (CCCP 16H and 25H), and production of oil and gas from the unconventional wells within the park began. Oil production was reported for nine unconventional wells (CCCP 5, 6H-8H, 9H-A, and 14H-16H) within the park (Figure 34) and accounted for production only in 2009, 2010, and 2012 (Figure 33). Unlike oil, natural gas production in the park has been continuous since 2009. Natural gas production for the first nine SPUD wells climaxed in 2011, and the overall production within the park decreased until 2014, which is most likely attributed to the additional 12 wells SPUD in 2012 and four wells SPUD in 2013 (Figure 33). Since 2014, natural gas production has remained steady around six million cubic feet (Mcf) per year. A total of 25 unconventional wells have been drilled in the park since 2007, but only 24 wells are still currently in production. Only nine wells have produced oil within the park (Figure 34).



Figure 32. Oil and natural gas production for unconventional wells within the Cross Creek Watershed.



Figure 33. Oil and natural gas production from unconventional wells within CCCP since 2007.



Figure 34. Oil and natural gas production in each well SPUD within CCCP between 2007 and 2015.

4.3.3 Water Use

For unconventional gas extraction, approximately 8-40 million liters of water can be used for the high volume hydraulic fracturing step in each well bore hole (Brittingham et al., 2014; Cluff et al., 2014; Sang et al., 2014; Warner et al., 2014). A review of well completion reports obtained from the Pennsylvania Department of Conservation and Natural Resources (PA DCNR) provided the quantities of water used in the hydraulic fracturing process. For this study, only the water volumes used for unconventional wells within Cross Creek County Park were evaluated. The sum of all base (water) fluids used was compared to the total recycled fluids (Figure 35). No data on water use was provided in the completion reports for well numbers 9H-A, 17H, 41H, 42H, 43H, 44H, 47H, and 51H. Based on the information provided by the completion reports, nine of the 24 unconventional wells are known to have recycled water at least once. Water was supplied to gas wells in CCCP for hydraulic fracturing via four known sources: (1) Cross Creek Lake; (2) the Chartiers Run/Fire Academy; (3) the Carol Baker Impoundment- Rain Water; and (4) the Kearns Impoundment-Rain Water (Appendix S: Water Use for Hydraulic Fracturing in).

Despite the information gained on water use within the park, the completion reports for eight unconventional gas wells (33.3%) did not provide any information regarding water use or its origin. The Cross Creek Lake was designed to hold approximately 316,525,711 L (414,000 yd³) (Figure 36). Since drilling began in the park, the known volume of freshwater taken from Cross Creek Lake, according to well completion reports, totaled to be 145,483,000 L. This freshwater volume used for hydraulically fracturing eight unconventional gas wells amounts to approximately 46% of the volume for which the Cross Creek Lake is designed to hold at one time. Although, this volume of water was not taken from the lake at once, but over a few years. As of the beginning of 2016, the PA DEP still does not report freshwater volumes used for

unconventional gas extraction other than within well completion reports. The FracFocus Chemical Disclosure Registry does provide water volumes used by drilling companies, but this information does not describe sources. The total volume of water taken from the park lake for unconventional shale gas operations is currently unknown.



Figure 35. Known water usage for unconventional gas extraction in Cross Creek County Park. The (#) represents the wellpad number indicated in Table 6.



Figure 36. The Cross Creek Watershed Multiple Purpose Dam was built under the Watershed Protection and Flood Prevention Act in 1979. This plaque was found at the top of the dam.

4.4 Chemical Analyses of Water Constituents

4.4.1 Surface Water

4.4.1.1 YSI-Multimeter

Using the YSI-Multimeter allowed for fast multi-analysis of water parameters that included temperature, dissolved oxygen, pressure, pH, conductivity, and specific conductivity. All recorded values can be seen in Appendix M: Surface Water YSI – Multimeter Data. Temperature, pH, and dissolved oxygen requirements for high quality waters and warm water fisheries, according to requirements under 025 Pa. Code § 93.7. for specific water quality criteria, were compared with stream water YSI data (Figure 37a-c). The rise and fall of temperature (°C) in surface waters followed weather patterns (Figure 37a), and 62 (42.2%) stream samples exceeded the maximum temperature limits for HQ and WWF waters. For dissolved oxygen concentrations, nine (6.1 %) stream samples were below the recommended limit (5.0 mg/L) for HQ and WWF waters (Figure 37b). Stream C dissolved oxygen levels increased after late August, 2015, and Stream B had less dissolved oxygen than other streams in CCCP. Fluctuations in pH were observed, but all samples were within the pH 6.0 - 9.0 limit for HQ and WWF waters (Figure 37c). Specific conductivity (µS), or the ability of water to conduct electricity due to halides, organic acids, and other substances dissolved in solution, was used to determine the total dissolved solids (TDS), a useful parameter when looking for potential impacts on water quality (Figure 37d). TDS remained consistently low (200-500 mg/L), particularly from the dam outflow of Cross Creek Lake (Figure 37d).



Figure 37. Four variables determined in the field by the YSI-Multimeter; (a) temperature, (b) DO (mg/L), (c) pH, (d) TDS. The red line indicates the required limits for waters to be considered high quality or having warm water fish.

4.4.1.2 Ion Chromatography

Ion chromatography was used to measure anions: fluoride, chloride, nitrate, bromide, nitrite, phosphate, and sulfate. All anion concentrations are included in Appendix N: Surface Water Ion Chromatography Data. Fluoride was detected in 117 (75%) of 155 surface water samples, and concentrations were low with an average of 0.06 mg/L. Fluoride concentration did increase briefly on 9/8/15, and concentrations for all streams increased during the colder months of late 2015 and early 2016. Chloride was detected in all surface water samples with an average concentration of 12.23 mg/L (Figure 38a). Concentrations were lower in Streams B and D and drops in concentration for all streams on 6/16/15 and 3/15/16 were most likely due to dilution of stream water from recent precipitation. Nitrite concentrations were below the detection limit for all stream waters. Bromide (Br) was detected in 41 (26.5%) surface water samples, mostly in Cross Creek 1 and Streams A and C (Figure 38b). The detection of bromide occurred after periods of low precipitation, such as August, 2015, that led to more concentrated levels above the detection limits. The maximum Br levels for Cross Creek 1 (0.264 mg/L), Stream A (0.230 mg/L), and Stream C (0.570 mg/L) could suggest intrusion of subsurface brine-like waters. Nitrate levels consistently increased after large precipitation events, suggesting surface runoff from agriculture nearby (Figure 38c). Sulfate levels were highest in Streams A and C, two streams that originate from areas very close to a mine dump and strip mine just north of Cross Creek County Park. Higher sulfate levels with these two streams suggests potential AMD impact, and sharp decreases in sulfate resulted from dilution via large precipitation events (Figure 38d). Phosphate was detected in only 5 (3.2%) of the total 155 surface water samples and it was detected only in Streams C and B. No anion levels exceeded their respective EPA SMCLs for all streams tested in CCCP.



Figure 38. Anion concentrations for CCCP surface waters (a) Cl, (b) Br, (c) NO₃, and (d) SO₄.

4.4.1.3 Inductively Coupled Plasma-Mass Spectrometry

For cation analysis, 31 metals were analyzed via ICP/MS (Appendix O: Surface Water ICP/MS Data). Some metals of interest, such as sodium (Na), calcium (Ca), barium (Ba), strontium (Sr), manganese (Mn), iron (Fe), aluminum (Al), and lead (Pb) were evaluated over time (Figure 39-Figure 40). Sodium concentrations never exceeded 30 mg/L and the maximum levels were detected in early September, 2015, was most likely the result of low precipitation in August, 2015, that led to more concentrated sodium levels (Figure 39a). Sodium levels began to increase in November 2015, potentially from the use of road salt application in the area around the park. Calcium levels fluctuated greatly but increased during the beginning of winter (Figure 39b). Barium levels were relatively steady and no stream exceeded the EPA MCL (Figure 39c). There was an increase in Ba in June, 2015, a time of frequent precipitation. Despite higher precipitation and more dilute waters, barium levels increased, suggesting another source. Stream B had the highest levels of barium and it was also the closest stream to the garbage pit containing various metal and electrical waste. Legacy issues with this buried waste could be responsible for the increase in barium. Strontium levels coincided with trends in precipitation, i.e. high precipitation frequency caused an increase in stream volume and thereby diluting water constituent levels, and periods of low precipitation decreased stream volume and water constituents became more concentrated. However, Stream C deviated from the conventional trend of other streams in terms of exhibiting much higher Sr levels both in May during the beginning of sampling and again at the end of July and through August, 2015 (Figure 39d).

Iron concentrations exceeded the EPA SMCL (0.3 mg/L) in 135 (87.1%) surface water samples, and manganese exceeded the EPA SMCL (0.05 mg/L) in 124 (80%) stream water samples. The maximum iron (13.05 mg/L) and manganese (10.8 mg/L) concentrations were detected in Stream A on 9/8/15 (Figure 40a-b). Aluminum was detected in 144 (93%) stream

water samples and 22 (14.2%) samples had Al concentrations exceeding the EPA MCL of 0.2 mg/L (Figure 40c). On average, Streams C and D had the highest Al concentrations. Like other cation concentrations, Al levels increased during the dry August period and decreased after the periods of heavy rain in September, 2015 (Figure 40c). Lead was detected in 143 (92.3%) surface water samples and 10 (6.45%) samples exceeded the EPA MCL of 0.02 mg/L (Figure 40d). Lead concentrations corresponded with precipitation, but Stream B had the highest Pb values (Figure 40d).



Figure 39. Cation concentrations for CCCP surface waters (a) Na, (b) Ca, (c) Ba, and (d) Sr.



Figure 40. Cation concentrations for CCCP surface waters (a) Fe, (b) Mn, (c) Al, and (d) Pb.

4.4.1.4 Gas Chromatography

Gas chromatography was used to measure methane, ethane, ethene, propane, propylene, and butane concentrations in water samples. All recorded values can be seen in Appendix P: Surface Water Gas Chromatography Data. Methane was detected in 141 (91%) of the total 155 surface water samples and concentrations remained well below EPA MCLs (Figure 41). Methane was consistently detected for Cross Creek 1, Stream A, and Stream C since initial sampling on 5/22/16. On 9/8/15, there was a significant increase in methane concentration for both Stream A and Cross Creek 1. Methane was detected in colder winter months in every stream except for Cross Creek 2. In addition to methane, higher chain hydrocarbons, such as ethane, ethene, propane, and propylene were detected in 20 (12.9%) surface water samples.



Figure 41. Methane concentrations for surface waters of CCCP since May, 2015.

4.4.1.5 GCxGC-TOFMS

Surface water samples taken from Stream A on 2/24/16 contained foam that appeared on the surface of the stream and were subsequently analyzed by Dr. F.L. Dorman and P. Piotrowski at the Pennsylvania State University using two-dimensional gas chromatography coupled to time of flight mass spectrometry (GCxGC-TOFMS) to determine the potential presence of surfactants. The analysis determined the presence of 2-(2-ethoxyethoxy)ethanol, butyl carbamate, 2ethylhexan-1-ol, and 2-(2-benzoyloxyethoxy)ethyl benzoate (Figure 42). In addition, both unsaturated and saturated hydrocarbons were detected, as well as a few esters, such as 1-oxopropan-2-yl benzoate.



Figure 42. Various organic chemicals detected in foam water of Stream A after GCxGC-TOFMS (figure courtesy of F.L. Dorman and P. Piotrowski).

4.4.2 Ground Water

Ground water analysis, through well water sampling, was much more variable in location and timing compared to the continuous sampling of surface waters in Cross Creek County Park. In addition, only 18 well water samples were acquired compared to 155 surface water (lake & stream water) samples taken from the park. Well water samples had been acquired from the area surrounding the park as early as 2013 for prior research in the Stolz lab of Duquesne University. In addition, acquisition of well water samples in the area also occurred more recently (2015-2016) when the availability and interest on the part of local homeowners was brought to the attention of this research via local outreach. All recorded values can be seen in Appendix Q: Well Water Data. From the YSI-Multimeter, well water temperature, pH, and TDS averages were 13.28 °C, 7.15, and 390.1 mg/L, respectively. One well water sample had a pH of 6.43, lower than the recommended MCL range of pH 6-8. Four (22.2%) of the 18 well water samples exceeded the 500 mg/L MCL for TDS, with a maximum of 544.1 mg/L. Detected anions had levels below EPA MCLs and nitrite, bromide, and phosphate were not detected (Figure 43).



Figure 43. Box plot for anion concentrations in well waters near CCCP. The red line indicates maximum contaminate levels.



Figure 44. Box plot showing cation concentrations for well water samples compared to primary & secondary MCLs (red line) set by the US EPA.

Of the 31 cations measured, only vanadium concentrations were below detection limits. Iron levels exceeded the SMCL in eight (44.4%) well water samples, and six (33.3%) well water samples had manganese levels above the MCL. All other cation levels were below primary and secondary MCLs set by the US EPA. Methane was detected in six (33.3%) of the 18 well water samples (Table 7). The maximum detected concentration of methane was 3.01 mg/L. Other hydrocarbons, such as ethane, ethene, propane, and propylene, were detected in five (27.8%) well water samples (Table 7).

Sample	Sample Date	Dissolved Gases (µg/L)					
		Methane	Ethane	Ethene	Propane	Propylene	Butane
CC1	8/10/13	3007.14	0.21	-	0.02	0.02	-
CC2	8/10/13	-	-	-	-	-	-
CC3	8/10/13	0.65	-	-	-	-	-
CC4	8/10/13	-	-	-	-	-	-
CC5	8/10/13	26.49	-	-	-	0.02	-
CC6	8/10/13	-	-	-	-	-	-
CC7	8/10/13	4.61	0.02	-	-	-	-
CC8	8/10/13	-	-	-	-	-	-
MS291	3/20/14	-	-	-	-	-	-
MS292	3/20/14	-	-	-	-	-	-
MS583	9/25/15	-	-	-	-	-	-
MS682	1/13/2016	-	-	-	-	-	-
MS681	1/13/2016	-	-	-	-	-	-
MS698	1/27/2016	-	-	-	-	-	-
MS699	1/27/2016	1300.98	0.51	-	-	-	-
MS725	2/24/2016	1.89	0.01	-	-	-	-
MS726	2/24/2016	26.62	0.01	0.09	-	0.02	-

Table 7. Dissolved Gases in well water samples near CCCP.

4.5 Geochemical Ratios

The use of indicator element concentrations and other environmental conditions (i.e. pH, TDS, etc.) can be helpful in determining whether a water source has been impacted by natural or human activities. However, the use of such analyses alone makes it difficult to distinguish between the potential sources of impact. One major reason is because the concentration of analytes within the water is strongly dependent on dilution of that water body. The use of mass ratios has been used in the past to distinguish between a wide variety of sources that impact ground water and surface water quality because the ratios remain the same, regardless of differences in concentration (Katz et al., 2011). For this research, mass ratios (e.g. Fe/Mn, Ca/Sr, Ca/Mg, Ba/Ca, Mg/Ca Sr/Ca, Na/Cl, Ca/Cl, Mg/Cl, Sr/Cl, Cl/Br, SO4/Cl, and Br/SO4) were utilized in an attempt to distinguish the sources of salinity in CCCP surface waters and surrounding local well waters. Waters of this research were also compared to southwestern PA flowback samples analyzed by Kondratyuk et al. (manuscript in progress).



Figure 45. Relationship between Fe and Mn concentrations for Cross Creek 1 (CC1), Cross Creek 2 (CC2), Stream A (SA), Stream B (SB), Stream C (SC), Stream D (SD), Cross Creek Lake (CCL), and well water (WW).



Figure 46. Ca/Sr and Ca/Mg ratio values for well water and CCCP surface waters compared to Venango County oil well brine and flowback waters.



Figure 47. Differences in (a) Ba and Sr and (b) Mg and Sr with Ca in CCCP surface water, well water, and Marcellus brines or wastewaters of PA (Chapman et al., 2012).



Figure 48. Relationship of (a) Ca and (b) Mg with Cl for brines, produced waters, CCCP surface water, and well water (Barbot et al., 2013).



Figure 49. Relationship of (a) Na and (b) Sr with Cl for brines, produced waters, CCCP surface water, and well water (Barbot et al., 2013).



Figure 50. Ba/Cl and Br/SO₄ ratios for (a) CCCP surface waters and (b) Cross Creek 1 over time compared to reference boundary lines of impacted waters by (Brantley et al., 2014).


Figure 51. Ba/Cl and Br/SO₄ ratios for (a) Stream A and (b) Stream C over time compared to reference boundary lines of impacted waters by (Brantley et al., 2014).



Figure 52. (a) SO₄/Cl and Br concentrations (mg/L) for CCCP surface water samples and (b) the trend for Cross Creek 1 over time compared to oil and gas flowback water, Venango County conventional oil well brine, and manually drawn clusters of saline groundwater and wastewaters from fossil fuel activities (Wilson, 2013).



Figure 53. SO₄/Cl and Br concentrations (mg/L) for (a) Stream A and (b) Stream C over time compared to oil and gas flowback water, Venango County conventional oil well brine, and manually drawn clusters of saline groundwater and wastewaters from fossil fuel activities (Wilson, 2013).



Figure 54. (a) Comparison of CCCP surface water samples and (b) Cross Creek 1 over time to binary mixing curves for the Cl/Br ratios of various salinity sources (Davis et al., 1998; Mullaney et al., 2009).



Figure 55. Comparison of (a) Stream A and (b) Stream C over time to binary mixing curves for the Cl/Br ratios of various salinity sources (Davis et al., 1998; Mullaney et al., 2009).

CHAPTER 5 – DISCUSSION

5.1 Unconventional Shale Gas Operations

5.1.1 Evaluating USGO in the Cross Creek Watershed

Constructing an accurate representation of all unconventional shale gas operations and mining within the Cross Creek Watershed allowed for the determination of where and how to analyze water quality. However, determining well locations, drilling paths, and which wells were permitted versus drilled, plugged, active or inactive, and producing oil or natural gas was difficult because of the general disorganized, and at times, lack of information for unconventional drilling. SPUD reports from the PA DEP were used to determine conventional and unconventional well locations within the watershed. PA DEP well location plats, well records, and well completion reports obtained from the PA DCNR were used to create a 2D representation of the drilled horizontal laterals for each unconventional well listed in the PA DEP SPUD reports. Determining the intensity of drilling through these features was focused primarily around Cross Creek County Park. However this was difficult because of the unorganized, inconsistent, and outdated manner in which these files were created. All well completion reports and well plats are submitted to the PA DEP by physical copy only and files acquired from the PA DCNR are scans, or images, of these documents. Because of this, there were several documents that had typed or hand-written information that was unreadable due to the poor picture quality of the document. Despite having the same American Petroleum Institute (API) number, some wells had several copies of various permits and well reports that appeared the same or had slightly different drilling paths or projected top and bottom bore holes. Some wells were given API number extensions labeled as "drill deeper", but in many cases it was difficult to determine which well location plat was the correct and permenant action taken by the drilling companies. In an attempt to solve the issue of determing which diagrams and data to use for drawing geospatial

representations of unconventional well laterals, PA DEP received date stamps applied to the paperwork were used to determine the most up-to-date information. However, a great deal of caution was still given for this option for most paperwork had multiple "received" or "approved" date stamps and signuratures from multiple contractors and PA DEP officials per document.

After requesting as much information about each gas or oil well as possible, many PA DEP documents only included well reports detailing the path of proposed drilling and no record of whether or not the well was hydraulically fractured. For some wells, only well location plats were available and the information provided for the well path and GPS coordinates was minimal. For example, older well location plats (i.e. early unconventional wells starting in 2007) displayed, at times, only the GPS coordinates for the proposed top and bottom bore holes but no information on the deviated path of the well lateral. In this case, GPS information was used from the well record for each stage of the drilling process in order to acurately draw the deviated path of the well. Wells that were more recently drilled had well location plats with much greater detail that included GPS coordinates for the top and bottom bore holes, landing points, and direction and length of the well laterals. Some well completion reports only indicated that the well had been drilled but provided little information on whether or not hydraulic fracturing of the well was completed. Documentation was then compared to data obtained from the PA DEP Oil & Gas Reporting application to determine whether or not if the well was producing gas or generating waste

5.1.2 Waste and Production Data

Like the PA DEP well completion reports and well location plats, evaluating data reported by the PA DEP on waste generation and oil and gas production for unconventional wells within the Cross Creek Watershed was difficult for a number of reasons. This information

obtained from the PA DEP Oil & Gas Reporting website is currently provided in an inconsistent format, with certain variables existing in reports where they shouldn't. After selecting the preferred PA county, one may choose to examine data from all oil & gas operations or unconventional only. However, after selecting "unconventional only", the reporting website provides waste data for conventional wells, unconventional wells, Marcellus only, annual O&G with Marcellus, annual O&G without Marcellus, and waste only: unconventional wells. In addition, waste data have been organized in inconsistent time periods, such as yearly, six-month periods, and monthly since 2009. While evaluating waste quantities, it was discovered that the units for various waste types changed at random times and this made any summation of total generated waste very difficult. For example, some reporting periods listed liquid wastes in barrels (Bbl), whereas others listed those same liquid wastes in tons.

In addition to unit problems, types of waste were labeled inconsistently. Early reporting periods labeled all liquid waste as "brine", while more recent waste reports separate liquid waste into drilling fluid, fracking fluid, and produced fluid. When attempting to evaluate the total waste generated since reporting began, it is impossible to tell how much waste included drilling fluids, fracking fluids, or produced fluids in early reporting periods because all options were only labeled as brine. Most reporting provided data in 12 month periods (January – December), but one waste report was only given as a 12-month period between July 2009 and June 2010. A waste report was provided for 2009 (January – December) as well as for the second half of 2010 (July – December), but this left a gap in the reporting of waste for the second half of 2009 (July – December). Because of this inconsistent reporting of waste, evaluating the trend in solid and liquid waste generated from unconventional shale gas operations could not be calculated with 100% accuracy for either a six-month or yearly basis. Many of the same issues regarding

inconsistent reporting periods were also evident when evaluating oil and gas production data, as provided by the PA DEP. These production and waste reports provided by the PA DEP are based on information provided by the oil and gas companies and these issues in data management could lead to incorrect representations on the total production capacity of unconventional drilling and the actual amount of waste is being generated. In addition, the issues detailed above on evaluating the data indicate the Department's poor ability to organize data on an industry that is quickly growing in the state of Pennsylvania. The importance of this issue is also exacerbated when it concerns accurately reporting waste generation and the methods used to treat and dispose of said waste.

5.1.3 Plugging CCCP 5 with Poz-o-Tec

Only one unconventional well, Cross Creek County Park 5 (Well API # 37-125-2618), has been plugged inside of the park since drilling began in 2007. In 2013, the drilling company submitted a "Notice of Intention by Well Operator to Plug a Well" form to the PA DEP, which was approved and the CCCP 5 well was subsequently plugged in 2014. The "Certificate of Well Plugging" (Appendix K: Plugging CCCP 5 with Poz-o-Tec (POZ)) obtained by Washington County indicates the manner in which this well was plugged. Along with Bentonite, NaCl slurry, and Pea-Gravel, a material called Poz-o-Tec (POZ) was used as the filling material to plug the CCCP 5 well. POZ is a clay-like substance similar to that of concrete and is made through the addition of lime to a mixture of coal fly ash and flue gas desulfurization (FGD) scrubber sludge (Kraner et al., 1982). While this technology is used in an attempt to stabilize the harmful contents of coal combustion products, it still has lower strength than concrete and exhibits more porous and permeable properties than that of concrete (Kraner et al., 1982). Because of the properties of POZ and the chemical constituents of coal fly ash, which can include inorganics

such as Ba, Cd, As, Cr, Fe, Mn, Al, Ti, and Se, the use of POZ as a filling material in the plugging of unconventional wells may develop additional risks to groundwater (Kingston et al., 2005; Rivera et al., 2015). This issue is particularly important due to the lower strength and additional porosity yielded by Poz-o-Tech when compared to concrete. This porosity in POZ and the very nature of using the material to fill and plug natural gas wells poses additional concern between methane in the well and harmful inorganics contained within the POZ. Anaerobic oxidation of methane (AOM) could be enacted by anaerobic bacteria present in the well to oxidize methane via dissimilatory reduction of metals within the POZ, which would serve as terminal electron acceptors in respiration (Lloyd and Lovley, 2001; Reimann et al., 2015; Stams et al., 2006). Anaerobic bacteria using this process for respiration could potentially reduce metals within the POZ to more soluble, or in some cases, more toxic species. For example, Fe(III) and Mn(IV) could be reduced to more soluble forms of Fe(II) and Mn(III), respectively. Arsenic found in the coal fly ash used within POZ could be reduced from As(V) to a more toxic and soluble As(III). Other metals, such as Hg(II), could be reduced to less toxic forms (Hg(0)), but still more soluble and mobile in the environment. With the lower strength and higher porosity of Poz-o-Tec and its use to plug the well and prevent methane escape, the potential for methane oxidation and reduction of harmful metals within POZ only further exacerbates the potential danger posed by using POZ to plug the CCCP 5 well within Cross Creek County Park. Aside from those dangers already posed by produced waters from hydraulic fracturing, in the event of failure on the part of well casing or filling due to lower Poz-o-Tec strength, potential reduction of metals in POZ by the oxidation of methane from anaerobic bacteria pose another danger to groundwater and thereby human health and environmental integrity.

5.1.4 Alternative Waste Management within CCCP

Other documents acquired from the file review included Request for Approval of Alternative Waste Disposal Practices forms that indicated alternative waste disposal practices were used for waste originating from unconventional wells at two separate wellpads within the park. This included disposal of "top hole" drilling cuttings generated from CCCP wellpads 2-3 (Table 6), or Well Nos. 6H, 7H, 8H, 9H, and 25H. All liquid waste fractions from the drill cuttings were mixed with Soli-Bond solidification material, placed within a reserve pit on the wellpad site, and a liner material was folded over the waste in a way that prevented future infiltration of water. The pit was then backfilled at least 18 inches over the top portion of the liner (Appendix I: Alternative Waste Management Practices).

While gas companies are allowed to request approval of alternative waste disposal practices, these cases within Cross Creek County Park are in direct violation of the lease Washington County agreed to for drilling within the park. Under Section 3.1 of Environmental Quality Control precautions required under Exhibit "A" Requirements for Protection and Conservation of County Park Lands of the 2003 Oil and Gas Lease for Cross Creek County Park, "The slush pit used to contain drilling fluids, mud, and water will be lined with plastic so that no escape of these fluids will occur. If said fluids contain oil or other chemical substances which are harmful to the forest environment, Lessee shall transport these fluids for disposal. All trash, rubbish, or waste materials from each drilling site shall be removed and disposed of in a properly licensed solid waste site" (Appendix J: CCCP Oil & Gas Lease Requirements for Waste). According to waste reports obtained from the PA DEP Oil & Gas Reporting website, all drill cuttings from the seven wellpads within CCCP were transported to the Arden Landfill Chartiers Township, Washington County, PA. Drill cuttings may have been transported for waste disposal, but fluid fractions from those drill cuttings were, in some cases (CCCP 6H, 7H, 8H, 9H-A, 25H), solidified and buried on the well pad sites within the park itself.

While drilling companies do have to follow or exceed the requirements stated under 25 Pa. Code § 78.61 (disposal of drill cuttings), 78.62 (disposal of residual waste – pits), or 78.63 (disposal of residual waste – land application) when applicable, there are a few concerns these rules fail to address. In the case of the disposal of "top hole" drill cuttings from five wells within the park, drill cuttings were disposed of in a pit on the well sites. The regulations under 25 Pa. Code § 78.61, 78.62, 78.63 require many characteristics of the pit used to bury the waste that include distance to streams or waterbodies or water supply resources, concentration of constituents, and liner use methods. However, there is no language in these regulations requiring oil and gas companies to mark or identify the location of these buried waste pits. Looking at aerial photographs obtained from Google Earth for CCCP 6H, 7H, 8H, 9H-A, 25H, pits on the wellpad sites are visible in 2008 and may have been used for chemical fluids or waste (Figure 56b,d). By 2015, these spits are absent in aerial photographs (Figure 56c,e), and their absence could be that they were filled in with the solidified drill cutting fluids approved as alternative waste management by the PA DEP. There is no proof indicating these pits are the location of the buried drill cutting fluids, but it is unlikely a separate pit on site to bury the waste when one already existed in 2008. Under 25 Pa. Code § 78.62 states that the pit must be "designed, constructed and maintained to be structurally sound and impermeable." With only the requirement of adding 18 inches of soil above the liner and no requirements for identifying the waste pit location, the future use of the land poses serious risks to the impermeability of the liner and the prevention of harmful constituents inside of the pit from impacting the surrounding environment.

Agriculture is the primary land use in this area (Figure 18), and if, in the future, this area is once again used for agriculture, the requirements for burying oil and gas drill cuttings or residual waste on site in this manner may not be enough to protect the environment or human wellbeing from the use of heavy farm equipment, farming practices, and erosion that follow agriculture.



Figure 56. Location of (a) CCCP wells approved for the use of alternative waste management and aerial photography from Google Earth shows the location (b,d) and absence (c,e) of chemical fluid or waste pits on wellpads between 5/27/2008 and 9/23/2015, respectively.

5.1.4 Water Quality in Proximity to USGO

A total of 155 surface water samples were taken from within Cross Creek County Park over the time of one year. In addition, 18 well water samples were acquired near the park from the nearby community and other homeowners nearby. Little baseline water quality data exist for the park or surrounding area and this made it difficult to compare with water chemistry prior to drilling. Investigating trends in chemical constituents within the water can potentially point to any source of impact, but they cannot differentiate whether or not this area was impaired before or after unconventional shale gas operations began in the park in 2007. However, with the inconsistent data record keeping, the continuous increase in natural gas production and generation of liquid wastes, the approval of alternative waste management (i.e. burying waste within the park), and the use of POZ for plugging CCCP 5, it was essential to monitor water quality to determine whether or not these issues are having an effect on the designated high quality waters of the Cross Creek Watershed. With no baseline water quality data to compare, the water sample chemistry for samples in this study were compared to MCLs and SMCLs set by the US EPA, requirements for high quality waters and warm water fish set by the PA DEP, and geochemical ratios of various impacted waters in previous literature.

Overall most water samples had good water quality and most analytes tested for met requirements for drinking waters or high quality water. Total dissolved solids (TDS), or total organic and inorganic contents dissolved in water, is just one of the standards used to check water quality, and it can be impacted by several natural and anthropogenic factors (Wilson, 2013). Liquid wastes generated from unconventional oil and gas wells, such as produced fluids, are very high in TDS content that can range in salinity from below to over 7 times that of seawater (Vengosh et al., 2014). For example, the produced fluids from Marcellus Shale have been recorded to vary in TDS up to 180,000 ppm (Vengosh et al., 2014). Some of the most

concentrated inorganic constituents of flowback/produced waste fluids from the Appalachian Basin are Na, Cl, Mg, and Ca (Brantley et al., 2014). At lower concentrations, Ba (2000 to 8000 mg/L), Sr (1000 to 7000 mg/L), and SO₄ are also present in brines from unconventional gas extraction wells. If a leak or spill into surface or groundwater were to occur from waste impoundments, faulty well casings, or the transportation of these wastewaters, then a significant increase in dissolved constituents (i.e. TDS) could be observed. All surface water samples had TDS levels lower than the US EPA SMCL of 500 mg/L. Only four well water samples exceeded 500 mg/L but never passed 600 mg/L. These TDS concentrations in surface and well waters were low enough throughout the sampling period to indicated very low, if any, impact on water quality. Although, evaluating TDS levels alone is, in general, a poor way of determining whether or not a water source has been impacted, especially when determining any contributions of TDS by produced water (Chapman et al., 2012). Despite most water samples exhibiting little signs of impact, there were potential issues in well water samples as well as Cross Creek 1, Stream A, and Stream C.

5.1.4.1 Dissolved Gases in Water Samples

As stated previously, methane was detected in most surface water samples, but Cross Creek 1, Stream A, and Stream C had the highest concentrations, with Stream A have the maximum concentration of 554.1 µg/L on 9/8/15. For well water, methane was detected in samples CC1, CC3, CC5, CC7, MS699, MS725, and MS726 with a maximum concentration of 3.01 mg/L of methane detected in sample CC1 on 8/10/13. In addition to methane, other higherchain hydrocarbons such as ethane, ethene, propane, and propylene were also detected in both surface and well water samples. Relative ratios between these higher-chain hydrocarbons and methane have been used to differentiate biogenic versus thermogenic gas. Biogenic, or microbial, gas is mainly comprised of CH₄ and CO₂, whereas thermogenic gas contains more higher-chain hydrocarbons (ethane, propane, butane, and pentane) from thermally mature rock formations (Osborn and McIntosh, 2010). Biogenic CH₄ is produced from methanogens that extract hydrogen from underground in situ formation water and organic rich shale matter. Methanogens can consume and produce CO₂, and because of this, gas accumulations in formation waters can contain very positive δ^{13} C-CO₂ values (> +20%). Methanogenesis is limited, however, by the toxicity of high SO₄ concentrations and salinity (2000 – 4000 mmol/L Cl) (Osborn and McIntosh, 2010).Even with low SO₄ concentrations (1 mmol/L), sulfatereducing bacteria start to out-compete methanogens for acetate and hydrogen. The various microbial activity, salinity and electron acceptor availability (SO₄) conditions, thermal maturity of organic-rich Devonian shale, and potential for gases mixing in formation waters demonstrates why obtaining a method for methane origin analysis is challenging. (Osborn & McIntosh, 2010)

While it has been noted that carbon isotope values (δ^{13} C-CH₄) and gas composition can be used to distinguish between biogenic and thermogenic gases, the analysis can be complicated by microbial oxidation modifications, production of higher chain hydrocarbons by microbial activity, and mixing and fractionation between other gas sources (Osborn and McIntosh, 2010). Previous research by (Jackson et al., 2013) demonstrated the use of methane/ethane (CH₄/C₂H₆) ratios to differentiate between biogenic and thermogenic gas. The lower ratios of methane to ethane (<100) usually suggest thermogenic source of gas in water, whereas higher ratios (>1,000) suggest microbial, or biogenic, origin of gas (Jackson et al., 2013). Venango County, PA conventional oil brine samples MISC 43, 44, 45, 46, and 47 best demonstrate the CH₄/C2H₆ ratio (i.e. ~<100) that suggests thermogenic gas origin with CH₄/C₂H₆ values of 1.38, 1.55, 0.462, 0.766, and 1.93, respectively. Ethane was detected in only eight (4.6%) of the total 173 combined surface and well water samples, and four of those eight samples exhibited higher CH_4/C_2H_6 ratios (>1000) that suggest biogenic origin. Two samples from Cross Creek 1, MS675 and MS703, had CH_4/C_2H_6 ratios of 184 and 467, respectively. Two well water samples, CC7 and MS725, had CH_4/C_2H_6 ratios of 231 and 189, respectively. These CH_4/C_2H_6 ratio values for Cross Creek 1 and two well water samples were much lower than the >1000 value indicating biogenic origin. Although, these samples were still higher than the <100 limit suggested by (Jackson et al., 2013) for thermogenic origin and much greater than the CH_4/C_2H_6 ratio values of the conventional oil brine from Venango County, PA. The CH_4/C_2H_6 ratio of 184 exhibited by Cross Creek 1 on 1/13/2016 could potentially indicate thermogenic origin. This sample was taken in early 2016 during colder weather and what should be minimal methanogenic activity. Such conditions further suggest thermogenic origin, but with only concentration data and without baseline data, it unreasonable to suggest methane or ethane in the surface waters of Cross Creek County Park was present due to unconventional shale gas extraction.

5.1.4.3 Surfactants in Surface Water

In addition to dissolved gases in water samples, the use of GCxGC-TOFMS from Pennsylvania State University determined the presence of surfactants in a Stream A sample acquired on 2/24/16 (Figure 42). Under the US EPA chemical data reporting program for the Toxic Substances Control Act (TSCA), diethylene glycol dibenzoate is used as coating and paint additives and plasticizers in the industry (US EPA, 2016c). For consumer use, diethylene glycol dibenzoate is found in floor coverings, adhesives, sealants, paints and coatings, and plastic and rubber products. In the industry 2-(2-ethoxyethoxy)ethanol is used as a chemical intermediate or solvent, and for consumer applications it is used in furnishing care products, paints and coatings, ink, toner, and other coloring products (US EPA, 2016c). Butyl carbamate is most commonly found in iodopropynyl butylcarbamate (IPBC), a paint and wood preservative. The 2-ethylhexan-1-ol (CAS 104-76-7) is used in the industry and is applicable by consumers as lubricant, chemical intermediates, non-pesticide agricultural chemicals, fuel additives, paint and coating additives, and solvents (US EPA, 2016c). The 2-ethylhexan-1-ol compound has been used in hydraulic fracturing fluids for 146 unconventional wells in Pennsylvania, as reported by the FracFocus Chemical Disclosure Registry. These chemicals were detected in foam waters of Stream A by GCxGC-TOFMS, and while they have many potential uses, some, like 2ethylhexan-1-ol, are used as lubricants in fracturing fluid. Analyzing water samples by GCxGC-TOFMS can only detect the presence of organics and is not enough to determine the source of constituents within the water or whether or not their origin is related to unconventional oil and gas operations. However, many of these substances detected in the foam of Stream A have industrial uses and one would not expect their presence in a small stream originating from groundwater in a county park, especially lubricants such as 2-ethylhexan-1-ol. Stream A and the location of the foam are shown in Figure 57. It is important to note that Stream A is at the bottom of a drainage area within the park, and the stream is surrounded on three sides by higher elevation accompanied by multiple USGO wellpads. Two of those wellpads in close, upper elevation proximity to Stream A are wellpad Nos. 2-3 (i.e. 6H, 7H, 8H, 9H-A, 25H) as reported in Table 6. As stated previously, Wellpad Nos. 2-3 were granted approval for using alternative waste disposal of drill cutting liquid wastes by the PA DEP. The detection of industrial chemicals, particularly 2-ethylhexan-1-ol, and the close proximity of buried waste pits near Stream A suggest that, despite what should be high quality waters, samples taken from CCCP, and Stream A in particular, are being impacted.



Figure 57. Unconventional wells, legacy mining, and environmental observations made near surface and well water sampling locations.

5.1.4.4 Geochemical Ratios

Unconventional drilling and hydraulic fracturing generate large quantities of both solid and liquid waste. Produced waters contain high total dissolved solids (TDS), with elevated levels of barium (Ba), bromide (Br), calcium (Ca), chloride (Cl), sodium (Na), and strontium (Sr) (Chapman et al., 2012). If produced waters cannot be reused, then treatment, transportation, injection disposal methods, and storage of this waste could potentially provide an opportunity to enter shallow groundwater and surface waters through releases or spills. In addition, if the gas well integritiy is compromised, deeper groundwater sources could also be affected. This issue is particularly concerning when considering the plugging of CCCP 5 with Poz-o-Tec, a material weaker than the typical concrete used to plug wells. Evaluating TDS levels or variations in water constituent concentrations alone is not enough to determine the sources of chemicals dissolved in water resources (Chapman et al., 2012). While natural gas extraction has become very prominent in the area surrounding Cross Creek County Park, other activities, such as agriculture, application of road salt, sewage, animal waste, mining, and sedimentation can all contribute to the total dissolved chemical components in water resources. These factors provide a difficult scenario for determining whether or not unconventional shale gas operations are having any impact on water resources. Several previous studies have used chemical ratios for key indicator elements to distinguish sources of salinity impact, and many of these ratios were combined with chemical data acquired in this research to evaluate water resources within and around Cross Creek County Park.

When comparing strontium and magnesium to calcium, surface waters of CCCP were much higher in Ca/Sr and had similar Ca/Mg concentrations to oil and gas flowback wastewaters or conventional oil well brine (Figure 46). Overall, surface waters within the park exhibited no similarity with unconventional produced waters or conventional oil brine. There was a clear separation in Ca/Sr and Ca/Mg concentrations for well water samples. Some exhibited a closer relationship with CCCP surface waters while another group was closer to that of conventional oil brine from Venango County, PA. This included samples CC1, CC3, CC5, and MS726, and these well water sample locations are shown in Figure 58.

As alkaline earth metals, Ba and Sr exhibit similar chemical characteristics to that of calcium (Ca) and magnesium (Mg). A previous study (Chapman et al., 2012) used Ba/Ca and Mg/Ca ratios to determine correlations with Sr/Ca in wastes from USGO in Washington County (wellhead produced water, impoundment water), Westmoreland County (wellhead produced water), Bradford County (wellhead produced and recycled produced water), and Green County (fracturing fluid and wellhead produced water). Produced water from wellheads and impoundment water in Washington County exhibited lower Ba/Ca and Sr/Ca ratios than wastewaters of other counties (Chapman et al., 2012). When comparing these wastewaters from Chapman et al., 2012 to surface waters of this study, the Ba/Ca ratio exhibited a general positive correlation with Sr/Ca ratios, but still lower than the wastewaters tested by Chapman et al., 2012 (Figure 47a). Well water samples CC1, CC3, CC5, MS252, and MS726 were closer to the Ba/Ca and Sr/Ca ratios of conventional oil well brines from Venango County, PA (Figure 47a). This suggests the mixing of groundwater with brine-like water. Well water sample MS725 demonstrated a Ba/Ca and Sr/Ca value very close to that of wellhead produced water and impoundment water of Washington County, as described by Chapman et al., 2012. Locations for these potentially impacted well waters are shown in Figure 58.

Chapman et al., 2012 described no regional trend within just samples from the Marcellus Basin for the Mg/Ca ratio. For this study, no corelation was made in the Mg/Ca and Sr/Ca ratios

between surface waters and those wastewaters tested by Chapman et al., 2012 (Figure 47b). Surface water samples exhibited a greater consistency in the Sr/Ca ratio albiet still much less than the Sr/Ca ratio of Marcellus Basin samples. The Mg/Ca ratio for surface and well waters were very similar to, and, in the case of Cross Creek 1, Cross Creek 2, Cross Creek Lake, Stream A, Stream C, and well water, were greater than the Mg/Ca ratio of Marcellus Basin samples analyzed by Chapman et al., 2012. Similar to the analysis of the Ba/Ca ratio, well water samples CC1, CC3, CC5, MS726, MS252, and MS292 demonstrated Mg/Ca ratios similar to the conventional oil well brines from Venango County, PA when compared to the Sr/Ca ratio (Figure 47b). The use of Ca/Sr, Ca/Mg, Ba/Ca, Sr/Ca, and Mg/Ca mass ratios suggests well water samples CC1, CC3, CC5, MS726, MS726, MS725, MS252, and MS292 are moving towards more brine-like waters.

The chemical composition of CCCP surface water and nearby well water samples were also compared to ions (i.e. Ba, Mg, Na, Sr, Cl) of Marcellus Shale brine and produced waters fom Southwestern (SW) and Northeastern (NE) regions of the Marcellus Basin, as analyzed by Barbot et al., 2013. Unlike the larger, positive correlations in Ca/Cl, Mg/Cl, Na/Cl, and Sr/Cl ratios of Marellus Basin brines and produced waters, CCCP surface waters and well water exibited much smaller ratios with no discernable correlation to oil and gas brines or wastes (Figure 48-Figure 49). Although, individual streams within CCCP expressed similar ratios with other streams. For example, Stream B and Stream D had similar ratio values, whereas Cross Creeks 1 and 2, Cross Creek Lake, Stream A, and Stream C exibited another cluster of samples with similar ratios. Due to different geographical regions and depths, the Ca/Cl, Mg/Cl, Na/Cl, and Sr/Cl ratios of well water samples near CCCP understandibly deviated from surface waters within the park (Figure 48-Figure 49).

Another important anion, bromide, was found consistently in Cross Creek 1, Stream A, and Stream C. Bromide is an ion typically found at low concentrations (averages of 0.014 to 0.20 mg/L) in surface waters, and it is 40-8000 times less abundant in nature when compared to other dissolved ions such as chloride (Katz et al., 2011; Wilson, 2013). Chloride and bromide migrate with ground water and surface water and have minimum interaction with other substrates (Panno et al., 2002). Bromide can concentrate as a result of clay-membrane effects and evaporation. Enrichment of bromide relative to chloride can occur upon the degradation of organic materials. Because of these properties, bromide can be used as a potential indicator in salinity sources for water resources (Panno et al., 2002). Increases in bromide concentrations in surface waters have been reported to be associated with fossil fuel extraction processes such as coal and shale gas (Katz et al., 2011).

While bromide alone is low in abundance and of little threat to human health, it can cause larger issues if increased concentrations reach surface waters used for drinking water. Water with bromides subjected to drinking water treatment methods result in the formation of halogenated disinfection byproducts (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) (Hua et al., 2006; Krasner et al., 2006). During the disinfection process, bromide is oxidized into a strong substitution group, hypobromous acid (HOBr), which can then be incorporated into THM formation (Hua et al., 2006; Krasner et al., 2006). According to the US EPA, the majority of DBPs include chlorinated, brominated, and iodinated halomethane species (Weinburg, 2002). Other priority DBPs can include chlorinated and brominated haloketones, haloacids, haloacetonitriles, and halonitromethanes. Over 500 different DBPs have been identified by previous literature for major disinfection processes, and more importantly, only a very small percentage of these compounds have been analyzed for adverse human health effects. Many of

the DBPs already studied have carcinogenic, cytotoxic, and genotoxic characteristics (Weinburg, 2002). A study conducted in 2008 by the Allegheny County Health Department (ACHD), the U.S. Environmental Protection Agency (US EPA), and the Pennsylvania Department of Environmental Protection (PA DEP) was launched to investigate disinfection byproducts (DBPs) in the effluent of drinking water treatment facilities on the Ohio, Allegheny, and Monongahela Rivers. According to the study, bromide concentrations as high as 0.17 mg/L in the water treatment system were generating brominated DBPs that were responsible for a large portion (85% - 94%) of all THM detected (Wilson, 2013). The detection of bromide concentrations in Cross Creek 1 and Streams A and C averaged at 0.11 mg/L with a maximum of 0.57 mg/L. Such concentrations are close to, and in some cases, exceeding the 0.17 mg/L of bromide responsible for generating brominated DBPs according to the study of drinking water effluent mentioned above. While these streams enter the Cross Creek Lake and the chemical constituents are nearly diluted to the point of below detection limits, the issue of bromide detection downstream from unconventional shale gas development is still important. Similar bromide levels in surface waters may be occurring in streams nearby that do not flow into highly diluting waters (i.e. Cross Creek Lake). This issue is especially pertinent when considering these waters are connected or part of Cross Creek, a tributary of the Ohio river and thereby communities downstream that may treat and use the water for drinking.

The inert chemistry of bromide makes it an ideal tracer for the evolution of seawater derived brines (Carpenter, 1978). Plots of the mass ratio of chloride to bromide (Cl/Br) and chloride concentrations have been used previously for distinguishing between pristine water sources and wastewater sources such as seawater, basin brines, and road salts. While studies have shown that Cl/Br ratio variations in rainwater can affect Cl/Br ratios and salinity in surface

and ground waters, other factors can include proximity of the water source to mining facilities, industrial and urban areas, Br-based pesticides, farm animal wastes, and the dissolution of evaporative rock outcroppings (Katz et al., 2011).

CCCP surface water Cl/Br values and Br concentrations were compared to binary mixing lines of halite, sewage or animal waste, landfill leachate, seawater, and basin brine sources of chloride (Mullaney et al., 2009) as well as flowback water (Davis et al., 1998) in Figure 54a. It was important to compare CCCP surface water samples to many forms of water impact because of the many activities in the region that can contribute to the constituents in water. Agriculture is a large land use both within the park and upstream from the waterbodies that flow into the lake. According to the US EPA 2000 National Water Quality Inventory, agriculture is the single largest source of water pollution for lakes, ponds, reservoirs, rivers, and streams in the United States (Ongley, 1996). All varying forms of agriculture can impact surface and groundwater through the use of water and land resources and the discharge of sediment, nutrients, and chemical pollutants (Cunningham and Cunningham, 2012; Ongley, 1996). Agriculture techniques and land use are considered a "non-point" source water pollution problem. The nonpoint source water pollutant can be defined as diffuse pollution, and it originates from many human activities for which the pollution in question has no apparent point of entry into the receiving water body (Ongley, 1996). Such pollution sources are difficult to control or measure directly, are responsive to hydrological conditions, and, in the case of agriculture, focus on land and other management practices.

From the stand point of a water pollution problem, the major agricultural practices responsible can include clear cutting, animal feedlots, fertilization, cultivation, irrigation, pastures, dairy farming, orchards, and aquaculture (Ongley, 1996). Non-source pollutants from

these practices are transported through soil and over land via snow melt and rainwater. Some of the most pressing agriculturally-related water pollution problems can be associated with pollutants that can include salinity, nitrates and phosphates, decomposing organic wastes, erosion and sedimentation, nutrient enrichment, trace elements, and pesticides (Rickert, 1993). Eventually, these pollutants enter wetlands, groundwater, lakes, rivers, and streams (Ongley, 1996).

The Cl/Br and Cl concentrations of Stream A and Stream C expressed the closest similarity to the binary mixing curves of flowback water, basin brines, seawater, and landfill leachate. Both Cross Creek 1 and Cross Creek 2 had Cl/Br and Br values indicative of sewage or animal waste, while Cross Creek 1 was also close to the flowback and seawater mixing curves. Comparing Cl/Br and Br concentrations over time showed the trend in potential sources of salinity. Cross Creek 1, for the most part, displayed Cl/Br and Br values similar to the binary mixing curves of sewage and animal waste, which suggests water intrusion by bromide from mostly agriculture, which is very common in the area and incorporates livestock (Figure 54b). The Cross Creek 1 sample acquired on 9/8/15 demonstrated a stronger similarity with the lower Cl/Br ratios of flowback, basin brine, and seawater mixing curves. Stream A showed characteristics of animal waste or sewage near the start of sampling, and, over time, changed chemistry to more exemplify lower Cl/Br concentrations of basin brine, seawater, and landfill leachate (Figure 55a). Bromide was detected most frequently in Stream C and Figure 55b suggests most Cl/Br values and Br concentrations of Stream C are similar to the binary mixing lines of flowback water, basin brine, seawater, and landfill leachate during the 1-year study.



Figure 58. Potentially impacted well water locations compared to unconventional shale gas operations.

5.2 Potential Abandoned Mine Drainage Impact

Abandoned mine drainage (AMD) has been a serious water related issue resulting from abandoned mine lands (AML) and industrial operations in several countries (Johnson and Hallberg, 2005). Pennsylvania in particular has a long history of coal mining and waters draining from abandoned and active mines (Cravotta III, 2008). Thus far, AMD accounts for the degradation of more than 5000 km of Pennsylvanian streams. The estimated total cost for the reclamation of AML would be approximately \$15 billion and the cleanup of AMD an additional \$5 billion (Cravotta III, 2008). While strict land reclamation and water quality requirements are currently enforced for environmental protection, historical coal and other mineral mining was completed with little regard for environmental protection. Mine voids were left open or poorly plugged. Subsequent storm water runoff produced flooded mines with drainage waters that are typically low in pH, have high concentrations of manganese, aluminum, iron, and specific conductivity, and lower concentrations of heavy metals (Akcil and Koldas, 2006; Cravotta III, 2008; Johnson and Hallberg, 2005). The properties of AMD are the result of exposing sulfide minerals within or near coal beds to weathering through oxygen and water. This results in dissolved metal ions and soluble sulfates that produce sulfuric acid laden waters. Pyrite (FeS₂) is the most common sulfide mineral but others can include pyrrhotite (FeS), chalcocite (Cu₂S), marcasite (FeS), arsenopyrite (FeAsS), chalcopyrite (CuFeS₂), bornite (Cu₃FeS₄), sphalerite (ZnS), covellite (CuS), millerite (NiS), cinnabar (HgS), and molybdenite (MoS₂). AMD can also be produced by non-sulfide minerals such as iron hydroxide, aluminum hydroxide, and sulfate salts of iron, manganese, and aluminum. Depending on the dissolved metals within the mine drainage, the water can have color. For example, drainage waters containing dissolved iron from pyrite (Fe₂S) have a distinguishable orange red color. With such properties as low pH and high

metal concentrations, AMD contamination can severely impact soil, groundwater, and surface water (Akcil and Koldas, 2006). Since at least 1920, there have been approximately 28 coal mines within the Cross Creek Watershed that have obtained resources from the Pittsburgh Coal Seam (PCS), the most extensive and thickest coal bed in the entire Appalachian Basin (Tewalt et al., 2000).

Two large signatures of AMD, iron and manganese, were found at higher concentrations in this study. Figure 40a-b demonstrates this water quality issue for most surface water samples exhibited Fe and Mn concentrations above MCLs of 0.3 mg/L and 0.05 mg/L, respectively. Iron and manganese concentrations also exceeded MCLs in multiple cases for well water samples (Figure 44). Iron and manganese concentrations are largely controlled by reduction and oxidation reactions and various geological conditions. Reduction and oxidation reactions can impact the speciation of anions, metals, and gases in water (Lindsey et al., 2014). Conditions such as slightly acidic (pH 4-7) and anoxic (low oxygen content) water are usually favorable for dissolved iron and manganese in surface or groundwater (WHO, 2004). Under higher oxygen conditions, iron is oxidized from Fe(II) to Fe(III) and appears in a solid, suspended form with colors of red and orange. Evidence of iron and manganese precipitation was observed within Stream A and nearby low-lying areas of Cross Creek County Park (Figure 57). For well water, iron and manganese can be an aesthetic issue by staining fixtures and piping within homes, promoting bacteria growth in water systems, and affect drinking water smell, taste, and color (Clemens et al., 2009; Dvorak et al., 2007; Lindsey et al., 2014). Elevated concentrations of manganese in aerobic sources, such as those found in surface and well water samples of this study, can potentially be connected with activities such as industry and mining (WHO, 2004).

A positive correlation between iron and manganese found in surface water samples of Cross Creek County Park further exemplifies the common relationship in which these two elements are found together (Figure 45). No correlation was found for ground water samples. Ba/Cl and Br/SO₄ ratios were used to indicate water types as described by Brantley et al., 2014 (Figure 50a). Bromide was only detected in surface waters of Cross Creek County Park, and its correlation with relatively low levels of Ba and SO₄ suggest both "non-impact" and "abandoned mine drainage (AMD)" waters. CCCP surface waters are lower in Br/SO₄ ratio but have a higher Ba/Cl ratio. No samples from this research exhibited Ba/Cl and Br/SO₄ ratios similar to that of oil and gas brine impacted water described by Brantley et al., 2014. Analysis of the Ba/Cl and Br/SO₄ ratio relationship over time demonstrates the frequency in which surface waters exhibited chemistry similar to that of AMD. In Figure 50b and Figure 51a-b, the Ba/Cl and Br/SO₄ concentrations for Cross Creek 1, Stream A, and Stream C best exemplify the alternating trend between non-impacted water and AMD impacted water over time.

Another geochemical ratio relationship (Wilson, 2013) was used to describe the alternating trend between non-impact water and AMD impacted water of CCCP surface waters. Wilson described the use of chloride and sulfate concentrations for distinction between natural waters, coal-related wastewaters, and oil and gas wastewaters. Oil and gas produced wastewaters are amplified in sulfate compared to chloride (Wilson, 2013). Contrastly, coal-related wastewaters are amplified in chloride compared to sulfate. However, as stated by Wilson, 2013, the SO₄/Cl ratio can only be used to distinguish between coal-related wastewaters and oil and gas produced waters. More information in distinguishing these fossil fuel wastewaters and natural waters can be acquired when comparing SO₄/Cl ratios to bromide concentrations. This format of analysis led to the comparison of CCCP surface water samples and highlighted clusters of

traditional and Marcellus oil and gas produced water, coal-fired power plant effluent, brine treatment plant effluent, abandoned mine drainage, and saline groundwater described by Wilson, 2013 (Figure 52a). In addition, the SO₄/Cl ratio and Br concentrations of conventional oil well brine from Venango County, PA and oil and gas flowback samples were investigated. Three of the four flowback samples (i.e. FB092012, FB102612, and FB110112) showed similarity between oil and gas produced water and brine treatment plant effluent clusters; whereas the flowback sample FB100412 exibited clear produced water characteristics. Venango County, PA conventional oil well brine samples also displayed clear similarity in SO₄/Cl and Br to produced water and brine treatment plant clusters. Water samples from CCCP were much higher in SO₄/Cl than oil and gas produced waters and were comparable to saline groundwater, AMD, and coalrelated wastewaters. Although, when SO₄/Cl was compared to Br concentrations, CCCP surface waters exibited a closer similarity to AMD. Similar to the use of Ba/Cl and Br/SO4 ratios described by Brantley et al., 2014, the SO₄/Cl and Br concentrations of Cross Creek 1, Stream A, and Stream were analyzed over time. While Cross Creek 1 was outside any impacted water clusters (Figure 52b), Stream A (Figure 53a) and Stream C (Figure 53b) showed an alternating trend between non-impacted water and AMD water characteristics over time.

Current records of mining in the area indicate current or past activity to the west and downstream of the park, which suggests little potential for water quality impact, regardless of current operations or legacy issues (Figure 20). There is a flooded surface strip mine in the southern region of Cross Creek County Park, and maps obtained from the Washinton County file review indicate a mine dump and strip mine just north of the park (Figure 59). However, no information could be found on the history or actual layout of either mine sites. Historical aerial photographs obtained from the United States Department of Agriculture via Pennsylvania

Geological Survey's Penn Pilot project show disturbed landscape and suggest active operations for both of these mine sites in 1958 (Figure 59). The resource obtained from these mines was likely coal. Although, it is unknown whether or not these mines have issues with AMD impacting the surrounding environment or water resources. The mine dump just north of CCCP is very close to where Stream C begins and it is also very close to vertical unconventional wells Cowden 50 and 53 (Figure 59). In addition, unconventional drilling and hydraulic fracturing (i.e. Cowden 47H-48H) occurred beneath the strip mine located just north of CCCP. Other vertical unconventional wells (i.e. Cowden 46, 75, 76) also surround the strip mine. The use of Ba/Cl, Br/SO4, and SO4/Cl ratios in conjunction with Br exemplify AMD-impacted surface waters, which could suggest that the legacy mine operations just north of where Streams A and C begin have been distrubed by the nearby high density unconventional drilling. It is also important to note that if any abandoned or improperly sealed shallow oil or gas wells exist near these mining areas, there is the potential that groundwater, and thereby surface water, could potentially be impacted by deeper basin brines (Poth, 1973).

There is strong evidence from observations made within the park (Figure 10) and from comparing geochemical ratios to previous literature that surface waters of Cross Creek County Park (i.e. Cross Creek 1, Stream A, and Stream C) are being impacted by abandoned mine drainage. However, without baseline data, the true source of potential AMD intrusion or whether or not surface waters within the park have been impacted before unconventional drilling began in 2007 is currently unknown.



Figure 59. Legacy mining near unconventional shale gas operations within CCCP.

5.3 Special Protection Watershed: Cross Creek

Cross Creek County Park is located within the Cross Creek Watershed, which, under 025 Pa. Code § 93.9w, is designated as a special protected use as high quality (HQ) waters with warm water fishes (WWF). To hold this special protection designation, waters must be better than those water quality requirements described in 025 Pa. Code § 93.7, Table 3 or § 93.8a(b) for at least 99% of the time. There seems to be no special requirements for which oil and gas operators must operate to ensure a Special Protection Watershed is compliant with state rules. Although, the PA DEP does provide a letter to drilling companies when they expect to develop oil and gas wells in a Special Protection Watershed with waters classified as high quality (Appendix L: PA DEP Letter Regarding High Quality Water). Surface water samples from within CCCP in this study were compared to the requirements for high quality waters with warm water fishes based on a 1-year study. Only temperature, dissolved oxygen, and pH were compared to HQ and WWF requirements. Dissolved metals, such as Al, Ni, Cu, Cd, Zn, Pb, and As, have maximum limits that are based on stream hardness as $CaCO_3$ (25 Pa. Code § 93.8a(b)), which was not determined in this study. Stream temperatures were below the maximum recommended limits set under 25 Pa. Code § 93.7 Table 3 for only 57.8% of the time within the 1-year study (Figure 37a). This was most likely due to the relatively warmer winter temperatures between 2015 and 2016. Dissolved oxygen was closer to meeting the water quality requirement with concentrations exceeding the 5.0 mg/L minimum 93.9% of the time during the 1-year study (Figure 37b). The pH for all surface waters never deviated outside of the pH 6.0-9.0 limit (Figure 37c). While both temperature and dissolved oxygen deviated from water quality requirements over 99% of the time during a 1-year study, evaluation of other water quality requirements (i.e.

dissolved metals) would have been required to make a full determination as to whether or not surface waters of Cross Creek County Park are actually qualifying as high quality waters.

5.4 Aluminum and Lead in Surface Waters

Lead and aluminum levels were higher than expected for Streams B and D. Up until 10/20/15, Stream B samples were taken after the outflow from a metal pipe that transported the stream under the trail path for a short distance (Figure 60). Dense vegetation prevented the acquisition of Stream B water from upstream from the pipe prior to 10/20/15. Initially, the Al and Pb levels in Stream B were thought to be the result of the metal pipe, which could have leached metals into the water and provided higher concentrations of these metals than other streams within the park. On 10/20/15, the vegetation had decreased enough from the changing season to access Stream B before the pipe. Similar levels of Al and Pb were found in the water upstream from the pipe, which suggests that the pipe was not the source of these higher metal concentrations above EPA MCLs in Stream B. (Figure 40c-d). Aluminum levels in Stream D were also high and had the most samples with concentrations exceeding the MCL than any other stream. While Al and Pb levels in Streams B and D could be attributed to natural origins in the surface or subsurface geology, other factors could potentially be the cause of levels higher than MCL. Figure 57 shows the location of the buried garbage pits found nearby, which could be one potential source of metals in the water. Most of the items found at the pile in Figure 12 were electrical and metal scrap. While the owner of this land could have buried these items before the park existed, there is also a chance that additional scrap could be located elsewhere in the park and leaching metals into groundwater and surface waters.


Figure 60. Drainage pipe outflow that was used to sample water from Stream B until 10/20/15.

CHAPTER 6 – SUMMARY AND FUTURE DIRECTION

Washington County, PA, like many other regions of western Pennsylvania, has both past and present human activities that present challenges for protecting water resources. Agriculture, coal mining, and oil and gas operations are some of the largest potential sources of impact on surface and groundwater. The Cross Creek Watershed, which contains Cross Creek County Park, is no exception to impact from human activities. With the Department of Agriculture's project to construct several dams within the watershed in an attempt to reduce flooding, prevent erosion and sedimentation, and develop a watershed with high quality water and warm water fish, the Cross Creek County Park was conceived (Grant, 1973). The park was finished in 1984 and it has served as an important recreation attraction for the nearby communities.

Coal mining in the Pittsburgh Coal Seam has existed in the area since at least 1920. A surface coal strip mine exists within the park, and another strip mine and mine dump are located just north of the park. Agriculture dominates the countryside within and upstream from the park and accounts for approximately 65.2 km² (28.4%) of the land use within the Cross Creek Watershed. After the Renz well was the hydraulically fractured in 2004 and subsequently began producing natural gas in Mount Pleasant Township of Washington County, PA, unconventional drilling for oil and natural gas spread throughout Pennsylvania. The first unconventional well within Cross Creek County Park began with CCCP 5 in 2007, and currently seven wellpads containing 25 unconventional wells are located within the park. According to SPUD data reported by the WV DEP and the PA DEP approximately 212 unconventional wells have been developed within the Cross Creek Watershed as of May, 2015. Some unconventional wells were developed on already existing conventional wells, while others were drilled through or in close proximity to mining areas. Poz-o-Tec (POZ), a material similar to concrete, but made of lime,

flue gas desulfurization scrubber sludge and coal fly ash, was used as filler for plugging CCCP 5, a vertical unconventional well within the Cross Creek County Park in 2014. The use of POZ could complicate the integrity of the well plugging, and the presence of methane and anaerobic bacteria could potentially mobilize or increase the toxicity of metal species within the material. In addition, the PA DEP approved the use of use alternative waste management for drill cutting fluids within the park, and the waste was subsequently solidified and buried in unmarked pits on two wellpad sites within the park. This was in direct violation of the lease Washington County agreed to for drilling within the park, which indicated that no permanent containment of waste within the park would be tolerated. Finally, despite what is considered an area of high quality water with warm water fish, no additional rules from the PA DEP require drilling companies to make any additional measures to ensure this level of water quality was still present during unconventional shale gas operations.

This poor regulation of waste within the park, combined with the recent introduction of high density unconventional drilling and hydraulic fracturing in an area with legacy mining and agriculture, increased the concern for the protection and analysis of water quality. A total of 173 water samples within and near the Cross Creek County Park were collected and analyzed over a 1-year study (May, 2015-2016) via surface and well water sampling. Water chemistry was analyzed via YSI-Multimeter, ion chromatography, inductively coupled plasma mass spectrometry, gas chromatography, and two-dimensional gas chromatography coupled to time of flight mass spectrometry. The results were compared to US EPA Primary or Secondary Maximum Contaminate Levels as well as requirements for high quality waters with warm water fish under 25 Pa. Code § 93.

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Temperature (42.2%) and dissolved oxygen (6.1%) in surface water samples failed to meet requirements for high quality waters. Of the 155 surface water samples, iron (87%), manganese (80%), aluminum (14.2%), and lead (6.45%) exceeded the Primary or Secondary Maximum Contaminate Levels. Of the 18 well water samples, TDS (22.2%), iron (44.4%), and manganese (33.3%) exceeded Secondary Maximum Contaminate Levels. Methane was detected in both surface water (91%) and well water (39%) with maximum concentrations of 0.554 mg/L in Stream A and 3.01 mg/L in well water sample CC1, respectively. Other hydrocarbons, such as ethane, ethene, propane, and propylene were detected in surface water (12.9%) and well water (55.5%) samples. Well water samples CC7 and MS725 had lower CH_4/C_2H_6 ratios of 231 and 189, respectively that could potentially indicate biogenic gas origin (Jackson et al., 2013). Well water sample MS725 was also similar to wellhead produced water and impoundment water of Washington County, PA when comparing the Ba/Ca ratio to Sr/Ca (Chapman et al., 2012). Well water samples CC1, CC3, CC5, MS252, MS292, and MS726 were similar to conventional oil brine from Venango County, PA when comparing Ba/Ca and Mg/Ca ratios to Sr/Ca (Chapman et al., 2012), and when comparing Ca/Sr to Ca/Mg ratios. These mass ratios suggest water chemistry from residential wells very close to unconventional shale gas operations near Cross Creek County park are moving towards more brine-like waters.

Two samples from Cross Creek 1 (i.e. MS675 and MS703) had lower CH₄/C₂H₆ ratios of 184 and 467, respectively that could potentially suggest thermogenic gas origin (Jackson, et al., 2013), particularly MS675 which was collected during colder weather and what should be low methanogenic activity. Organic chemicals, such as diethylene glycol dibenzoate, 2-(2-ethoxyethoxy)ethanol, butyl carbamate, and 2-ethylhexan-1-ol, have many industrial and consumer uses, and they were detected in foam water in Stream A on 2/24/16. The presence of 2-

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ethylhexan-1-ol, a lubricant used in 146 unconventional wells within PA (FracFocus Chemical Disclosure Registry) is particularly concerning and demonstrates that Stream A is being impacted. Bromide was detected mostly in Cross Creek 1, Stream A, and Stream C, and concentrations were similar to, and at times, exceeding the minimum 0.17 mg/L of bromide responsible for the formation of trihalomethanes in drinking water treatment, according to the 2008 study by the ACHD, US EPA, and the PA DEP. Comparing Cl/Br ratios to Br concentrations for Cross Creek 1 show similarity with the binary mixing lines of sewage or animal waste, which supports the notion that Cross Creek 1 flows through areas of land used for agriculture and livestock before entering Cross Creek County Park (Davis et al., 1998; Mullaney et al., 2009). In addition, Cl/Br ratios and Br levels suggest Stream A was similar to the binary mixing lines of sewage or animal waste, but over time, began to more exemplify characteristics of Stream C, which was similar to the binary mixing lines of flowback water, basin brine, seawater, and landfill leachate. Evidence of high iron and manganese precipitation in Stream A and other low-lying wet areas of the park, and the use of Ba/Cl, Br/SO₄, and SO₄/Cl ratios in conjunction with Br suggest surface waters within CCCP are being impacted by abandoned mine drainage (Brantley et al., 2014; Wilson, 2013). This could be the result of unconventional drilling operations disturbing legacy mining operations within or very close to the park. With the legacy issues of abandoned mines and the continuous development of oil and gas operations near Cross Creek County Park, it is essential that continuous water quality monitoring projects should be conducted to better understand whether or not waters within the park and the watershed are being impacted and whether or not they are meeting recommended requirements for high quality water classification.

Limitations for this study included one sample collection for every two weeks despite the continuous changing quality of surface waters within the park over time. In addition, only 18 well water samples were collected from the area near the park. Changes to these limitations would improve water quality data and the overall understanding of surface and groundwater in an area with high density unconventional oil and gas operations. Sampling of surface waters within the park has stopped but the acquisition of groundwater samples via well water will be continued in the area surrounding the park when public interest is optimal. As stated earlier in the results, methane, and at times, other higher chain hydrocarbons were detected within CCCP. While at small concentrations, methane was still detected in surface waters during cold winter months when microbial generation of methane should be non-existent. Even some well water samples had higher levels of detected methane. In terms of a drinking water health hazard and ingestion, dissolved methane in water is of little known concern. However, methane is a fire and explosion hazard and an asphyxiate in closed spaces (Osborn et al., 2011). Because of this, it is critical to analyze methane dissolved in surface or groundwater to determine its source (either deeper thermogenic gas or shallow biogenic gas). In a recent study groundwater samples were taken from shallow formations near shale gas exploration in northeastern PA and subsequently analyzed for concentrations of dissolved-methane gas, methane hydrogen and carbon isotope ratios, and higher chain hydrocarbons (Osborn et al., 2011). The ratio of methane and other higher-chain hydrocarbons (ethane, butane, and propane) and δ^2 H-CH₄ and δ^{13} C-CH₄ values were used to distinguish between deeper thermogenic (physically derived) and shallower biogenic (biologically derived) methane gas (Osborn et al., 2011).

The combination of low δ^{13} C-CH₄ values and higher negative δ^{2} H-CH₄ values than -175 % typically indicate a purer biogenic origin of methane. Less negative δ^{13} C-CH₄ values than -54

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% indicate deeper thermogenic methane while more negative values than -64 % greatly indicate microbial methane (Osborn et al., 2011). One other indication used for distinguishing the source of methane is the presence of higher-chain hydrocarbons with low methane-to-ethane ratios (<100). This can indicate deeper thermogenic methane because higher-chain hydrocarbons like ethane or propane are not usually coproduced from microbial methanogenesis (Osborn et al., 2011). From the gas data obtained, the Osborn et al., 2011 study found that Middle Devonian and older thermally mature organic matter was the most likely source of thermogenic gas to cause high concentrations of dissolved methane in the shallow water wells observed (Osborn et al., 2011). To distinguish between biogenic and thermogenic methane in CCCP surface waters and surrounding well water, the methods outlined by Osborn et al., 2011 may be potentially used in the future.

Besides determining water quality and potential sources of impact, management practices and policies in place for unconventional oil and gas operations should be improved to better protect human health and the environment. This includes changing the requirements for alternative waste management practices, limitation on water use from within the park, prevention of the use of dangerous substances, such as coal fly ash, to plug recently fractured unconventional wells, and the addition of new rules to better ensure requirements for high quality waters are met. Geochemical ratios proved to be a useful tool in identifying sources of potential water impact. While many characteristics of water quality determined in this study were similar to data collected by the PA DEP, the addition of ratios analysis could aid in a better understanding of water quality and indicators of potential contamination. With the rise in unconventional oil and gas exploration within Cross Creek County Park and the Cross Creek Watershed, issues over chemicals used, solid and liquid waste generated, and protection of

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human health and the environment has become a significant issue for the present and the future. Continued water quality analysis in the area near shale gas exploration and the continued analysis of inorganics, organics, and hydrocarbons involved in this industrial process will be essential in understanding the potential effects of this industry for the future of public health and environmental integrity.

CHAPTER 7 – REFERENCES

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APPENDIX A: GIS SOURCES BY LAYER

Data Layer	Source
Cross Creek County Park	Washington County Department of Parks and Recreation. Cross Creek County Park Map, 2014.
Land Cover	U.S. Geological Survey, 2014-10-10, NLCD 2006 Land Cover (2011 Edition, amended 2014) – National Geospatial Data Asset (NGDA) Land Use Land Cover: None None, U.S. Geological Survey, Sioux Falls, SD.
Oil & Gas Development	Total area used for oil and gas operations within CCCP was drawn from tracing aerial images obtained from the USGS National Map Viewer.
Hydrology	U.S. Geological Survey, 2014-12-20, National Hydrography Dataset (NHD) Best Resolution for HU8-05030101 HU-8 Sub basin (12/04/2000 – 06/26/2014).
riyurology	USDA/NRCS – National Geospatial Center of Excellence, 2014, 8 Digit Watershed Boundary Dataset, U.S. Department of Agriculture, Service Center Agencies, Fort Worth, TX, obtained 10/6/14.
Digital Elevation Model (DEM) Data	USGS National Map Viewer, http://viewer.nationalmap.gov/viewer/
PA Local & State Roads	Pennsylvania Spatial Data Access, PASDA. The Pennsylvania Geospatial Data Clearinghouse http://www.pasda.psu.edu
PA Counties	Pennsylvania Spatial Data Access, PASDA. The Pennsylvania Geospatial Data Clearinghouse http://www.pasda.psu.edu
PA Municipalities	Pennsylvania Spatial Data Access, PASDA. The Pennsylvania Geospatial Data Clearinghouse http://www.pasda.psu.edu
U.S. States	US Department of Commerce, US Census Bureau, 2014 TIGER/Line Shapefiles
Marcellus Formation Elevation & Thickness	U.S. Energy Information Administration, 2015-1-8, Marcellus shale play boundaries, elevations and isopachs. <u>http://www.eia.gov/pub/oil_gas/natural_gas/analysis_publications/maps/maps.</u> <u>htm</u>
PA SPUD Oil and Gas Wells	Pennsylvania Department of Environmental Protection, Office of Oil and Gas Management, http://www.depreportingservices.state.pa.us/ReportServer/Pages/ReportViewe r.aspx?/Oil_Gas/Spud_External_Data
Conventional & Unconventional Oil & Gas Wells of PA	Pennsylvania Spatial Data Access, PASDA. The Pennsylvania Geospatial Data Clearinghouse http://www.pasda.psu.edu
Oil and Gas Fields	Carter, K. M., Moore, M. E., Harper, J. A., and others, 2015, Oil and gas fields and pools of Pennsylvania—1859–2011: Pennsylvania Geological Survey, 4 th ser., Open-File Report OFOG 15–01.0, 10 p., geodatabase and shapefiles.
Abandoned Mine Lands	Pennsylvania Spatial Data Access, PASDA. The Pennsylvania Geospatial Data Clearinghouse http://www.pasda.psu.edu
Digitizing Mining Areas	Pennsylvania Spatial Data Access, PASDA. The Pennsylvania Geospatial Data Clearinghouse http://www.pasda.psu.edu

APPENDIX B: LETTER OF CONSENT FORM



SUMMARY OF RESULTS:	You will be provided a summary of your well water test results that we conduct and an explanation of these results.				
VOLUNTARY CONSENT:	I have read the above statements and understand what is being requested of me. I also understand that my participation is voluntary and that I am free to withdraw my consent at any time, for any reason. On these terms, I certify that I am willing to participate in this research project.				
	I understand that should I have any further questions about my participation in this study, I may call Dr. Joseph Kush, Chair of the Duquesne University Institutional Review Board (412- 3961151).				
	Please feel free to contact me (Dr. Stolz) if you have any questions (412 396 4367; stolz@duq.edu)				
SIGNATURES:	Both the researcher and subject copy with original signatures.	should sign, and each should hold a			
Participant's Signature		Date			
Participant's Name (Printed)		Date			
Participant's Name (Printed) Researcher's Signature		Date Date			
Participant's Name (Printed) Researcher's Signature Participant's Address		Date			



DUQUESNE UNIVERSITY

Office of Research

301 ADMINISTRATION BUILDING . PITTSBURGH, PA 15282-0202

Dr. Joseph C. Kush Chair, IRB-Human Subjects Office of Research Phone (412) 396-6326 Fax (412) 396-5176 E-mail: kush@duq.edu

November 6, 2012

Re: Well Water Survey of Six Counties in Western Pennsylvania - (PROTOCOL # 12-140)

Dr. John F. Stolz Center for Environmental Research and Education Duquesne University Pittsburgh PA 15282

Dear Dr. Stolz,

Thank you for submitting your research proposal to the Institutional Review Board at Duquesne University.

Based on the review of IRB representative Dr. Becky L. Morrow and my own review, your study is approved as **Exempt** based on 45-CFR-46.101.b.2 regarding research involving the use of educational tests, survey procedures, interview procedures or observations of public behavior.

The consent form is attached, stamped with IRB approval and expiration date. You should use the stamped form as the original for copies you display or distribute.

The approval pertains to the submitted protocol. If you wish to make changes to the research, you must first submit an amendment and receive approval from this office. In addition, if any unanticipated problems arise in reference to human subjects, you should notify the IRB chair before proceeding. In all correspondence, please refer to the protocol number shown after the title above.

Once the study is complete, please provide our office with a short summary (one page) of your results for our records.

Thank you for contributing to Duquesne's research endeavors.

Sincerely yours, ye e. 1

Joseph C. Kush, Ph.D.

C: Dr. Becky L. Morrow IRB Records

APPENDIX C: YSI FIELD DATA SHEET & WELL WATER SURVEY

	YSI DATA SHEET	•		
Homeowner I	nformation	Well Information		
Address:		GPS Latitude:		
City, State, Zip:	GPS Longitude:			
Mailing Address:	Elevation (ft):			
County:	MS Number:			
Township:	MS Number:			
	Sample Information			
Date:	Sample Source:			
Time:				
Pre/Post Drill:	Sampled By:	#2	Average	
Tomp (%C)		#2	Average	
DO(ma/l)				
nH	nH			
Pressure (mmHa)	Pressure (mmHa)			
Sof Cond (uS/cm)	Spf Cond (uS/cm)			
Cond. (uS)	Cond. (uS)			
	(µ)	TDS		
	Survey Questions:			
1. Do you have well water ar	nd where is your well locat	ed?		
2. What type of well is it? (e.	.g. artesian, rotary, cable to	ool)?		
3. Do you know how deep th	ne well is? Have you notice	d any change in your w	ell depth?	
4. Have you noticed any cha	ange in water quality, if so v	when?		
5. Have you noticed any cha	ange in the water flow of qu	antity?		
6. Have you had the water te	ested? Would you be willin	g to share those results	?	
	Notes:			
	Notes:			

Analyte	EPA Maximum Detection Limit (mg/L)
рН	6.5-8.5
Silver (Ag)	0.1
Aluminum (Al)	0.2
Arsenic (As)	0.01
Barium (Ba)	2
Cadmium (Cd)	0.01
Chloride (Cl)	250
Chromium (Cr)	0.1
Copper (Cu)	1.3
Iron (Fe)	0.3
Fluoride (F)	2
Mercury (Hg)	0.002
Manganese (Mn)	0.05
Nitrite (NO ₂)	3.3
Nitrate (NO ₃)	44.3
Lead (Pb)	0.02
Antimony (Sb)	0.01
Selenium (Se)	0.05
Sulfate (SO ₄)	250
Total Dissolved Solids (TDS)	500
Uranium (U)	0.03
Zinc (Zn)	5

APPENDIX D: EPA MAXIMUM DETECTION LIMITS (MCL)



APPENDIX E: WATER SAMPLING LOCATIONS IN CROSS CREEK COUNTY PARK



APPENDIX F: WATERSHEDS OF PENNSYLVANIA WITH RESPECT TO CCCP



APPENDIX G: MARCELLUS FORMATION GEOLOGY AND RESOURCE FIELDS







APPENDIX H: WELL LOCATION PLAT EXAMPLE



APPENDIX I: ALTERNATIVE WASTE MANAGEMENT PRACTICES

	E WASTE DISPOS			
B. ALTERNATIV	E WASTE DISPOS	ALPRACTICES		
Complete this section well site. Describe th that will demonstrate Code § 78.61, 78.62,	to it requesting approvance type of waste, include the proposed practice of or 78.63.	I of an alternative pract ding any additives, and will provide protection ed	ice to dispose of drill cuttings or the proposed alternative practice quivalent or superior to the practic	residual wastes at th a. Include informatio ces identified in 25 Pa
The waste is "top hole the well site where the disposed is the reserv	e" drill cuttings from the e drill cuttings are being ve pit on the well site ar	Cross Creek County Pa disposed, as required ad the pit has been cons	ark Wells Nos. 6H and 8H. These by §78.62(a)(1). The pit in which tructed in accordance with §78.62	e wells are located or the waste will be 2 of the regulations.
The material will be di removed and dispose Bond will then be add material is attached to	isposed in accordance d. The free liquid fract ed to the remaining ma o this submittal.	with §78.62(a)(14), which ion will be removed from iterial to stabilize and so	ch requires that all free liquid fract the pit and a solidification mater lidify the material. The MSDS for	ion of the waste be ial known as Soli- the Soli-Bond
Once the material has completely cover the confined about the line	s been stabilized, the lir waste and the waste wi er as required by §78.6	her shall be folded over, Il be shaped so that wat 2(a)(15) of the regulatio	or an additional liner will be adde ter does not infiltrate the liner and ns.	d if required, to does not get
The pit will then be ba low spots that would a	ckfilled at least 18 inch accumulate or pond wa	es over the top of the lir ter.	ner and graded to promote runoff,	with depressions or
		4 E184		
SIGNATURE OF	APPLICANT			
SIGNATURE OF J Signature of Applicant / We	APPLICANT Suszhowski	Print or Type Signer Carla L. Suszkowsk	's Name and Title I, P.E.	D 12-14-09
SIGNATURE OF J Signature of Applicant / We	APPLICANT Il Operator Juszhowski	Print or Type Signer Carla L. Suszkowsk	's Name and Title i, P.E.	D 12-14-09
Signature of Applicant / We Callass	Denied	Print or Type Signer Carla L. Suszkowsk	's Name and Title , P.E.	D 12-14-D9 Date
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SIGNATURE OF J Signature of Applicant / We Callady Approved DEP Representative: A Conditions:	Denied	Print or Type Signer Carla L. Suszkowsk	's Name and Title , P.E. VLY YES, see below or attached. NO	D 12-14-09 Date 12/29/09
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B. ALTERNATI	VE WASTE DISPOSA	L PRACTICES		
Complete this section well site. Describe that will demonstrate Code § 78.61, 78.62	on if requesting approval of the type of waste, includin the proposed practice will b, or 78.63.	f an alternative practice to disp ig any additives, and the propo I provide protection equivalent of	pose of drill cuttings or re osed alternative practice. or superior to the practice	sidual wastes at the Include information s identified in 25 Pa
The waste is "top ho located on the well s will be disposed is th regulations.	ele" drill cuttings from the C site where the drill cuttings a ne reserve pit on the well si	ross Creek County Park Wells are being disposed, as required te and the pit has been constru	Nos. 7H, 9H, and 25H. T d by §78.62(a)(1). The pit icted in accordance with §	hese wells are in which the waste 78.62 of the
The material will be removed and dispos Bond will then be ad material is attached	disposed in accordance wil ed. The free liquid fraction ded to the remaining mater to this submittal.	th §78.62(a)(14), which require a will be removed from the pit a rial to stabilize and solidify the a	s that all free liquid fractio nd a solidification materia material. The MSDS for t	n of the waste be I known as Soli- he Soli-Bond
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The pit will then be b	ackfilled at least 18 inches	over the top of the liner and gr	raded to promote runoff, w	vith depressions or
low spots that would	accumulate or pond water			
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SIGNATURE OF Signature of Applicant / V Called Approved DEP Representative: Conditions: Conditions: Conditions: See this form to apply 8.63. Complete this form ar ie information item it end your application PA DEP Oil & Gas Manag Northwest Regio 230 Chestnut Str Meadville, PA	APPLICANT Vell Operator Just for Walk Denied Denied Decied Decied Decied Decied Altown Operator should not 412-417-7944, 48 h solidification. of approval of alternative and submit it with all other new refers to. to the Oil and Gas Manage gement Program inal Office reet 16335-3481 main and the submit it with all to the Oil and Cas Manage reet 16335-3481 main and the submit it with all the submit it with all other new refers to. to the Oil and Gas Manage performance of the submit it with all other new refers to. to the Oil and Gas Manage reet 16335-3481 main and the submit it with all other new reet 16335-3481 main and the submit it with all other new refers to. to the Oil and Gas Manage refers to. to the Oil and Cas Manage refers to. to the Oil and Cas Manage refers to. to the Oil and Cas Manage the submit it with all other new the submit it with al	Print or Type Signer's Name an Carla L. Suszkowski, P.E. DEP USE ONLY Conditions: YES, s NO tify Michael Morgart at hours prior to beginning waste management practices ecessary documentation. Label ement Program at the appropri PA DEF Oil & G Southw 400 Wa Pittsbur	d Title ee below or attached. RECE DEC 1 DEP, SOUTHW OIL & under 25 Pa. Code § 78.5 each attachment with app ate DEP regional office: b as Management Program rest Regional Office aterfront Drive rgh, PA 15222-4745	D 12-10-09 Date 12/17/04 IVED 1 2009 VEST REGION GAS 6, 78.61, 78.62, or plicant's name and

APPENDIX J: CCCP OIL & GAS LEASE REQUIREMENTS FOR WASTE

ANIMALS

2.1 Lessee shall prevent access of humans or animals to pits or excavations dug for Lessee's operations by erecting, maintaining fences, or by other means approved by County.

SLUSH PIT

3.1 Each slush pit will consist of two compartments; one to contain fluids from the drilling operations and the second to contain surface runoff from the drilling site. Unless authorized by County, all slush pits will be located at approximately the same elevation as the drilling site. Depending on the topography and slope conditions, the slush pit to contain surface runoff may be located below the drilling site and a safe and reasonable distance from the stream in which the effluent will be discharged. The slush pit used to contain drilling fluids, mud, and water will be lined with plastic so that no escape of these fluids will occur. If said fluids contain oil or

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other chemical substances which are harmful to the forest environment, Lessee shall transport these fluids for disposal. All trash, rubbish, or waste materials from each drilling site shall be removed and disposed of in a properly licensed solid waste site. All pits shall be filled with earth and developed per County specifications at Lessee's expense upon completion of each well.

3.2 Before any operations commence, the location, design, construction, and maintenance of any slush pit must be approved by Lessor.

3.3 If drilling operations are conducted by air, gas, or airfoam, Lessee shall also provide sufficient means by which dust and/or foam dispersal are abated, kept to a minimum, and shall not become a nuisance.

SILTATION

4.1 Lessee realizes that as a result of its operation, areas of land which may be cleared to provide for roads, rights-of-way, and drilling sites, and which will be exposed to the forces of erosion for varying periods of time, could create siltation to nearby streams. Lessee agrees, therefore,

APPENDIX K: PLUGGING CCCP 5 WITH POZ-O-TEC (POZ)

pennsylvania	DE	PARTMEN	T OF ENVIRON	MENTAL PROT	TECTION	Site ID #	Pr	imary Facility ID #	
DEPARTMENT OF ENVIRONMENTAL PROTECTION		OFFICE	OF OIL AND GA	AS MANAGEME	ENT	eFACTS Client #	SL	do-facility ID #	
CERTIFICATE OF WELL PLUGGING					Bonded Well? Yes No	Bo	Bond Agreement #		
		W	ELL INFO	RMATION					
Well Operator Range Resources - Appalach	a, LLC	10# 141142	Well API# 37-125-226	18		Well Farm Name Cross Creek C	County	Well # Park 5	
Address 2000 Town Conter Blud			LAT 40°15' 02.5"		Project Number		Serial #		
3000 Town Center Biva.		LONG - 80°			NAD 83				
City	State	Zip	Municipality Municipality			County	County		
Canonsburg Phone	PA Fax	15317	Hopewell Township Email		Washington USGS 7.5 min. quadrangle map				
724/743-6700	724/743-6790	licable	srantovich@	rangeresources	i.com	Avella		10-	
Complete the next sec	tion (coal) if app	Cont D	Operator M	Owner Di					
Coal Operator Owner Lessee Coal Coal Coal Address Address Address CoWashCountyBd-100 W Beau St #702 CNX C		Reserv Address CNX C	e Coal Prope TR-1000 Cor	rties Co/Don	Puglio Dr	uddress	ial Operator Owner Lessee		
City, State, Zip Washington PA 15301		City, State	Zip shura PA 15	317	0	City, State, Zip			
The undersigned represent	atatives of the We	Canons	codilu that w	a participated	lin pluggin	a this well and	that the u	work was started	
on (date) 02/06/2014, an	d that the well was	plugged a	s follows:	e participateo	i in pluggini	g mis well, and	that the v	VOIR Was started	
				De	pth	Casing and Tubing			
Filling	Material and P	lugs		From	To	Size	Pulled	Left	
50/50 POZ, 2% Bentoni	te Gel, 10% NaC	Islurry		4,600'	6,400'	4-1/2"	4,500	2,066	
50/50 POZ, 2% Bentoni	te Gel, 10% NaC	Islurry		3,450'	4,450'	7"	0'	2,852'	
50/50 POZ, 2% Bentoni	te Gel, 10% NaC	Islurry		2,450'	3,450'	9-5/8"	0'	1,157'	
50/50 POZ, 2% Bentoni	te Gel, 10% NaC	Islurry		1,450'	2,450'	13-3/8"	0'	440'	
50/50 POZ, 2% Bentoni	te Gel, 10% NaC	Islurry		40'	2,450'				
Pea-Gravel				0'	40'	Depth to	Depth to coal seams, if any		
						Des	cribe Mo	nument	
Dept. ap	proved Attainable	Bottom			6,400'	Metal plate welded to 7" with permit number attached. Well buried 5' belo ground level			
					TD T				
Signature of Partic	ipants	(here a lot	and the second					1. N.S.	
Signature - Well Operator	nuch	Signature	are - Qualified Participant			Signature - Obalified Participant			
Sherry Rantovich, Attor	ney-In-Fact	Matthew	Type Signer's Name, Title, & Co. Print or Type Signer's Name, Title, & Co. ww A. Ockree, Production Robert Foulk, Completions ger, Range Resources-Appalachia Supervisor, Range Resources-Appalachia					ions sources-Appal	
Signers certify that the wo	rk of plugging this	well was		No.	DEP	USE ONLY		· Re- Call Con-	
completed on (date) 02/10/2014, and that the			Approved Denied						
information above is true	and accurate.		DEP Hep:			Date:			
Upon completion of plugging, mail one copy of this certificate to each coal operator, owner, or lessee, if any, and one copy to the appropriate DEP Regional Oil and Gas Management Program office.			Dept. of Environmental Protection NW District Oil & Gas Operations 230 Chestnut Street Meadville, PA 16335-3481 Dept. of Environmental Protect SW District Oil & Gas Operatio 400 Waterfront Drive Pittsburgh, PA 15222-4745				ental Protection Gas Operations Ive		
APPENDIX L: PA DEP LETTER REGARDING HIGH QUALITY WATER



Sample	Name	Date	Temp. (°C)	DO (%)	DO (mg/L)	рН	Pressure (mmHg)	Conductivity (µS)	Specific Cond. (µS/cm)	TDS (mg/L)
MS460	CC1	5/22/15	13.6	79.3	8	7.3	737.2	539.7	427.7	350.8
MS468	CC1	6/3/15	17.2	78.5	7.5	7.7	737.1	528.5	453.6	343.5
MS481	CC1	6/16/15	23.1	47.3	4	7.4	734.4	389.2	376.5	252.9
MS489	CC1	6/30/15	18.3	69.2	6.5	7.9	731.1	569.2	497.7	369.9
MS509	CC1	7/17/15	17.8	79	7.8	7.41	734.1	533.1	460.4	346.5
MS519	CC1	7/29/15	24.6	68	5.67	7.7	734.4	535.0	532.0	347.8
MS533	CC1	8/13/15	20.7	52	4.64	7.48	738.2	526.1	482.3	341.9
MS549	CC1	8/25/15	21.5	68.2	5.92	7.52	733.4	548.0	511.0	356.2
MS573	CC1	9/8/15	26.8	68.3	5.33	7.33	734.7	472.5	499.7	307.1
MS585	CC1	9/25/15	17.7	83.7	7.79	7.85	740.3	556.7	483.7	361.9
MS598	CC1	10/6/15	16.8	70.4	6.82	7.51	735.6	517.8	436.9	336.8
MS619	CC1	10/20/15	8.20	75.00	8.73	7.45	741.9	588.9	401.1	382.8
MS637	CC1	11/3/15	12.10	77.50	8.27	7.46	739.0	515.6	390.1	335.1
MS642	CC1	11/17/15	10.50	79.20	8.80	7.39	740.9	531.3	386.9	345.3
MS655	CC1	12/4/15	8.30	85.50	10.14	7.65	747.3	503.5	343.7	327.3
MS661	CC1	12/15/15	9.40	83.10	9.47	7.83	731.0	533.5	375.5	346.8
MS667	CC1	12/31/15	8.50	83.20	9.68	7.43	740.1	532.2	364.3	345.9
MS675	CC1	1/13/16	7.10	98.20	11.56	7.71	734.8	472.8	349.6	307.3
MS691	CC1	1/27/16	2.50	100.4	13.33	7.86	740.2	587.3	336.1	381.7
MS703	CC1	2/10/16	0.80	194.5	22.17	7.94	730.3	557.7	300.7	362.5
MS719	CC1	2/24/16	8.70	100.5	11.59	7.44	720.2	439.5	305.2	285.7
MS733	CC1	3/15/16	11.40	85.30	9.30	7.02	729.8	316.1	234.7	205.5
MS752	CC1	3/29/16	9.20	100.7	11.59	7.97	740.3	463.0	324.1	300.9
MS768	CC1	4/19/16	14.50	76.80	7.84	7.83	738.1	454.3	365.1	295.3
MS775	CC1	5/3/16	14.30	74.80	7.66	7.86	731.1	433.3	345.5	281.6

APPENDIX M: SURFACE WATER YSI – MULTIMETER DATA

Sample	Name	Date	Temp. (°C)	DO (%)	DO (mg/L)	рН	Pressure (mmHg)	Conductivity (µS)	Specific Cond. (µS/cm)	TDS (mg/L)
MS463	CC2	5/22/15	19.1	69.8	6.3	8.2	739.6	376.5	338.3	19.1
MS471	CC2	6/3/15	22.0	65.8	5.7	8.2	738.6	355.4	336.4	22.0
MS486	CC2	6/16/15	26.5	57.5	4.6	8.2	736.2	348.7	362.5	26.5
MS493	CC2	6/30/15	24.0	59.1	5.1	8.3	732.0	434.2	427.6	24.0
MS517	CC2	7/17/15	26.2	58.9	4.7	8.0	735.3	368.7	377.7	26.2
MS521	CC2	7/29/15	28.7	66.4	5.1	7.8	735.9	372.8	400.7	28.7
MS537	CC2	8/13/15	24.8	69.0	5.7	7.9	739.3	365.7	365.2	24.8
MS553	CC2	8/25/15	23.0	75.1	6.4	8.0	735.4	357.1	342.7	23.0
MS571	CC2	9/8/15	25.5	58.0	4.7	7.9	737.0	350.3	354.7	25.5
MS582	CC2	9/25/15	21.8	59.0	5.2	8.0	742.4	346.3	326.7	21.8
MS596	CC2	10/6/15	19.8	72.5	6.6	7.9	737.9	343.6	309.7	19.8
MS623	CC2	10/20/15	15.2	75.8	7.5	7.8	742.9	396.6	322.9	15.2
MS635	CC2	11/3/15	16.2	79.0	7.7	7.6	741.2	364.4	306.6	16.2
MS646	CC2	11/17/15	13.5	80.2	8.3	7.8	741.2	377.2	296.7	13.5
MS660	CC2	12/4/15	9.0	95.6	11.0	7.9	748.5	396.5	275.4	9.0
MS665	CC2	12/15/15	8.0	87.7	10.3	7.6	733.0	399.8	270.4	8.0
MS671	CC2	12/31/15	7.3	89.6	10.7	7.7	740.7	400.7	265.6	7.3
MS679	CC2	1/13/16	10.7	91.1	9.8	7.6	734.7	375.4	274.7	10.7
MS697	CC2	1/27/16	2.4	103.7	13.7	7.8	740.5	409.0	227.7	2.4
MS707	CC2	2/10/16	3.1	104.0	13.6	7.9	731.9	405.5	236.0	3.1
MS724	CC2	2/24/16	6.0	102.5	12.5	7.7	717.7	366.1	234.8	6.0
MS738	CC2	3/15/16	9.6	102.5	11.4	7.8	731.7	375.8	266.3	9.6
MS756	CC2	3/29/16	9.8	88.0	10.0	7.9	742.4	382.9	271.8	9.8
MS773	CC2	4/19/16	14.4	58.4	6.0	8.0	740.1	382.1	307.3	14.4
MS780	CC2	5/3/16	16.6	59.3	5.8	8.1	731.9	356.2	299.6	16.6

Sample	Name	Date	Temp. (°C)	DO (%)	DO (mg/L)	рН	Pressure (mmHg)	Conductivity (µS)	Specific Cond. (µS/cm)	TDS (mg/L)
MS461	SA	5/22/15	15.0	76.8	7.6	8.0	737.7	520.1	425.5	338.1
MS470	SA	6/3/15	17.5	73.8	7.0	7.9	737.0	533.4	458.1	346.7
MS484	SA	6/16/15	20.1	64.2	5.8	7.4	734.4	413.0	376.9	268.5
MS492	SA	6/30/15	17.7	70.4	6.7	8.1	730.9	620.0	537.0	403.0
MS514	SA	7/17/15	18.2	70.2	6.6	7.6	733.8	532.7	465.7	346.3
MS523	SA	7/29/15	21.1	70.0	6.2	7.8	734.1	546.0	508.0	354.9
MS536	SA	8/13/15	17.9	66.4	6.3	7.5	737.9	522.3	452.3	339.5
MS552	SA	8/25/15	17.4	84.0	7.8	7.6	733.5	528.2	452.9	343.3
MS576	SA	9/8/15	24.9	17.7	1.4	6.9	733.8	735.0	738.0	477.8
MS588	SA	9/25/15	19.2	52.6	4.9	7.3	739.7	536.6	478.9	348.8
MS601	SA	10/6/15	17.8	62.6	5.9	7.6	734.9	512.0	441.8	332.8
MS622	SA	10/20/15	11.5	75.4	8.2	7.5	741.5	609.7	455.3	396.3
MS640	SA	11/3/15	15.6	70.2	6.9	7.5	738.3	515.8	426.3	335.3
MS645	SA	11/17/15	12.1	76.0	8.1	7.7	740.4	518.6	393.3	337.1
MS658	SA	12/4/15	8.0	91.6	10.7	7.6	747.2	500.5	339.7	325.3
MS664	SA	12/15/15	8.6	93.0	10.5	7.5	731.2	535.6	367.5	348.1
MS670	SA	12/31/15	7.2	83.0	9.9	7.4	739.6	486.4	320.9	316.2
MS678	SA	1/13/16	8.2	98.6	11.6	7.4	734.6	477.2	324.8	310.2
MS694	SA	1/27/16	2.7	83.7	11.2	7.8	739.4	495.7	285.8	322.2
MS706	SA	2/10/16	1.0	136.4	17.6	7.8	729.8	511.5	277.7	332.5
MS720	SA	2/24/16	8.1	90.0	10.5	7.4	720.0	373.6	254.1	242.8
MS736	SA	3/15/16	11.5	81.1	8.8	7.2	730.2	321.4	239.1	208.9
MS755	SA	3/29/16	9.4	94.7	10.8	7.7	740.6	440.6	310.0	286.4
MS771	SA	4/19/16	16.8	54.7	5.3	7.7	738.2	448.4	379.9	291.5
MS778	SA	5/3/16	14.7	54.4	5.6	7.8	730.7	419.4	337.2	272.6

Sample	Name	Date	Temp. (°C)	DO (%)	DO (mg/L)	pН	Pressure (mmHg)	Conductivity (µS)	Specific Cond. (µS/cm)	TDS (mg/L)
MS462	SB	5/22/15	13.2	83.6	8.9	7.8	737.0	569.7	443.6	370.3
MS469	SB	6/3/15	14.0	81.0	8.4	7.7	736.4	575.0	456.3	373.8
MS482	SB	6/16/15	17.2	74.5	7.1	7.6	733.9	537.5	459.3	349.4
MS491	SB	6/30/15	14.5	81.3	8.3	8.0	730.2	690.0	555.0	448.5
MS512	SB	7/17/15	16.4	75.0	7.3	7.4	733.3	583.1	491.2	379.0
MS522	SB	7/29/15	17.2	76.6	7.3	7.7	733.6	596.0	511.0	387.4
MS535	SB	8/13/15	15.4	77.9	7.8	7.7	737.4	570.9	468.0	371.1
MS551	SB	8/25/15	15.6	85.7	8.4	7.8	733.0	568.9	467.7	369.8
MS575	SB	9/8/15	20.4	65.0	5.8	7.7	733.3	570.0	521.0	370.5
MS587	SB	9/25/15	17.4	71.0	6.7	7.8	739.0	573.4	491.8	372.7
MS600	SB	10/6/15	17.3	73.7	7.1	7.8	734.5	567.9	484.3	369.1
MS621	SB	10/20/15	14.3	52.6	5.4	7.1	740.8	647.0	515.0	420.6
MS639	SB	11/3/15	16.1	51.9	5.0	7.1	737.5	593.0	496.5	385.5
MS644	SB	11/17/15	12.8	76.1	8.0	7.7	739.9	578.9	446.1	376.3
MS657	SB	12/4/15	10.4	61.1	6.8	7.2	746.3	597.8	430.5	388.6
MS663	SB	12/15/15	10.2	59.8	6.6	7.3	730.4	612.0	438.8	397.8
MS669	SB	12/31/15	9.7	63.4	6.9	7.3	738.7	530.8	375.4	345.0
MS677	SB	1/13/16	8.9	90.7	10.4	7.4	734.7	522.2	364.2	339.4
MS693	SB	1/27/16	7.8	56.8	6.7	7.7	738.7	558.2	374.4	362.8
MS705	SB	2/10/16	9.0	62.7	7.3	7.1	736.5	493.6	338.0	320.8
MS722	SB	2/24/16	10.6	65.7	7.2	7.2	717.8	475.2	346.2	308.9
MS735	SB	3/15/16	10.3	63.9	7.1	7.0	729.3	422.4	304.1	274.6
MS754	SB	3/29/16	10.2	62.1	6.9	7.4	739.6	509.6	365.6	331.2
MS770	SB	4/19/16	14.3	53.6	5.4	7.3	737.4	526.3	422.0	342.1
MS777	SB	5/3/16	12.8	46.2	4.9	7.4	730.0	519.9	399.7	337.9

Sample	Name	Date	Temp. (°C)	DO (%)	DO (mg/L)	рН	Pressure (mmHg)	Conductivity (µS)	Specific Cond. (µS/cm)	TDS (mg/L)
N/A	SC	5/22/15	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
MS472	SC	6/3/15	19.5	80.7	7.4	7.8	736.7	636.0	570.0	413.4
MS485	SC	6/16/15	22.4	79.2	6.8	7.5	734.7	472.4	449.7	307.1
MS495	SC	6/30/15	23.8	74.5	6.3	8.0	729.1	699.0	686.0	454.4
MS518	SC	7/17/15	22.3	75.1	6.6	7.5	733.3	619.0	587.0	402.4
MS524	SC	7/29/15	29.0	58.3	4.5	7.3	733.2	630.0	683.0	409.5
MS538	SC	8/13/15	24.3	63.4	5.2	7.6	737.6	557.0	551.0	362.1
MS554	SC	8/25/15	24.0	177.3	14.9	8.0	733.2	447.2	438.3	290.7
MS572	SC	9/8/15	28.5	107.9	8.3	7.6	734.7	442.7	474.0	287.8
MS584	SC	9/25/15	21.5	131.0	11.5	8.1	740.1	474.5	443.1	308.4
MS597	SC	10/6/15	20.1	125.0	11.3	7.8	735.6	591.0	535.0	384.2
MS624	SC	10/20/15	13.5	129.6	13.4	7.9	740.3	683.0	535.0	444.0
MS636	SC	11/3/15	14.2	96.2	9.8	7.6	739.0	618.4	492.3	402.0
MS647	SC	11/17/15	12.2	119.0	12.6	7.9	738.9	617.5	468.0	401.4
MS659	SC	12/4/15	8.8	111.1	12.7	7.8	746.6	621.3	429.7	403.8
MS666	SC	12/15/15	9.2	97.8	11.0	7.7	731.2	647.1	452.0	420.6
MS672	SC	12/31/15	7.4	90.3	10.7	7.8	738.2	576.1	382.3	374.5
MS680	SC	1/13/16	11.0	93.4	10.1	7.6	734.6	583.9	432.6	379.5
MS695	SC	1/27/16	2.9	90.2	11.9	7.7	738.6	640.3	371.6	416.2
MS708	SC	2/10/16	2.8	190.4	20.1	7.8	729.2	628.9	352.2	408.8
MS723	SC	2/24/16	10.2	109.0	12.0	7.5	717.0	503.3	362.3	327.1
MS737	SC	3/15/16	11.6	89.7	9.4	7.4	729.8	403.9	301.9	262.5
MS757	SC	3/29/16	10.7	107.6	12.0	8.0	740.0	541.3	392.7	351.8
MS772	SC	4/19/16	16.6	67.7	6.6	7.7	738.1	501.0	420.9	325.7
MS779	SC	5/3/16	14.8	58.6	5.9	7.8	730.1	547.6	447.4	355.9

Sample	Name	Date	Temp. (°C)	DO (%)	DO (mg/L)	рН	Pressure (mmHg)	Conductivity (µS)	Specific Cond. (µS/cm)	TDS (mg/L)
N/A	SD	5/22/15	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
N/A	SD	6/3/15	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
MS483	SD	6/16/15	17.7	68.4	6.5	7.7	734.4	427.6	369.8	277.9
MS490	SD	6/30/15	16.2	78.3	7.7	8.1	730.8	643.0	536.0	418.0
MS510	SD	7/17/15	17.8	69.5	6.5	7.5	734.0	565.3	489.2	367.4
MS520	SD	7/29/15	19.8	72.8	6.6	7.7	734.3	530.6	478.9	344.9
MS534	SD	8/13/15	17.1	73.9	7.2	7.7	738.2	480.0	409.1	312.0
MS550	SD	8/25/15	16.7	84.0	8.1	7.7	733.7	480.1	404.3	312.1
MS574	SD	9/8/15	22.1	60.3	5.2	7.6	734.1	496.0	469.0	322.4
MS586	SD	9/25/15	18.2	60.6	5.7	7.5	739.9	506.2	441.9	329.0
MS599	SD	10/6/15	16.4	71.5	7.0	7.8	735.2	523.5	437.5	340.3
MS620	SD	10/20/15	12.0	77.3	8.5	7.8	741.7	604.5	444.0	392.9
MS638	SD	11/3/15	15.9	68.2	6.7	7.6	738.2	558.9	468.7	363.3
MS643	SD	11/17/15	12.4	78.3	8.3	7.6	740.7	554.8	422.7	360.6
MS656	SD	12/4/15	8.3	98.3	11.4	7.7	747.3	552.6	376.8	359.2
MS662	SD	12/15/15	8.9	77.6	8.9	7.8	731.0	554.8	385.7	360.6
MS668	SD	12/31/15	7.9	83.3	9.8	7.7	739.8	532.0	358.0	345.8
MS676	SD	1/13/16	8.7	95.9	11.1	7.8	734.7	500.7	346.3	325.5
MS692	SD	1/27/16	3.6	81.4	10.7	8.0	739.9	512.0	303.5	332.8
MS704	SD	2/10/16	11.8	98.0	13.5	8.3	729.7	517.5	288.3	336.4
MS721	SD	2/24/16	8.9	97.1	11.1	7.6	719.2	413.7	287.1	268.9
MS734	SD	3/15/16	10.7	80.1	8.9	7.2	730.0	367.8	268.1	239.1
MS753	SD	3/29/16	8.7	95.0	11.0	7.7	740.4	468.3	322.8	304.4
MS769	SD	4/19/16	16.1	56.1	5.6	7.8	738.0	454.8	377.4	295.6
MS776	SD	5/3/16	12.9	59.3	6.3	7.8	730.9	435.0	334.9	282.8

Sample	Name	Analysis Date	Fluoride (mg/L)	Chloride (mg/L)	Nitrite (mg/L)	Bromide (mg/L)	Nitrate (mg/L)	Phosphate (mg/L)	Sulfate (mg/L)
MS460	CC1	5/26/15	bdl	20.48	bdl	bdl	2.2	bdl	30.19
MS468	CC1	6/4/15	bdl	20.31	bdl	bdl	2.34	bdl	27.14
MS481	CC1	6/17/15	bdl	10.78	bdl	bdl	2.61	bdl	14.55
MS489	CC1	7/1/15	bdl	16.44	bdl	bdl	6.54	bdl	37.17
MS509	CC1	7/20/15	0.01	21.39	bdl	bdl	2.95	bdl	30.44
MS519	CC1	7/30/15	0.03	24.32	bdl	bdl	2.62	bdl	30.27
MS533	CC1	8/14/15	0.01	29.09	bdl	0.05	1.76	bdl	30.08
MS549	CC1	8/26/15	0.01	32.8	bdl	0.07	1.37	bdl	27.77
MS573	CC1	9/8/15	0.03	36.37	bdl	0.15	0.38	bdl	22.56
MS585	CC1	9/25/15	0.03	38.8	bdl	0.03	1.79	bdl	28.22
MS598	CC1	10/7/15	bdl	28.07	bdl	0.06	6.08	bdl	36.87
MS619	CC1	10/21/15	0.02	29.47	bdl	bdl	1.41	bdl	33.98
MS637	CC1	11/4/15	0.02	24.87	bdl	bdl	3.11	bdl	32.93
MS642	CC1	11/17/15	0.05	23.17	bdl	bdl	2.64	bdl	31.32
MS655	CC1	12/7/15	0.06	16.01	bdl	bdl	3.34	bdl	27.99
MS661	CC1	12/16/15	0.08	17.01	bdl	0.06	1.98	bdl	28.10
MS667	CC1	1/14/16	0.11	13.19	bdl	bdl	6.12	bdl	25.48
MS675	CC1	1/14/16	0.09	17.80	bdl	bdl	5.21	bdl	27.32
MS691	CC1	2/10/16	0.08	33.20	bdl	bdl	3.88	bdl	30.65
MS703	CC1	2/11/16	0.07	23.41	bdl	bdl	3.18	bdl	36.43
MS719	CC1	2/25/16	0.09	25.36	bdl	0.05	4.50	bdl	28.13
MS733	CC1	3/16/16	0.06	12.73	bdl	0.26	7.40	bdl	22.41
MS752	CC1	3/29/16	0.08	15.25	bdl	bdl	4.37	bdl	32.27
MS768	CC1	4/20/16	0.07	11.33	bdl	bdl	3.06	bdl	27.76
MS775	CC1	5/4/16	0.05	8.20	bdl	bdl	1.45	bdl	14.07

APPENDIX N: SURFACE WATER ION CHROMATOGRAPHY DATA

Sample	Name	Analysis Date	Fluoride (mg/L)	Chloride (mg/L)	Nitrite (mg/L)	Bromide (mg/L)	Nitrate (mg/L)	Phosphate (mg/L)	Sulfate (mg/L)
MS463	CC2	5/26/15	bdl	14.77	bdl	bdl	0.84	bdl	28.15
MS471	CC2	6/4/15	bdl	13.75	bdl	bdl	0.54	bdl	25.10
MS486	CC2	6/17/15	bdl	14.46	bdl	0.03	0.31	bdl	27.32
MS493	CC2	7/1/15	bdl	15.24	bdl	bdl	0.07	bdl	39.82
MS517	CC2	7/20/15	0.02	15.52	bdl	bdl	0.82	bdl	27.21
MS521	CC2	7/30/15	0.01	12.23	bdl	bdl	0.30	bdl	21.59
MS537	CC2	8/14/15	0.02	16.41	bdl	bdl	0.24	bdl	27.65
MS553	CC2	8/26/15	0.03	16.30	bdl	bdl	0.27	bdl	26.30
MS571	CC2	9/8/15	0.03	16.38	bdl	bdl	0.28	bdl	25.66
MS582	CC2	9/25/15	0.03	16.53	bdl	bdl	0.92	bdl	24.65
MS596	CC2	10/7/15	bdl	15.48	bdl	bdl	0.71	bdl	24.53
MS623	CC2	10/21/15	bdl	16.24	bdl	bdl	1.10	bdl	23.96
MS635	CC2	11/4/15	0.01	15.24	bdl	bdl	0.27	bdl	22.32
MS646	CC2	11/17/15	0.07	16.43	bdl	bdl	0.16	bdl	22.44
MS660	CC2	12/7/15	0.07	13.93	bdl	0.02	0.26	bdl	22.33
MS665	CC2	12/16/15	0.08	13.27	bdl	bdl	0.36	bdl	21.01
MS671	CC2	1/14/16	0.10	12.25	bdl	0.03	0.52	bdl	17.11
MS679	CC2	1/14/16	0.11	13.09	bdl	bdl	1.09	bdl	20.99
MS697	CC2	2/10/16	0.09	14.35	bdl	bdl	1.08	bdl	28.23
MS707	CC2	2/11/16	0.09	14.25	bdl	bdl	1.13	bdl	27.72
MS724	CC2	2/25/16	0.08	13.59	bdl	0.08	1.80	bdl	25.26
MS738	CC2	3/16/16	0.08	14.04	bdl	bdl	2.87	bdl	27.12
MS756	CC2	3/29/16	0.09	13.87	bdl	bdl*	2.99	bdl	28.66
MS773	CC2	4/20/16	0.07	12.62	bdl	bdl	2.29	bdl	26.02
MS780	CC2	5/4/16	0.08	11.79	bdl	bdl	1.54	bdl	23.63

Sample	Name	Analysis Date	Fluoride (mg/L)	Chloride (mg/L)	Nitrite (mg/L)	Bromide (mg/L)	Nitrate (mg/L)	Phosphate (mg/L)	Sulfate (mg/L)
MS461	SA	5/26/15	bdl	8.72	bdl	bdl	0.97	bdl	42.96
MS470	SA	6/4/15	bdl	10.01	bdl	bdl	1.37	bdl	40.27
MS484	SA	6/17/15	bdl	0.73	bdl	bdl	1.39	bdl	10.88
MS492	SA	7/1/15	bdl	5.67	bdl	bdl	5.04	bdl	61.57
MS514	SA	7/20/15	0.01	10.43	bdl	bdl	1.30	bdl	41.99
MS523	SA	7/30/15	0.01	11.43	bdl	bdl	1.16	bdl	43.91
MS536	SA	8/14/15	0.02	13.87	bdl	0.03	0.84	bdl	47.54
MS552	SA	8/26/15	0.03	13.35	bdl	0.05	0.62	bdl	46.17
MS576	SA	9/8/15	0.07	10.83	bdl	0.10	0.49	bdl	1.61
MS588	SA	9/25/15	0.03	12.75	bdl	bdl	0.68	bdl	36.67
MS601	SA	10/7/15	bdl	9.50	bdl	0.08	1.90	bdl	48.31
MS622	SA	10/21/15	bdl	11.40	bdl	0.08	1.36	bdl	48.83
MS640	SA	11/4/15	0.01	8.58	bdl	Bdl	0.32	bdl	43.34
MS645	SA	11/17/15	0.06	8.51	bdl	Bdl	0.29	bdl	41.04
MS658	SA	12/7/15	0.07	5.95	bdl	Bdl	0.50	bdl	41.56
MS664	SA	12/16/15	0.09	6.95	bdl	0.09	0.27	bdl	39.47
MS670	SA	1/14/16	0.07	4.84	bdl	0.04	1.55	bdl	41.15
MS678	SA	1/14/16	0.09	5.90	bdl	0.03	1.30	bdl	36.56
MS694	SA	2/10/16	0.09	6.38	bdl	bdl	0.79	bdl	46.10
MS706	SA	2/11/16	0.07	5.93	bdl	bdl	0.67	bdl	43.31
MS720	SA	2/25/16	0.11	3.95	bdl	0.10	1.39	bdl	40.75
MS736	SA	3/16/16	0.10	3.01	bdl	0.23	2.19	bdl	33.64
MS755	SA	3/29/16	0.09	4.87	bdl	bdl	0.88	bdl	42.64
MS771	SA	4/20/16	0.07	4.85	bdl	0.03	0.50	bdl	39.77
MS778	SA	5/4/16	0.08	4.33	bdl	bdl	0.33	bdl	33.04

Sample	Name	Analysis Date	Fluoride (mg/L)	Chloride (mg/L)	Nitrite (mg/L)	Bromide (mg/L)	Nitrate (mg/L)	Phosphate (mg/L)	Sulfate (mg/L)
MS462	SB	5/26/15	bdl	1.32	bdl	bdl	4.26	bdl	35.41
MS469	SB	6/4/15	bdl	1.28	bdl	bdl	4.04	bdl	32.05
MS482	SB	6/17/15	bdl	0.60	bdl	bdl	3.86	bdl	15.94
MS491	SB	7/1/15	bdl	0.96	bdl	bdl	4.21	bdl	49.98
MS512	SB	7/20/15	0.02	1.05	bdl	bdl	3.60	bdl	32.62
MS522	SB	7/30/15	0.01	1.33	bdl	bdl	3.67	bdl	39.56
MS535	SB	8/14/15	0.01	1.48	bdl	bdl	3.77	bdl	40.29
MS551	SB	8/26/15	0.01	1.36	bdl	bdl	3.21	bdl	37.88
MS575	SB	9/8/15	0.03	1.50	bdl	bdl	1.87	0.15	36.47
MS587	SB	9/25/15	bdl	1.62	bdl	bdl	2.33	0.19	37.12
MS600	SB	10/7/15	bdl	1.44	bdl	bdl	5.66	0.19	38.30
MS621	SB	10/21/15	bdl	1.28	bdl	bdl	3.94	bdl	38.09
MS639	SB	11/4/15	bdl	1.26	bdl	bdl	4.57	bdl	37.02
MS644	SB	11/17/15	0.06	1.19	bdl	bdl	4.49	bdl	35.61
MS657	SB	12/7/15	0.07	0.87	bdl	bdl	3.52	bdl	34.04
MS663	SB	12/16/15	0.06	0.79	bdl	bdl	3.08	bdl	33.10
MS669	SB	1/14/16	0.10	0.76	bdl	bdl	4.09	bdl	26.15
MS677	SB	1/14/16	0.09	0.70	bdl	bdl	3.89	bdl	27.12
MS693	SB	2/10/16	0.07	0.61	bdl	bdl	3.67	bdl	33.24
MS705	SB	2/11/16	0.07	0.68	bdl	bdl	3.68	bdl	34.47
MS722	SB	2/25/16	0.08	0.62	bdl	0.07	4.92	bdl	29.15
MS735	SB	3/16/16	0.07	0.55	bdl	bdl	7.96	0.18	26.32
MS754	SB	3/29/16	0.09	0.59	bdl	bdl	4.98	bdl	31.59
MS770	SB	4/20/16	0.06	0.55	bdl	bdl	4.09	bdl	27.99
MS777	SB	5/4/16	0.06	0.68	bdl	bdl	3.65	bdl	25.83

Sample	Name	Analysis Date	Fluoride (mg/L)	Chloride (mg/L)	Nitrite (mg/L)	Bromide (mg/L)	Nitrate (mg/L)	Phosphate (mg/L)	Sulfate (mg/L)
N/A	SC	5/26/15	N/A	N/A	N/A	N/A	N/A	N/A	N/A
MS472	SC	6/4/15	bdl	41.61	bdl	bdl	1.43	bdl	72.02
MS485	SC	6/17/15	bdl	13.44	bdl	bdl	3.86	bdl	27.18
MS495	SC	7/1/15	bdl	14.75	bdl	bdl	5.55	bdl	60.80
MS518	SC	7/20/15	0.03	24.56	bdl	bdl	1.05	bdl	50.99
MS524	SC	7/30/15	0.01	32.22	bdl	bdl	1.01	bdl	56.43
MS538	SC	8/14/15	0.02	42.80	bdl	0.20	0.63	bdl	62.72
MS554	SC	8/26/15	0.01	44.28	bdl	0.19	0.21	bdl	60.81
MS572	SC	9/8/15	0.03	37.94	bdl	0.23	0.10	bdl	32.67
MS584	SC	9/25/15	bdl	37.45	bdl	0.12	0.64	bdl	52.75
MS597	SC	10/7/15	bdl	23.90	bdl	0.09	2.94	bdl	55.32
MS624	SC	10/21/15	bdl	35.74	bdl	0.57	1.38	bdl	73.77
MS636	SC	11/4/15	0.01	23.66	bdl	0.06	1.22	bdl	55.88
MS647	SC	11/17/15	0.08	22.95	bdl	0.04	1.32	bdl	56.19
MS659	SC	12/7/15	0.08	17.03	bdl	0.09	2.30	bdl	55.41
MS666	SC	12/16/15	0.07	18.03	bdl	0.16	1.01	bdl	55.72
MS672	SC	1/14/16	0.11	11.56	bdl	0.06	4.24	bdl	41.29
MS680	SC	1/14/16	0.09	15.88	bdl	0.15	3.54	bdl	52.88
MS695	SC	2/10/16	0.08	38.22	bdl	bdl	4.00	bdl	62.47
MS708	SC	2/11/16	0.08	23.49	bdl	0.07	2.47	bdl	70.45
MS723	SC	2/25/16	0.08	25.43	bdl	0.10	3.49	bdl	44.74
MS737	SC	3/16/16	0.06	13.68	bdl	bdl	7.92	0.07	39.90
MS757	SC	3/29/16	0.10	17.05	bdl	bdl	2.38	bdl	63.88
MS772	SC	4/20/16	0.08	14.65	bdl	0.07	0.10	bdl	61.01
MS779	SC	5/4/16	0.08	15.93	bdl	0.08	1.46	bdl	47.85

Sample	Name	Analysis Date	Fluoride (mg/L)	Chloride (mg/L)	Nitrite (mg/L)	Bromide (mg/L)	Nitrate (mg/L)	Phosphate (mg/L)	Sulfate (mg/L)
N/A	SD	5/26/15	N/A	N/A	N/A	N/A	N/A	N/A	N/A
N/A	SD	6/4/15	N/A	N/A	N/A	N/A	N/A	N/A	N/A
MS483	SD	6/17/15	bdl	3.84	bdl	bdl	2.43	bdl	30.34
MS490	SD	7/1/15	bdl	1.23	bdl	bdl	1.62	bdl	40.61
MS510	SD	7/20/15	bdl	1.76	bdl	bdl	1.94	bdl	31.71
MS520	SD	7/30/15	0.03	1.97	bdl	bdl	1.15	bdl	31.53
MS534	SD	8/14/15	0.01	2.09	bdl	bdl	1.60	bdl	31.87
MS550	SD	8/26/15	0.01	2.19	bdl	bdl	1.27	bdl	31.67
MS574	SD	9/8/15	0.03	2.69	bdl	bdl*	0.81	bdl	30.23
MS586	SD	9/25/15	bdl*	2.80	bdl	bdl	1.20	bdl	31.95
MS599	SD	10/7/15	bdl	2.04	bdl	bdl	3.34	bdl	31.90
MS620	SD	10/21/15	0.01	2.50	bdl	bdl	0.06	bdl	33.79
MS638	SD	11/4/15	0.02	1.91	bdl	bdl	0.34	bdl	28.08
MS643	SD	11/17/15	0.07	1.97	bdl	bdl	0.62	bdl	30.75
MS656	SD	12/7/15	0.07	1.27	bdl	bdl	1.27	bdl	28.66
MS662	SD	12/16/15	0.08	1.39	bdl	bdl	1.11	bdl	28.97
MS668	SD	1/14/16	0.11	1.29	bdl	bdl	1.84	bdl	25.19
MS676	SD	1/14/16	0.03	0.57	bdl	bdl	0.62	bdl	11.22
MS692	SD	2/10/16	0.08	1.23	bdl	bdl	1.50	bdl	31.04
MS704	SD	2/11/16	N/A	N/A	N/A	N/A	N/A	N/A	N/A
MS721	SD	2/25/16	0.09	0.97	bdl	0.06	2.70	bdl	24.05
MS734	SD	3/16/16	0.09	0.85	bdl	bdl	3.45	bdl	22.46
MS753	SD	3/29/16	0.08	1.20	bdl	bdl	2.28	bdl	28.49
MS769	SD	4/20/16	0.07	1.13	bdl	bdl	1.39	bdl	27.13
MS776	SD	5/4/16	0.06	1.07	bdl	bdl	1.00	bdl	21.76

								m	ig/L					
Sample	Name	Analysis Date	Li	В	Na	Mg	AI	Si	Ρ	К	Са	Ti	V	Cr
MS460	CC1	6/2/15	0.004	0.030	12.98	10.81	0.156	3.73	0.02	1.40	87.33	0.001	0.0010	0.004
MS468	CC1	6/25/15	0.004	0.026	13.30	11.07	0.099	3.80	0.01	1.72	76.89	0.001	0.0014	0.002
MS481	CC1	6/24/15	0.003	0.029	13.41	8.06	0.518	4.27	0.14	3.15	75.43	0.004	0.0040	0.004
MS489	CC1	7/14/15	0.003	0.054	13.79	9.38	0.304	4.67	0.06	2.64	69.36	0.004	0.0017	0.002
MS509	CC1	8/11/15	0.003	0.032	12.82	10.84	0.066	4.15	0.01	1.88	77.97	0.002	0.0006	0.001
MS519	CC1	8/11/15	0.003	0.028	12.46	11.46	0.052	3.78	0.01	2.91	81.79	0.001	0.0009	0.001
MS533	CC1	9/1/15	0.004	0.011	15.08	12.80	0.028	3.75	0.02	3.02	73.20	0.002	bdl	0.002
MS549	CC1	9/1/15	0.003	0.002	18.31	14.34	0.012	4.30	0.03	3.51	88.64	0.002	bdl	0.004
MS573	CC1	9/24/15	0.003	0.030	20.48	13.49	0.030	4.64	0.04	5.56	69.28	0.002	0.0005	<0.001
MS585	CC1	10/13/15	0.003	0.028	25.67	14.96	0.038	3.99	0.03	5.73	82.43	0.002	0.0009	0.002
MS598	CC1	10/13/15	0.002	0.023	19.30	12.82	0.006	4.89	0.01	3.32	91.89	0.002	<0.001	0.003
MS619	CC1	10/27/15	0.003	0.019	17.16	12.92	0.016	3.33	0.06	3.74	87.98	0.002	<0.001	0.002
MS637	CC1	11/18/15	0.003	0.028	15.53	10.49	0.055	3.94	bdl	2.59	69.13	bdl	bdl	bdl
MS642	CC1	11/18/15	0.003	0.026	13.35	10.54	0.044	3.25	bdl	2.21	70.88	bdl	bdl	bdl
MS655	CC1	12/23/15	0.003	0.017	14.82	10.71	0.089	3.90	0.00	2.17	84.30	<0.001	bdl	bdl
MS661	CC1	12/23/15	0.003	0.014	16.93	12.24	0.046	3.23	<0.01	2.42	95.93	bdl	bdl	0.001
MS667	CC1	2/25/16	0.004	0.025	14.24	9.10	0.131	4.09	0.00	2.50	69.28	0.001	0.0007	bdl
MS675	CC1	2/25/16	0.004	0.022	16.96	10.37	0.107	3.97	bdl	1.61	76.11	bdl	<0.001	bdl
MS691	CC1	2/25/16	0.004	0.020	26.72	9.64	0.002	3.58	bdl	1.86	68.15	bdl	<0.001	bdl
MS703	CC1	2/25/16	0.004	0.018	20.79	10.66	0.074	3.36	bdl	1.23	74.78	bdl	0.0005	bdl
MS719	CC1	2/25/16	0.004	0.017	24.10	9.01	0.280	3.24	bdl	1.76	65.89	bdl	0.0011	bdl
MS733	CC1	3/30/16	0.002	0.023	10.48	6.39	0.351	3.71	0.06	2.40	52.19	0.002	0.0013	bdl
MS752	CC1	3/30/16	0.004	0.015	11.93	9.36	0.073	3.64	<0.01	1.54	78.93	0.001	<0.001	0.001
MS768	CC1	4/22/16	0.004	0.017	10.16	10.75	0.098	3.45	0.03	1.04	84.76	bdl	<0.001	0.002
MS775	CC1	6/2/16	0.004	0.029	12.03	9.93	0.121	3.36	0.02	1.21	76.20	<0.001	<0.001	bdl

APPENDIX O: SURFACE WATER ICP/MS DATA

		-						mg/L					
Sample	Name	Analysis Date	Mn	Fe	Со	Ni	Cu	Zn	As	Se	Rb	Sr	Мо
MS460	CC1	6/2/15	0.22	0.73	0.0006	0.004	0.007	0.49	0.001	0.002	0.001	0.38	0.0073
MS468	CC1	6/25/15	0.22	0.66	0.0006	0.003	0.002	<0.01	0.002	0.001	0.001	0.44	0.0071
MS481	CC1	6/24/15	0.79	1.46	0.0030	0.005	0.014	0.02	0.003	0.004	0.002	0.35	0.0136
MS489	CC1	7/14/15	0.33	1.19	0.0011	0.003	0.004	0.02	0.002	0.002	0.001	0.28	0.0119
MS509	CC1	8/11/15	0.11	0.58	0.0002	0.002	0.002	0.01	0.001	0.002	0.001	0.31	0.0064
MS519	CC1	8/11/15	0.17	0.51	0.0002	0.004	0.002	0.01	0.001	0.001	0.001	0.34	0.0049
MS533	CC1	9/1/15	0.23	0.62	0.0004	0.003	0.002	bdl	bdl	0.002	0.001	0.40	0.0067
MS549	CC1	9/1/15	0.35	0.75	0.0005	0.003	0.003	bdl	bdl	0.002	0.001	0.44	0.0069
MS573	CC1	9/24/15	0.83	0.84	0.0007	0.003	0.003	bdl	0.003	0.002	0.001	0.30	0.0065
MS585	CC1	10/13/15	0.34	1.11	0.0006	0.004	0.002	bdl	0.001	0.001	0.001	0.34	0.0089
MS598	CC1	10/13/15	0.08	0.59	0.0003	0.003	0.002	bdl	<0.001	0.001	0.001	0.29	0.0081
MS619	CC1	10/27/15	0.16	0.71	0.0004	0.003	0.002	bdl	0.001	0.002	0.001	0.33	0.0051
MS637	CC1	11/18/15	0.09	0.38	0.0004	0.003	0.004	<0.01	bdl	bdl	<0.001	0.32	0.0063
MS642	CC1	11/18/15	0.08	0.38	0.0004	0.002	0.008	0.01	bdl	bdl	<0.001	0.32	0.0056
MS655	CC1	12/23/15	0.21	0.60	0.0004	0.003	0.006	0.01	0.001	0.001	0.001	0.33	0.0098
MS661	CC1	12/23/15	0.14	0.50	0.0003	0.003	0.013	0.02	<0.001	0.001	0.001	0.39	0.0104
MS667	CC1	2/25/16	0.18	0.46	0.0006	0.004	0.008	0.02	0.001	0.001	0.001	0.38	0.0069
MS675	CC1	2/25/16	0.12	0.39	0.0004	0.003	0.003	0.01	0.001	bdl	<0.001	0.42	0.0062
MS691	CC1	2/25/16	0.04	0.18	0.0003	0.023	0.006	<0.01	0.001	<0.001	0.001	0.38	0.0059
MS703	CC1	2/25/16	0.16	0.38	0.0005	0.003	0.002	<0.01	<0.001	<0.001	0.000	0.42	0.0048
MS719	CC1	2/25/16	0.21	0.50	0.0009	0.011	0.005	0.01	0.001	<0.001	0.001	0.36	0.0070
MS733	CC1	3/30/16	0.31	0.75	0.0014	0.004	0.008	0.01	0.001	<0.001	0.001	0.27	0.0095
MS752	CC1	3/30/16	0.10	0.47	0.0004	0.004	0.005	0.01	<0.001	0.001	0.001	0.33	0.0095
MS768	CC1	4/22/16	0.10	0.48	0.0008	0.001	bdl	0.62	<0.001	0.001	<0.001	0.40	0.0044
MS775	CC1	6/2/16	0.19	0.67	0.0006	0.002	0.002	<0.01	<0.001	0.001	0.001	0.38	0.0120

						mg	J/L			
Sample	Name	Analysis Date	Ag	Cd	Sn	Sb	Ва	W	Pb	U
MS460	CC1	6/2/15	bdl	bdl	0.007	0.0001	0.12	0.0007	0.0006	0.0005
MS468	CC1	6/25/15	bdl	bdl	0.001	0.0001	0.17	0.0003	0.0008	0.0006
MS481	CC1	6/24/15	bdl	0.0003	<0.001	0.0002	0.38	0.0005	0.0077	0.0003
MS489	CC1	7/14/15	0.0020	0.0002	0.003	0.0004	0.14	0.0047	0.0025	0.0003
MS509	CC1	8/11/15	bdl	0.0001	0.003	0.0003	0.11	0.0036	0.0010	0.0002
MS519	CC1	8/11/15	bdl	0.0001	<0.001	0.0001	0.13	bdl	0.0007	0.0002
MS533	CC1	9/1/15	0.0007	0.0001	0.002	0.0003	0.11	0.0027	0.0004	0.0006
MS549	CC1	9/1/15	bdl	<0.0001	0.001	0.0002	0.12	0.0001	0.0004	0.0004
MS573	CC1	9/24/15	bdl	bdl	0.002	0.0002	0.12	0.0001	0.0007	0.0004
MS585	CC1	10/13/15	bdl	<0.0001	0.001	0.0004	0.10	0.0002	0.0009	0.0005
MS598	CC1	10/13/15	bdl	<0.0001	0.001	0.0002	0.08	0.0002	0.0002	0.0004
MS619	CC1	10/27/15	<0.0001	<0.0001	0.003	0.0002	0.08	0.0002	0.0005	0.0005
MS637	CC1	11/18/15	<0.0001	0.0002	0.005	0.0001	0.09	0.0001	0.0002	0.0004
MS642	CC1	11/18/15	<0.0001	0.0002	0.027	0.0001	0.10	<0.0001	0.0005	0.0004
MS655	CC1	12/23/15	<0.0001	<0.0001	0.018	0.0002	0.10	0.0003	0.0005	0.0004
MS661	CC1	12/23/15	<0.0001	0.0001	0.028	0.0002	0.11	0.0002	0.0010	0.0005
MS667	CC1	2/25/16	<0.0001	0.0013	0.002	0.0004	0.12	0.0006	0.0010	0.0004
MS675	CC1	2/25/16	<0.0001	0.0001	0.001	0.0002	0.12	0.0002	0.0006	0.0005
MS691	CC1	2/25/16	bdl	<0.0001	<0.001	0.0001	0.12	0.0001	<0.0001	0.0005
MS703	CC1	2/25/16	bdl	0.0001	0.001	0.0001	0.12	<0.0001	0.0007	0.0006
MS719	CC1	2/25/16	<0.0001	0.0001	<0.001	0.0018	0.13	<0.0001	0.0024	0.0006
MS733	CC1	3/30/16	bdl	<0.0001	0.001	0.0032	0.11	0.0003	0.0027	bdl
MS752	CC1	3/30/16	bdl	bdl	0.002	0.0011	0.11	<0.0001	0.0006	<0.0001
MS768	CC1	4/22/16	<0.0001	bdl	<0.001	0.0002	0.11	0.0002	0.0004	0.0006
MS775	CC1	6/2/16	0.0001	<0.0001	0.001	0.0015	0.11	0.0019	0.0009	0.0004

			mg/L												
Sample	Name	Analysis Date	Li	В	Na	Mg	Al	Si	Р	К	Са	Ti	V	Cr	
MS463	CC2	6/2/15	0.002	0.020	9.92	7.75	0.044	0.46	bdl	1.55	54.32	<0.001	0.0006	0.004	
MS471	CC2	6/25/15	0.002	0.021	10.04	7.92	0.057	0.62	bdl	1.59	48.93	<0.001	0.0008	0.001	
MS486	CC2	6/24/15	0.002	0.004	10.78	8.70	0.020	0.49	0.03	1.68	57.12	0.001	0.0007	0.005	
MS493	CC2	7/14/15	0.002	0.026	9.55	7.61	0.054	1.24	<0.01	1.73	48.53	0.001	0.0006	0.002	
MS517	CC2	8/11/15	0.001	0.021	9.80	7.57	0.037	1.49	bdl	1.86	51.20	<0.001	0.0004	0.001	
MS521	CC2	8/11/15	0.001	0.022	9.56	7.75	0.038	1.51	bdl	1.89	51.00	<0.001	0.0005	0.001	
MS537	CC2	9/1/15	0.002	bdl	10.19	8.31	bdl	1.78	bdl	1.99	52.44	0.001	bdl	0.001	
MS553	CC2	9/1/15	0.001	bdl	11.26	9.97	bdl	2.19	0.01	2.18	64.67	0.001	bdl	0.003	
MS571	CC2	9/24/15	0.002	0.017	11.76	8.98	0.019	2.08	0.01	2.20	50.59	0.001	0.0003	<0.001	
MS582	CC2	10/13/15	0.002	0.014	11.78	8.91	bdl	2.07	0.01	2.32	52.75	0.001	<0.001	0.002	
MS596	CC2	10/13/15	0.001	0.013	11.89	9.17	bdl	1.98	bdl	2.25	58.44	0.001	bdl	0.003	
MS623	CC2	10/27/15	0.001	0.008	10.92	8.26	bdl	2.52	bdl	2.48	56.34	0.001	bdl	0.002	
MS635	CC2	11/18/15	0.002	0.024	9.71	7.86	0.037	2.27	bdl	2.46	47.94	bdl	bdl	bdl	
MS646	CC2	11/18/15	0.002	0.023	10.13	8.11	0.041	2.51	bdl	2.51	48.61	bdl	bdl	bdl	
MS660	CC2	12/23/15	0.002	0.010	13.45	9.08	0.020	2.51	bdl	2.44	68.27	bdl	bdl	<0.001	
MS665	CC2	12/23/15	0.002	0.009	11.63	9.65	0.034	2.46	bdl	2.51	73.53	bdl	bdl	0.001	
MS671	CC2	2/25/16	0.003	0.025	14.29	8.34	0.060	1.80	0.04	2.15	57.77	bdl	<0.001	bdl	
MS679	CC2	2/25/16	0.003	0.028	13.69	8.54	0.063	1.74	bdl	2.09	67.30	bdl	0.0006	bdl	
MS697	CC2	2/25/16	0.003	0.023	14.10	8.64	0.065	1.56	bdl	2.11	62.48	bdl	<0.001	bdl	
MS707	CC2	2/25/16	0.003	0.022	14.03	8.41	0.024	1.41	bdl	1.96	57.24	bdl	<0.001	bdl	
MS724	CC2	2/25/16	0.003	0.020	13.50	8.55	0.034	1.17	bdl	2.06	57.73	bdl	<0.001	bdl	
MS738	CC2	3/30/16	0.003	0.018	10.65	8.25	0.039	0.68	0.03	2.15	63.16	bdl	<0.001	0.001	
MS756	CC2	3/30/16	0.003	0.016	10.13	8.16	0.047	1.00	bdl	2.05	68.84	<0.001	<0.001	0.003	
MS773	CC2	4/22/16	0.002	0.018	10.07	8.86	0.056	0.41	0.02	1.63	71.23	bdl	bdl	0.001	
MS780	CC2	6/2/16	0.003	0.021	9.88	8.60	0.045	0.14	0.01	1.59	64.12	bdl	bdl	0.001	

		_						mg/L					
Sample	Name	Analysis Date	Mn	Fe	Со	Ni	Cu	Zn	As	Se	Rb	Sr	Мо
MS463	CC2	6/2/15	0.04	0.34	0.0003	0.001	0.003	0.01	0.001	0.002	0.001	0.28	0.0047
MS471	CC2	6/25/15	0.08	0.34	0.0003	0.001	0.003	0.01	0.001	0.002	0.001	0.29	0.0046
MS486	CC2	6/24/15	0.04	0.45	0.0003	0.003	0.002	bdl	0.001	0.004	0.001	0.32	0.0053
MS493	CC2	7/14/15	0.02	0.42	0.0002	0.003	0.002	bdl	0.001	0.002	0.001	0.23	0.0056
MS517	CC2	8/11/15	0.02	0.24	bdl	0.001	0.002	0.01	0.001	0.002	0.001	0.22	0.0050
MS521	CC2	8/11/15	0.03	0.23	bdl	0.002	0.001	0.01	0.001	0.001	0.001	0.21	0.0048
MS537	CC2	9/1/15	0.03	0.30	0.0002	0.002	0.001	bdl	bdl	0.001	0.001	0.22	0.0050
MS553	CC2	9/1/15	0.04	0.34	0.0002	0.002	0.001	bdl	bdl	0.001	0.001	0.23	0.0053
MS571	CC2	9/24/15	0.03	0.24	0.0002	0.002	0.001	bdl	0.002	0.001	0.001	0.20	0.0049
MS582	CC2	10/13/15	0.03	0.57	0.0002	0.002	0.002	0.01	0.001	0.001	0.001	0.21	0.0047
MS596	CC2	10/13/15	0.02	0.31	0.0001	0.002	0.001	bdl	0.001	0.001	0.001	0.20	0.0046
MS623	CC2	10/27/15	0.14	0.21	0.0002	0.001	0.002	bdl	0.001	0.001	0.001	0.21	0.0053
MS635	CC2	11/18/15	0.14	0.19	0.0003	0.002	0.008	0.01	bdl	bdl	0.001	0.24	0.0049
MS646	CC2	11/18/15	0.32	0.22	0.0003	0.002	0.028	0.02	bdl	bdl	0.001	0.24	0.0035
MS660	CC2	12/23/15	0.44	0.26	0.0002	0.002	0.002	<0.01	0.001	0.001	0.001	0.28	0.0052
MS665	CC2	12/23/15	0.45	0.27	0.0002	0.003	0.008	0.01	bdl	0.001	0.001	0.30	0.0048
MS671	CC2	2/25/16	0.47	0.25	0.0003	0.002	0.002	0.01	0.002	<0.001	0.001	0.35	0.0050
MS679	CC2	2/25/16	0.33	0.25	0.0004	0.002	0.002	0.10	0.001	<0.001	0.001	0.35	0.0079
MS697	CC2	2/25/16	0.27	0.22	0.0003	0.002	0.004	0.04	0.001	bdl	0.001	0.35	0.0048
MS707	CC2	2/25/16	0.22	0.16	0.0003	0.002	0.001	<0.01	0.001	<0.001	0.001	0.34	0.0045
MS724	CC2	2/25/16	0.14	0.17	0.0003	0.003	0.006	0.04	0.001	<0.001	0.001	0.34	0.0042
MS738	CC2	3/30/16	0.06	0.33	0.0003	0.004	0.005	<0.01	0.001	<0.001	0.001	0.33	0.0059
MS756	CC2	3/30/16	0.08	0.28	0.0003	0.003	0.071	0.04	0.001	0.002	0.001	0.37	0.0060
MS773	CC2	4/22/16	0.05	0.32	0.0006	<0.001	bdl	0.65	<0.001	<0.001	0.001	0.33	0.0044
MS780	CC2	6/2/16	0.04	0.41	0.0003	0.001	0.011	0.01	<0.001	0.001	0.001	0.31	0.0047

						mg	J∕L			
Sample	Name	Analysis Date	Ag	Cd	Sn	Sb	Ва	W	Pb	U
MS463	CC2	6/2/15	bdl	bdl	0.003	0.0001	0.08	0.0004	0.0001	0.0005
MS471	CC2	6/25/15	bdl	bdl	0.002	0.0001	0.09	0.0005	0.0001	0.0004
MS486	CC2	6/24/15	bdl	bdl	0.003	0.0002	0.10	0.0003	0.0001	0.0004
MS493	CC2	7/14/15	0.0003	<0.0001	0.003	0.0001	0.08	0.0010	0.0001	0.0003
MS517	CC2	8/11/15	bdl	<0.0001	0.002	0.0001	0.07	bdl	bdl	0.0001
MS521	CC2	8/11/15	bdl	<0.0001	0.002	0.0002	0.07	bdl	0.0002	0.0001
MS537	CC2	9/1/15	bdl	<0.0001	0.002	0.0001	0.07	0.0006	bdl	0.0004
MS553	CC2	9/1/15	bdl	<0.0001	0.003	0.0001	0.07	<0.0001	bdl	0.0004
MS571	CC2	9/24/15	bdl	bdl	0.002	0.0002	0.06	0.0001	0.0001	0.0004
MS582	CC2	10/13/15	bdl	<0.0001	0.001	0.0006	0.06	0.0003	0.0003	0.0004
MS596	CC2	10/13/15	bdl	<0.0001	0.002	0.0002	0.05	0.0001	<0.0001	0.0004
MS623	CC2	10/27/15	<0.0001	<0.0001	0.002	0.0002	0.06	0.0001	<0.0001	0.0003
MS635	CC2	11/18/15	<0.0001	0.0001	0.022	0.0001	0.07	0.0001	0.0004	0.0004
MS646	CC2	11/18/15	<0.0001	0.0002	0.031	0.0001	0.08	<0.0001	0.0012	0.0004
MS660	CC2	12/23/15	<0.0001	<0.0001	0.004	0.0002	0.07	0.0002	<0.0001	0.0004
MS665	CC2	12/23/15	<0.0001	<0.0001	0.029	0.0002	0.08	0.0001	0.0004	0.0005
MS671	CC2	2/25/16	<0.0001	<0.0001	0.002	0.0003	0.10	0.0003	0.0004	0.0005
MS679	CC2	2/25/16	bdl	<0.0001	0.002	0.0002	0.10	0.0001	0.0003	0.0005
MS697	CC2	2/25/16	bdl	0.0001	0.003	0.0001	0.10	<0.0001	0.0002	0.0005
MS707	CC2	2/25/16	bdl	0.0001	0.002	0.0001	0.10	<0.0001	0.0001	0.0005
MS724	CC2	2/25/16	bdl	0.0002	0.002	0.0014	0.10	<0.0001	0.0003	0.0005
MS738	CC2	3/30/16	bdl	bdl	0.001	0.0012	0.09	0.0001	0.0002	bdl
MS756	CC2	3/30/16	bdl	bdl	0.003	0.0002	0.09	<0.0001	0.0028	bdl
MS773	CC2	4/22/16	bdl	bdl	<0.001	0.0001	0.09	0.0001	<0.0001	0.0005
MS780	CC2	6/2/16	0.0001	bdl	0.001	0.0004	0.10	0.0005	0.0007	0.0004

			mg/L												
Sample	Name	Analysis Date	Li	В	Na	Mg	AI	Si	Р	К	Са	Ti	V	Cr	
MS461	SA	6/2/15	0.006	0.030	7.98	12.77	0.503	4.49	0.10	2.04	159.01	0.003	0.0022	0.004	
MS470	SA	6/25/15	0.006	0.025	7.72	11.05	0.096	4.63	0.02	0.98	86.25	0.001	0.0010	0.001	
MS484	SA	6/24/15	0.004	0.020	5.10	7.66	0.414	4.64	0.12	1.22	87.71	0.004	0.0017	0.005	
MS492	SA	7/14/15	0.004	0.033	6.10	9.47	0.160	4.48	0.03	0.98	87.51	0.003	8000.0	0.002	
MS514	SA	8/11/15	0.003	0.022	7.74	9.71	0.068	4.38	bdl	0.95	83.05	0.001	0.0004	<0.001	
MS523	SA	8/11/15	0.004	0.025	7.81	11.25	0.061	4.95	0.01	1.27	95.92	0.001	0.0007	0.001	
MS536	SA	9/1/15	0.004	bdl	8.98	12.09	bdl	4.72	0.02	1.25	85.56	0.002	bdl	0.001	
MS552	SA	9/1/15	0.004	bdl	10.73	14.89	0.011	5.73	0.04	1.82	111.06	0.002	bdl	0.004	
MS576	SA	9/24/15	0.001	0.015	11.19	14.93	0.094	10.36	0.03	1.72	144.57	0.003	0.0001	0.001	
MS588	SA	10/13/15	0.003	0.024	12.26	13.98	bdl	5.33	0.04	3.15	98.98	0.002	bdl	0.002	
MS601	SA	10/13/15	0.003	0.015	9.47	12.41	0.007	5.29	0.01	1.85	109.99	0.002	bdl	0.003	
MS622	SA	10/27/15	0.003	0.011	8.49	12.02	bdl	6.93	0.04	2.00	109.66	0.002	bdl	0.002	
MS640	SA	11/18/15	0.003	0.023	5.86	10.00	0.059	5.08	0.01	1.51	81.58	bdl	bdl	bdl	
MS645	SA	11/18/15	0.004	0.021	6.86	10.23	0.023	4.84	bdl	1.23	80.15	bdl	bdl	bdl	
MS658	SA	12/23/15	0.004	0.008	6.53	10.72	0.055	4.56	<0.01	1.15	99.72	bdl	bdl	bdl	
MS664	SA	12/23/15	0.004	0.006	8.91	12.24	0.030	4.60	bdl	1.16	114.59	bdl	bdl	0.001	
MS670	SA	2/25/16	0.005	0.022	7.80	9.48	0.145	4.69	0.00	0.89	85.86	<0.001	0.0006	bdl	
MS678	SA	2/25/16	0.005	0.017	8.10	10.03	0.099	4.25	bdl	0.67	86.05	bdl	<0.001	bdl	
MS694	SA	2/25/16	0.006	0.017	9.12	10.09	0.074	4.09	bdl	0.71	84.34	bdl	<0.001	bdl	
MS706	SA	2/25/16	0.006	0.016	8.76	10.37	0.042	4.02	bdl	0.62	84.03	bdl	<0.001	bdl	
MS720	SA	2/25/16	0.003	0.015	7.55	6.74	0.135	3.58	bdl	1.21	68.30	bdl	<0.001	bdl	
MS736	SA	3/30/16	0.003	0.019	4.24	6.30	0.188	4.06	0.05	1.49	59.80	0.001	<0.001	bdl	
MS755	SA	3/30/16	0.005	0.012	5.98	8.98	0.121	4.14	bdl	0.94	88.47	0.001	<0.001	0.002	
MS771	SA	4/22/16	0.005	0.018	5.82	9.97	0.126	4.32	0.02	0.52	93.63	bdl	<0.001	0.001	
MS778	SA	6/2/16	0.005	0.021	5.97	9.37	0.131	4.08	0.01	0.60	85.58	bdl	<0.001	0.001	

		-						mg/L					
Sample	Name	Analysis Date	Mn	Fe	Со	Ni	Cu	Zn	As	Se	Rb	Sr	Мо
MS461	SA	6/2/15	0.39	1.33	0.0009	0.006	0.032	0.91	0.002	0.002	0.002	0.56	0.0009
MS470	SA	6/25/15	0.45	0.96	0.0006	0.002	0.001	<0.01	0.002	0.001	0.001	0.54	0.0010
MS484	SA	6/24/15	0.37	0.90	0.0017	0.004	0.010	0.01	0.001	0.003	0.001	0.39	0.0006
MS492	SA	7/14/15	0.29	1.04	0.0008	0.003	0.004	bdl	0.001	0.002	<0.001	0.36	0.0012
MS514	SA	8/11/15	0.20	0.64	0.0001	0.002	0.003	0.03	0.001	0.001	<0.001	0.36	0.0007
MS523	SA	8/11/15	0.31	0.79	0.0002	0.005	0.005	0.01	0.001	0.001	0.001	0.49	0.0008
MS536	SA	9/1/15	0.43	1.11	0.0004	0.003	0.001	bdl	bdl	0.002	<0.001	0.51	0.0014
MS552	SA	9/1/15	0.52	1.66	0.0005	0.003	0.003	bdl	bdl	0.002	0.001	0.57	0.0013
MS576	SA	9/24/15	10.77	13.05	0.0023	0.004	0.002	<0.01	0.010	0.001	0.001	0.49	0.0015
MS588	SA	10/13/15	0.87	2.13	0.0005	0.004	0.002	bdl	0.001	0.001	0.001	0.41	0.0012
MS601	SA	10/13/15	0.15	0.72	0.0003	0.004	0.001	bdl	bdl	0.001	0.000	0.34	0.0008
MS622	SA	10/27/15	0.38	1.39	0.0004	0.003	0.002	bdl	0.001	0.002	<0.001	0.38	0.0008
MS640	SA	11/18/15	0.15	0.46	0.0004	0.003	0.008	0.01	bdl	bdl	<0.001	0.37	0.0007
MS645	SA	11/18/15	0.13	0.45	0.0004	0.003	0.001	0.01	bdl	bdl	<0.001	0.38	0.0006
MS658	SA	12/23/15	0.16	0.54	0.0003	0.003	0.006	0.01	0.001	0.001	<0.001	0.40	0.0005
MS664	SA	12/23/15	0.23	0.64	0.0003	0.005	0.001	<0.01	bdl	0.001	<0.001	0.47	0.0006
MS670	SA	2/25/16	0.19	0.52	0.0005	0.004	0.002	0.01	<0.001	0.001	<0.001	0.47	0.0005
MS678	SA	2/25/16	0.16	0.51	0.0005	0.003	0.003	<0.01	<0.001	bdl	<0.001	0.50	0.0004
MS694	SA	2/25/16	0.14	0.43	0.0003	0.003	0.022	0.01	<0.001	0.001	<0.001	0.50	0.0005
MS706	SA	2/25/16	0.12	0.41	0.0003	0.003	0.001	<0.01	<0.001	<0.001	<0.001	0.50	0.0004
MS720	SA	2/25/16	0.07	0.31	0.0004	0.003	0.004	0.01	<0.001	<0.001	0.001	0.31	0.0006
MS736	SA	3/30/16	0.11	0.43	0.0006	0.004	0.004	<0.01	<0.001	bdl	0.001	0.32	0.0006
MS755	SA	3/30/16	0.13	0.52	0.0004	0.004	0.004	<0.01	0.001	0.001	<0.001	0.38	0.0006
MS771	SA	4/22/16	0.16	0.60	0.0008	<0.001	bdl	0.65	bdl	<0.001	<0.001	0.46	0.0004
MS778	SA	6/2/16	0.24	0.75	0.0006	0.002	0.001	0.01	0.001	0.001	<0.001	0.42	0.0009

						mg	/L			
Sample	Name	Analysis Date	Ag	Cd	Sn	Sb	Ва	W	Pb	U
MS461	SA	6/2/15	bdl	0.0001	0.025	0.0002	0.15	0.0006	0.0011	0.0005
MS470	SA	6/25/15	bdl	bdl	0.002	0.0001	0.16	0.0002	0.0007	0.0006
MS484	SA	6/24/15	bdl	0.0002	<0.001	0.0001	0.25	0.0003	0.0047	0.0002
MS492	SA	7/14/15	0.0003	<0.0001	0.001	0.0001	0.14	0.0014	0.0011	0.0003
MS514	SA	8/11/15	bdl	0.0013	0.001	0.0001	0.11	0.0005	0.0072	bdl
MS523	SA	8/11/15	bdl	0.0001	0.001	0.0001	0.14	bdl	0.0012	0.0001
MS536	SA	9/1/15	<0.0001	<0.0001	0.002	0.0001	0.11	0.0008	<0.0001	0.0004
MS552	SA	9/1/15	bdl	<0.0001	0.002	0.0001	0.12	<0.0001	0.0002	0.0004
MS576	SA	9/24/15	bdl	bdl	0.002	0.0001	0.23	0.0001	0.0004	0.0001
MS588	SA	10/13/15	bdl	<0.0001	0.002	0.0003	0.10	0.0001	0.0001	0.0004
MS601	SA	10/13/15	bdl	<0.0001	0.002	0.0001	0.08	<0.0001	0.0001	0.0004
MS622	SA	10/27/15	<0.0001	<0.0001	0.001	0.0002	0.10	0.0001	0.0002	0.0004
MS640	SA	11/18/15	<0.0001	0.0002	0.025	0.0001	0.10	<0.0001	0.0004	0.0003
MS645	SA	11/18/15	<0.0001	0.0002	0.001	<0.0001	0.10	<0.0001	0.0001	0.0003
MS658	SA	12/23/15	<0.0001	<0.0001	0.020	0.0002	0.10	0.0002	0.0003	0.0004
MS664	SA	12/23/15	<0.0001	<0.0001	0.002	0.0001	0.10	0.0001	0.0001	0.0004
MS670	SA	2/25/16	<0.0001	0.0001	0.001	0.0003	0.14	0.0004	0.0006	0.0004
MS678	SA	2/25/16	<0.0001	<0.0001	0.001	0.0001	0.13	0.0002	0.0007	0.0005
MS694	SA	2/25/16	bdl	0.0001	0.002	0.0001	0.13	0.0001	0.0006	0.0005
MS706	SA	2/25/16	bdl	0.0001	0.001	0.0001	0.12	<0.0001	0.0003	0.0005
MS720	SA	2/25/16	bdl	0.0001	0.002	0.0057	0.11	<0.0001	0.0008	0.0005
MS736	SA	3/30/16	bdl	bdl	<0.001	0.0044	0.10	0.0002	0.0010	bdl
MS755	SA	3/30/16	bdl	bdl	0.002	0.0001	0.12	<0.0001	0.0007	bdl
MS771	SA	4/22/16	bdl	<0.0001	<0.001	0.0002	0.13	0.0002	0.0006	0.0005
MS778	SA	6/2/16	0.0002	<0.0001	0.001	0.0005	0.11	0.0007	0.0008	0.0004

			mg/L												
Sample	Name	Analysis Date	Li	В	Na	Mg	AI	Si	Р	К	Са	Ti	V	Cr	
MS462	SB	6/2/15	0.006	0.012	3.98	8.64	0.191	4.37	0.06	0.75	104.22	0.002	0.0007	0.004	
MS469	SB	6/25/15	0.007	0.013	3.86	8.78	0.290	4.45	0.12	0.73	104.00	0.002	0.0010	0.001	
MS482	SB	6/24/15	0.007	0.014	4.01	9.13	0.533	5.19	0.44	1.34	128.00	0.005	0.0023	0.005	
MS491	SB	7/14/15	0.006	0.023	3.87	8.73	0.217	4.48	0.13	0.86	105.00	0.004	0.0008	0.002	
MS512	SB	8/11/15	0.004	0.016	4.19	8.54	0.148	4.60	0.11	1.02	102.84	0.002	0.0004	0.001	
MS522	SB	8/11/15	0.004	0.014	4.27	9.09	0.094	4.77	0.07	1.07	116.74	0.002	0.0004	0.002	
MS535	SB	9/1/15	0.004	bdl	4.01	9.16	0.122	4.71	0.13	1.02	112.38	0.003	bdl	0.002	
MS551	SB	9/1/15	0.004	bdl	4.69	10.88	0.104	5.42	0.15	1.23	147.36	0.003	bdl	0.004	
MS575	SB	9/24/15	0.005	0.008	5.37	10.59	0.135	5.47	0.18	1.82	122.32	0.003	0.0003	0.001	
MS587	SB	10/13/15	0.005	0.006	6.12	10.70	0.144	5.11	0.20	1.93	127.67	0.003	<0.001	0.002	
MS600	SB	10/13/15	0.005	0.007	5.77	11.27	0.210	5.28	0.20	1.56	138.04	0.004	<0.001	0.003	
MS621	SB	10/27/15	0.005	0.000	5.04	9.73	bdl	5.00	0.03	1.11	128.51	0.002	bdl	0.003	
MS639	SB	11/18/15	0.005	0.028	3.47	8.98	0.117	4.67	0.06	1.22	103.97	bdl	bdl	bdl	
MS644	SB	11/18/15	0.005	0.014	4.58	9.26	0.107	4.79	0.08	1.12	102.77	bdl	bdl	bdl	
MS657	SB	12/23/15	0.005	0.018	4.56	9.89	0.086	4.69	0.08	1.31	132.13	<0.001	bdl	0.001	
MS663	SB	12/23/15	0.005	0.001	5.82	10.06	0.093	4.51	0.02	0.86	147.19	0.001	bdl	0.002	
MS669	SB	2/25/16	0.006	0.020	5.88	8.06	0.068	4.65	0.01	0.98	98.04	<0.001	<0.001	bdl	
MS677	SB	2/25/16	0.007	0.016	8.25	8.37	0.070	4.49	bdl	0.79	103.70	<0.001	<0.001	bdl	
MS693	SB	2/25/16	0.006	0.014	4.18	8.71	0.058	4.51	bdl	0.78	107.09	bdl	<0.001	bdl	
MS705	SB	2/25/16	0.007	0.019	5.76	8.85	0.072	4.45	bdl	0.72	108.53	bdl	<0.001	bdl	
MS722	SB	2/25/16	0.006	0.015	5.57	8.00	0.089	4.56	bdl	1.00	92.93	bdl	<0.001	bdl	
MS735	SB	3/30/16	0.005	0.015	3.62	6.75	0.143	4.63	0.09	1.41	87.07	0.001	<0.001	<0.001	
MS754	SB	3/30/16	0.006	0.004	4.10	7.92	0.043	4.44	0.01	1.03	111.08	0.001	<0.001	0.002	
MS770	SB	4/22/16	0.005	0.009	3.60	8.56	0.052	4.68	0.03	0.52	115.89	bdl	bdl	0.002	
MS777	SB	6/2/16	0.006	0.014	3.74	8.79	0.042	4.42	0.02	0.72	117.01	<0.001	bdl	<0.001	

		-						mg/L					
Sample	Name	Analysis Date	Mn	Fe	Со	Ni	Cu	Zn	As	Se	Rb	Sr	Мо
MS462	SB	6/2/15	0.06	0.76	0.0008	0.002	0.007	<0.01	0.001	0.002	0.001	0.38	0.0005
MS469	SB	6/25/15	0.10	0.76	0.0009	0.006	0.005	0.01	0.001	0.002	0.001	0.40	0.0005
MS482	SB	6/24/15	0.33	1.29	0.0026	0.006	0.018	0.05	0.001	0.003	0.002	0.46	0.0006
MS491	SB	7/14/15	0.08	1.09	0.0009	0.004	0.004	0.01	0.001	0.001	0.001	0.33	0.0011
MS512	SB	8/11/15	0.06	0.70	0.0004	0.003	0.004	0.02	0.001	0.001	0.001	0.29	0.0006
MS522	SB	8/11/15	0.07	0.61	0.0003	0.003	0.005	0.02	<0.001	0.001	0.001	0.33	0.0003
MS535	SB	9/1/15	0.08	0.79	0.0008	0.004	0.005	bdl	bdl	0.001	0.001	0.38	0.0008
MS551	SB	9/1/15	0.08	0.83	0.0008	0.004	0.005	bdl	bdl	0.001	0.001	0.40	0.0004
MS575	SB	9/24/15	0.06	0.72	0.0007	0.004	0.003	<0.01	0.001	0.001	0.001	0.30	0.0006
MS587	SB	10/13/15	0.09	0.91	0.0008	0.005	0.003	<0.01	bdl	0.001	0.001	0.31	0.0006
MS600	SB	10/13/15	0.12	0.93	0.0010	0.005	0.004	0.01	bdl	0.001	0.001	0.30	0.0004
MS621	SB	10/27/15	0.02	0.57	0.0003	0.003	0.002	<0.01	<0.001	0.001	0.001	0.30	0.0003
MS639	SB	11/18/15	0.06	0.71	0.0008	0.003	0.006	0.01	bdl	bdl	0.001	0.34	0.0003
MS644	SB	11/18/15	0.05	0.45	0.0007	0.004	0.002	0.01	bdl	bdl	<0.001	0.34	0.0004
MS657	SB	12/23/15	0.05	0.76	0.0005	0.005	0.011	0.01	0.001	0.001	0.001	0.39	0.0003
MS663	SB	12/23/15	0.03	0.71	0.0005	0.004	0.003	0.01	bdl	0.001	0.001	0.42	0.0003
MS669	SB	2/25/16	0.02	0.44	0.0004	0.005	0.002	0.01	<0.001	<0.001	0.001	0.42	0.0006
MS677	SB	2/25/16	0.02	0.48	0.0004	0.004	0.004	0.00	0.005	0.001	0.001	0.44	0.0004
MS693	SB	2/25/16	0.02	0.38	0.0003	0.003	0.011	0.01	<0.001	<0.001	0.001	0.46	0.0002
MS705	SB	2/25/16	0.03	0.53	0.0005	0.004	0.002	<0.01	<0.001	<0.001	0.001	0.47	0.0003
MS722	SB	2/25/16	0.01	0.36	0.0003	0.003	0.005	0.01	<0.001	bdl	0.001	0.40	0.0006
MS735	SB	3/30/16	0.02	0.50	0.0004	0.005	0.006	0.01	<0.001	0.001	0.001	0.28	0.0008
MS754	SB	3/30/16	0.01	0.52	0.0004	0.005	0.004	<0.01	0.003	0.001	0.001	0.36	0.0004
MS770	SB	4/22/16	0.01	0.51	0.0007	0.001	bdl	0.64	bdl	<0.001	<0.001	0.42	0.0002
MS777	SB	6/2/16	0.01	0.75	0.0004	0.002	0.003	<0.01	bdl	0.001	0.001	0.42	0.0007

						mg	ı/L			
Sample	Name	Analysis Date	Ag	Cd	Sn	Sb	Ва	W	Pb	U
MS462	SB	6/2/15	bdl	bdl	0.001	0.0001	0.25	0.0005	0.0087	0.0007
MS469	SB	6/25/15	bdl	0.0001	<0.001	0.0002	0.32	0.0003	0.0269	0.0006
MS482	SB	6/24/15	bdl	0.0004	<0.001	0.0003	0.73	0.0004	0.0760	0.0003
MS491	SB	7/14/15	0.0004	0.0001	0.001	0.0002	0.26	0.0018	0.0194	0.0004
MS512	SB	8/11/15	bdl	0.0001	0.001	0.0024	0.22	0.0008	0.0146	0.0003
MS522	SB	8/11/15	bdl	0.0001	<0.001	0.0001	0.24	bdl	0.0123	0.0003
MS535	SB	9/1/15	0.0001	0.0001	0.001	0.0002	0.22	0.0011	0.0227	0.0006
MS551	SB	9/1/15	bdl	0.0001	0.000	0.0001	0.22	<0.0001	0.0192	0.0005
MS575	SB	9/24/15	bdl	<0.001	<0.001	0.0002	0.18	0.0001	0.0179	0.0005
MS587	SB	10/13/15	bdl	<0.0001	<0.001	0.0004	0.16	0.0001	0.0181	0.0006
MS600	SB	10/13/15	bdl	<0.0001	<0.001	0.0003	0.18	<0.0001	0.0259	0.0005
MS621	SB	10/27/15	<0.0001	<0.0001	<0.001	0.0002	0.17	0.0001	0.0054	0.0005
MS639	SB	11/18/15	<0.0001	0.0002	0.014	0.0001	0.24	<0.0001	0.0227	0.0005
MS644	SB	11/18/15	<0.0001	0.0002	0.001	0.0001	0.20	<0.0001	0.0125	0.0006
MS657	SB	12/23/15	<0.0001	<0.0001	0.010	0.0002	0.23	0.0003	0.0112	0.0006
MS663	SB	12/23/15	<0.0001	<0.0001	0.003	0.0001	0.23	0.0001	0.0221	0.0007
MS669	SB	2/25/16	0.0001	<0.0001	0.002	0.0003	0.25	0.0004	0.0060	0.0006
MS677	SB	2/25/16	<0.0001	0.0001	0.001	0.0002	0.27	0.0002	0.0091	0.0007
MS693	SB	2/25/16	<0.0001	<0.0001	0.015	0.0001	0.28	0.0001	0.0025	0.0007
MS705	SB	2/25/16	0.0028	0.0001	0.001	<0.0001	0.29	<0.0001	0.0140	0.0008
MS722	SB	2/25/16	0.0002	0.0001	0.002	0.0024	0.24	<0.0001	0.0073	0.0006
MS735	SB	3/30/16	bdl	bdl	<0.001	0.0023	0.19	0.0002	0.0042	bdl
MS754	SB	3/30/16	bdl	bdl	0.002	0.0001	0.24	<0.0001	0.0068	0.0001
MS770	SB	4/22/16	0.0001	bdl	<0.001	0.0001	0.23	0.0002	0.0025	0.0006
MS777	SB	6/2/16	0.0003	<0.0001	<0.001	0.0006	0.23	0.0009	0.0033	0.0006

			mg/L											
Sample	Name	Analysis Date	Li	В	Na	Mg	AI	Si	Р	К	Са	Ti	V	Cr
N/A	SC	6/2/15	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
MS472	SC	6/25/15	0.005	0.026	14.35	11.42	0.037	2.81	bdl	1.54	96.73	0.001	0.0009	0.001
MS485	SC	6/24/15	0.003	0.030	12.38	7.69	0.453	4.73	0.12	2.32	99.86	0.004	0.0030	0.005
MS495	SC	7/14/15	0.003	0.027	11.61	9.17	0.093	4.37	0.07	2.70	96.11	0.003	0.0010	0.003
MS518	SC	8/11/15	0.003	0.025	11.08	10.40	0.057	4.00	0.01	1.64	103.53	0.001	0.0006	0.001
MS524	SC	8/11/15	0.003	0.024	12.07	11.22	0.021	4.03	<0.01	1.94	101.50	0.001	0.0007	0.002
MS538	SC	9/1/15	0.003	bdl	13.20	11.86	bdl	2.98	0.02	2.47	85.86	0.001	bdl	0.002
MS554	SC	9/1/15	0.003	bdl	16.54	14.07	0.014	2.95	0.03	3.78	85.35	0.002	bdl	0.003
MS572	SC	9/24/15	0.003	0.028	15.55	12.60	0.024	2.40	0.03	4.15	60.40	0.001	0.0005	0.001
MS584	SC	10/13/15	0.003	0.023	17.93	12.25	0.022	1.81	0.03	3.69	68.87	0.001	<0.001	0.001
MS597	SC	10/13/15	0.003	0.019	14.76	12.47	0.012	4.15	0.01	2.69	116.18	0.002	<0.001	0.003
MS624	SC	10/27/15	0.003	0.008	12.69	12.16	bdl	3.09	bdl	2.03	116.76	0.001	bdl	0.002
MS636	SC	11/18/15	0.004	0.029	11.07	10.49	0.063	3.72	0.02	2.16	98.26	bdl	bdl	<0.001
MS647	SC	11/18/15	0.004	0.028	11.53	10.72	0.045	3.81	0.01	1.81	99.96	bdl	bdl	<0.001
MS659	SC	12/23/15	0.004	0.012	13.32	11.35	0.083	4.11	0.01	1.90	123.59	bdl	bdl	<0.001
MS666	SC	12/23/15	0.004	0.008	14.79	12.79	0.029	3.45	bdl	1.91	143.89	bdl	bdl	0.002
MS672	SC	2/25/16	0.005	0.023	11.54	9.77	0.150	4.28	0.00	1.52	99.54	bdl	0.0007	bdl
MS680	SC	2/25/16	0.005	0.019	13.10	11.02	0.049	3.85	bdl	1.26	105.42	bdl	<0.001	bdl
MS695	SC	2/25/16	0.004	0.018	24.96	10.41	0.079	3.53	bdl	1.77	101.77	bdl	0.0006	bdl
MS708	SC	2/25/16	0.005	0.017	17.45	10.81	0.058	3.14	bdl	1.17	101.82	bdl	<0.001	bdl
MS723	SC	2/25/16	0.003	0.016	21.38	8.43	0.371	3.42	bdl	1.78	80.65	bdl	0.0009	bdl
MS737	SC	3/30/16	0.003	0.023	9.78	6.46	0.278	3.89	0.06	2.76	71.42	0.001	0.0008	<0.001
MS757	SC	3/30/16	0.004	0.014	11.44	9.88	0.088	3.79	bdl	1.53	110.45	0.001	0.0006	0.003
MS772	SC	4/22/16	0.004	0.018	9.41	10.87	0.075	3.09	0.02	0.91	96.97	bdl	<0.001	0.001
MS779	SC	6/2/16	0.004	0.023	11.97	10.33	0.081	3.48	<0.01	1.24	108.25	bdl	<0.001	0.001

		-						mg/L					
Sample	Name	Analysis Date	Mn	Fe	Со	Ni	Cu	Zn	As	Se	Rb	Sr	Мо
N/A	SC	6/2/15	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
MS472	SC	6/25/15	0.16	0.65	0.0005	0.002	0.001	<0.01	0.002	0.002	0.001	0.48	0.0013
MS485	SC	6/24/15	0.49	1.04	0.0018	0.005	0.007	0.01	0.001	0.004	0.001	0.38	0.0010
MS495	SC	7/14/15	0.31	0.98	0.0006	0.004	0.004	bdl	0.001	0.002	0.001	0.32	0.0012
MS518	SC	8/11/15	0.19	0.65	0.0002	0.003	0.002	0.01	0.001	0.001	0.001	0.35	0.0009
MS524	SC	8/11/15	0.23	0.61	0.0001	0.002	0.001	0.01	0.001	0.001	0.001	0.37	0.0011
MS538	SC	9/1/15	0.30	0.74	0.0006	0.004	0.003	bdl	bdl	0.002	0.001	0.41	0.0053
MS554	SC	9/1/15	0.51	0.79	0.0007	0.003	0.002	bdl	bdl	0.002	0.001	0.40	0.0015
MS572	SC	9/24/15	0.83	0.62	0.0006	0.003	0.001	bdl	0.005	0.002	0.001	0.26	0.0011
MS584	SC	10/13/15	0.36	0.84	0.0006	0.003	0.002	<0.01	0.001	0.001	<0.001	0.28	0.0012
MS597	SC	10/13/15	0.12	0.69	0.0004	0.004	0.002	bdl	0.001	0.001	<0.001	0.31	0.0010
MS624	SC	10/27/15	0.12	0.60	0.0003	0.003	0.002	bdl	0.001	0.003	<0.001	0.35	0.0009
MS636	SC	11/18/15	0.20	0.58	0.0006	0.004	0.004	0.01	bdl	bdl	<0.001	0.37	0.0007
MS647	SC	11/18/15	0.14	0.49	0.0006	0.004	0.001	<0.01	bdl	bdl	<0.001	0.38	0.0007
MS659	SC	12/23/15	0.17	0.56	0.0004	0.004	0.007	<0.01	<0.001	0.001	<0.001	0.41	0.0005
MS666	SC	12/23/15	0.27	0.58	0.0005	0.005	0.004	<0.01	bdl	0.002	<0.001	0.47	0.0007
MS672	SC	2/25/16	0.17	0.51	0.0006	0.004	0.002	0.01	<0.001	0.001	0.001	0.46	0.0006
MS680	SC	2/25/16	0.10	0.42	0.0004	0.004	0.006	<0.01	<0.001	<0.001	<0.001	0.49	0.0006
MS695	SC	2/25/16	0.10	0.41	0.0004	0.003	0.003	0.01	<0.001	0.001	0.001	0.48	0.0005
MS708	SC	2/25/16	0.13	0.44	0.0004	0.004	0.002	<0.01	<0.001	<0.001	<0.001	0.48	0.0005
MS723	SC	2/25/16	0.15	0.43	0.0007	0.004	0.005	0.01	<0.001	<0.001	0.001	0.38	0.0006
MS737	SC	3/30/16	0.12	0.49	0.0008	0.004	0.006	<0.01	<0.001	<0.001	0.001	0.32	0.0008
MS757	SC	3/30/16	0.20	0.55	0.0005	0.005	0.005	0.01	0.001	0.002	<0.001	0.50	0.0008
MS772	SC	4/22/16	0.17	0.55	0.0007	0.001	bdl	0.65	<0.001	<0.001	<0.001	0.42	0.0005
MS779	SC	6/2/16	0.33	0.88	0.0006	0.002	0.002	<0.01	<0.001	0.001	0.001	0.44	0.0010

						mg	g/L			
Sample	Name	Analysis Date	Ag	Cd	Sn	Sb	Ва	W	Pb	U
N/A	SC	6/2/15	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
MS472	SC	6/25/15	bdl	bdl	0.002	0.0001	0.16	0.0002	0.0001	0.0006
MS485	SC	6/24/15	bdl	0.0002	0.001	0.0002	0.33	0.0003	0.0043	0.0002
MS495	SC	7/14/15	0.0002	<0.0001	0.001	0.0001	0.13	0.0007	0.0006	0.0003
MS518	SC	8/11/15	bdl	0.0001	0.001	0.0001	0.12	bdl	0.0003	0.0002
MS524	SC	8/11/15	bdl	<0.0001	0.002	0.0001	0.12	bdl	bdl	0.0002
MS538	SC	9/1/15	bdl	0.0001	0.002	0.0001	0.12	0.0005	0.0007	0.0004
MS554	SC	9/1/15	bdl	<0.0001	0.003	0.0001	0.10	<0.0001	0.0004	0.0004
MS572	SC	9/24/15	bdl	bdl	0.003	0.0002	0.08	0.0001	0.0004	0.0002
MS584	SC	10/13/15	bdl	<0.0001	0.002	0.0004	0.08	0.0003	0.0006	0.0004
MS597	SC	10/13/15	bdl	<0.0001	0.001	0.0002	0.08	0.0001	0.0003	0.0004
MS624	SC	10/27/15	<0.0001	<0.0001	0.002	0.0002	0.08	0.0001	0.0002	0.0005
MS636	SC	11/18/15	<0.0001	0.0002	0.019	0.0001	0.11	0.0001	0.0004	0.0004
MS647	SC	11/18/15	<0.0001	0.0002	0.001	0.0001	0.10	<0.0001	0.0004	0.0005
MS659	SC	12/23/15	<0.0001	<0.0001	0.019	0.0002	0.11	0.0002	0.0004	0.0005
MS666	SC	12/23/15	<0.0001	<0.0001	0.002	0.0002	0.10	0.0001	0.0002	0.0006
MS672	SC	2/25/16	<0.0001	<0.0001	0.001	0.0002	0.14	0.0003	0.0007	0.0006
MS680	SC	2/25/16	bdl	0.0008	0.001	0.0001	0.14	0.0001	0.0005	0.0007
MS695	SC	2/25/16	bdl	0.0001	0.001	0.0001	0.14	0.0001	0.0004	0.0007
MS708	SC	2/25/16	0.0006	<0.0001	0.001	0.0001	0.13	<0.0001	0.0007	0.0007
MS723	SC	2/25/16	bdl	0.0003	<0.001	0.0023	0.13	<0.0001	0.0020	0.0005
MS737	SC	3/30/16	bdl	bdl	<0.001	0.0018	0.11	0.0001	0.0012	bdl
MS757	SC	3/30/16	bdl	bdl	0.002	0.0001	0.12	<0.0001	0.0005	0.0002
MS772	SC	4/22/16	bdl	<0.0001	0.001	0.0002	0.09	0.0001	0.0001	0.0006
MS779	SC	6/2/16	0.0001	bdl	<0.001	0.0004	0.12	0.0006	0.0013	0.0005

			mg/L											
Sample	Name	Analysis Date	Li	В	Na	Mg	AI	Si	Р	К	Са	Ti	V	Cr
N/A	SD	6/2/15	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
N/A	SD	6/25/15	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
MS483	SD	6/24/15	0.003	0.013	4.15	6.13	0.544	4.56	0.12	0.71	99.01	0.003	0.0021	0.005
MS490	SD	7/14/15	0.003	0.029	4.83	7.88	0.297	4.98	0.09	0.75	106.12	0.004	0.0014	0.002
MS510	SD	8/11/15	0.003	0.020	4.62	7.99	0.202	4.65	0.06	0.69	102.37	0.002	0.0009	0.001
MS520	SD	8/11/15	0.002	0.019	4.71	8.65	0.157	4.80	0.07	0.80	113.35	0.002	0.0011	0.001
MS534	SD	9/1/15	0.003	bdl	4.86	8.85	0.153	4.69	0.06	0.82	88.97	0.002	bdl	0.001
MS550	SD	9/1/15	0.002	bdl	5.63	10.24	0.125	5.35	0.05	1.08	112.54	0.003	bdl	0.004
MS574	SD	9/24/15	0.002	0.017	6.89	9.98	0.301	5.75	0.12	1.72	103.93	0.004	0.0014	0.001
MS586	SD	10/13/15	0.003	0.014	7.30	10.75	0.416	5.31	0.20	1.73	129.54	0.005	0.0023	0.002
MS599	SD	10/13/15	0.003	0.010	6.38	10.14	0.066	5.36	0.03	1.11	123.82	0.003	bdl	0.003
MS620	SD	10/27/15	0.003	0.004	5.36	9.62	0.010	5.25	0.03	1.43	118.54	0.001	bdl	0.002
MS638	SD	11/18/15	0.003	0.019	3.87	8.16	0.075	5.15	0.02	0.94	97.79	bdl	bdl	bdl
MS643	SD	11/18/15	0.003	0.018	5.07	8.23	0.067	4.91	0.02	0.80	99.31	bdl	bdl	<0.001
MS656	SD	12/23/15	0.003	0.005	4.38	8.74	0.109	4.62	0.02	0.75	120.32	bdl	bdl	bdl
MS662	SD	12/23/15	0.003	0.002	6.12	10.00	0.075	4.75	0.02	0.80	131.86	bdl	bdl	0.001
MS668	SD	2/25/16	0.004	0.016	5.71	7.59	0.238	4.42	0.03	0.36	102.02	0.001	0.0007	bdl
MS676	SD	2/25/16	0.004	0.013	5.91	7.80	0.085	4.07	bdl	0.33	98.55	bdl	<0.001	bdl
MS692	SD	2/25/16	0.004	0.012	4.41	7.58	0.153	3.94	bdl	0.28	98.71	bdl	<0.001	bdl
MS704	SD	2/25/16	0.004	0.011	5.98	8.09	0.048	3.89	bdl	0.27	93.47	bdl	<0.001	bdl
MS721	SD	2/25/16	0.003	0.012	5.42	6.07	0.588	3.75	bdl	0.38	81.35	<0.001	0.0009	bdl
MS734	SD	3/30/16	0.003	0.013	3.75	5.12	0.277	4.02	0.06	0.85	76.59	0.001	<0.001	bdl
MS753	SD	3/30/16	0.004	0.005	5.26	7.14	0.129	4.05	0.02	0.58	102.42	0.001	<0.001	0.001
MS769	SD	4/22/16	0.004	0.012	4.13	7.90	0.160	4.33	0.04	0.29	99.80	bdl	<0.001	0.001
MS776	SD	6/2/16	0.004	0.018	4.12	7.53	0.188	4.04	0.02	0.34	96.30	<0.001	<0.001	<0.001

		-						mg/L					
Sample	Name	Analysis Date	Mn	Fe	Со	Ni	Cu	Zn	As	Se	Rb	Sr	Мо
N/A	SD	6/2/15	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
N/A	SD	6/25/15	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
MS483	SD	6/24/15	0.49	1.12	0.0023	0.005	0.034	0.02	0.001	0.004	0.001	0.36	0.0004
MS490	SD	7/14/15	0.19	1.16	0.0013	0.004	0.005	bdl	0.001	0.002	0.001	0.31	0.0016
MS510	SD	8/11/15	0.16	0.76	0.0008	0.005	0.004	0.01	0.001	0.001	0.001	0.31	0.0010
MS520	SD	8/11/15	0.23	0.65	0.0009	0.004	0.007	0.02	<0.001	0.001	0.001	0.35	0.0009
MS534	SD	9/1/15	0.17	0.69	0.0010	0.004	0.005	bdl	bdl	0.001	<0.001	0.36	0.0011
MS550	SD	9/1/15	0.19	0.71	0.0008	0.004	0.006	bdl	bdl	0.001	<0.001	0.39	0.0007
MS574	SD	9/24/15	0.51	0.97	0.0019	0.004	0.005	<0.01	0.001	0.001	0.001	0.30	0.0010
MS586	SD	10/13/15	0.92	1.38	0.0036	0.009	0.008	0.02	0.001	0.001	0.001	0.35	0.0006
MS599	SD	10/13/15	0.10	0.68	0.0005	0.004	0.002	bdl	bdl	0.001	0.000	0.30	0.0006
MS620	SD	10/27/15	0.07	0.50	0.0003	0.003	0.001	0.01	<0.001	0.001	<0.001	0.31	0.0007
MS638	SD	11/18/15	0.08	0.41	0.0006	0.004	0.006	0.01	bdl	bdl	<0.001	0.34	0.0005
MS643	SD	11/18/15	0.14	0.56	0.0007	0.003	0.001	0.01	bdl	bdl	<0.001	0.34	0.0005
MS656	SD	12/23/15	0.09	0.55	0.0005	0.004	0.008	0.03	<0.001	<0.001	<0.001	0.36	0.0004
MS662	SD	12/23/15	0.10	0.50	0.0005	0.004	0.002	0.02	bdl	0.001	<0.001	0.39	0.0006
MS668	SD	2/25/16	0.14	0.52	0.0008	0.004	0.003	<0.01	<0.001	0.001	<0.001	0.43	0.0005
MS676	SD	2/25/16	0.06	0.39	0.0004	0.004	0.004	0.01	<0.001	<0.001	<0.001	0.42	0.0004
MS692	SD	2/25/16	0.07	0.39	0.0005	0.003	0.011	0.01	<0.001	<0.001	<0.001	0.42	0.0003
MS704	SD	2/25/16	0.04	0.30	0.0003	0.003	0.002	<0.01	<0.001	bdl	<0.001	0.41	0.0004
MS721	SD	2/25/16	0.14	0.37	0.0010	0.004	0.008	0.01	<0.001	bdl	0.001	0.34	0.0002
MS734	SD	3/30/16	0.08	0.48	0.0007	0.004	0.005	<0.01	<0.001	0.001	<0.001	0.31	0.0012
MS753	SD	3/30/16	0.07	0.47	0.0006	0.005	0.006	0.01	0.028	0.001	<0.001	0.42	0.0005
MS769	SD	4/22/16	0.08	0.50	0.0010	0.001	0.003	0.65	bdl	<0.001	<0.001	0.39	0.0005
MS776	SD	6/2/16	0.11	0.68	0.0007	0.002	0.004	<0.01	<0.001	0.001	<0.001	0.37	0.0008

						mg	/L			
Sample	Name	Analysis Date	Ag	Cd	Sn	Sb	Ba	W	Pb	U
N/A	SD	6/2/15	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
N/A	SD	6/25/15	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
MS483	SD	6/24/15	bdl	0.0002	<0.001	0.0001	0.33	0.0004	0.0061	0.0002
MS490	SD	7/14/15	0.0010	0.0001	0.001	0.0001	0.21	0.0028	0.0024	0.0003
MS510	SD	8/11/15	bdl	0.0002	0.001	0.0002	0.21	0.0019	0.0048	0.0002
MS520	SD	8/11/15	bdl	0.0003	bdl	0.0001	0.27	bdl	0.0032	0.0001
MS534	SD	9/1/15	0.0003	0.0001	0.001	0.0001	0.15	0.0016	0.0021	0.0004
MS550	SD	9/1/15	bdl	0.0001	0.000	0.0001	0.14	0.0001	0.0015	0.0004
MS574	SD	9/24/15	bdl	<0.001	<0.001	0.0002	0.15	0.0001	0.0045	0.0004
MS586	SD	10/13/15	bdl	<0.0001	<0.001	0.0003	0.24	0.0002	0.0070	0.0003
MS599	SD	10/13/15	bdl	<0.0001	0.001	0.0001	0.11	0.0001	0.0007	0.0004
MS620	SD	10/27/15	<0.0001	<0.0001	0.001	0.0002	0.11	0.0001	0.0002	0.0004
MS638	SD	11/18/15	<0.0001	0.0002	0.015	0.0001	0.14	0.0001	0.0006	0.0004
MS643	SD	11/18/15	<0.0001	0.0002	0.001	<0.0001	0.14	<0.0001	0.0008	0.0004
MS656	SD	12/23/15	0.0009	0.0001	0.013	0.0005	0.14	0.0003	0.0012	0.0005
MS662	SD	12/23/15	<0.0001	<0.0001	0.001	0.0002	0.13	0.0002	0.0005	0.0006
MS668	SD	2/25/16	<0.0001	0.0001	0.001	0.0004	0.18	0.0005	0.0014	0.0006
MS676	SD	2/25/16	<0.0001	0.0001	0.001	0.0001	0.16	0.0002	0.0006	0.0006
MS692	SD	2/25/16	bdl	<0.0001	0.002	0.0001	0.17	0.0001	0.0011	0.0007
MS704	SD	2/25/16	bdl	<0.0001	0.001	0.0001	0.15	<0.0001	0.0003	0.0007
MS721	SD	2/25/16	0.0025	0.0001	<0.001	0.0036	0.16	<0.0001	0.0034	0.0005
MS734	SD	3/30/16	bdl	bdl	<0.001	0.0030	0.13	0.0002	0.0011	bdl
MS753	SD	3/30/16	bdl	bdl	0.001	0.0003	0.16	<0.0001	0.0012	<0.0001
MS769	SD	4/22/16	<0.0001	0.0001	<0.001	0.0002	0.16	0.0002	0.0044	0.0006
MS776	SD	6/2/16	0.0003	<0.0001	<0.001	0.0009	0.14	0.0012	0.0013	0.0005

			μg/L					
Sample	Description	Analysis Date	Methane	Ethane	Ethene	Propane	Propylene	Butane
MS460	CC1	5/29/15	8.49	ND	ND	ND	ND	ND
MS468	CC1	6/10/15	12.4	ND	ND	ND	ND	ND
MS481	CC1	6/22/15	1.52	ND	ND	ND	ND	ND
MS489	CC1	7/6/15	2.67	ND	ND	ND	ND	ND
MS509	CC1	7/23/15	8.00	ND	ND	ND	ND	ND
MS519	CC1	7/30/15	14.85	ND	ND	ND	ND	ND
MS533	CC1	8/20/15	25.62	ND	0.01	ND	ND	ND
MS549	CC1	9/1/15	37.84	ND	ND	ND	ND	ND
MS573	CC1	9/11/15	246.53	ND	0.03	ND	ND	ND
MS585	CC1	10/1/15	98.26	ND	0.01	ND	ND	ND
MS598	CC1	10/8/15	8.33	ND	ND	ND	ND	ND
MS619	CC1	10/22/15	13.47	ND	ND	ND	ND	ND
MS637	CC1	11/5/15	6.29	ND	ND	ND	ND	ND
MS642	CC1	11/19/15	6.77	ND	ND	ND	ND	ND
MS655	CC1	12/8/15	6.37	ND	ND	ND	ND	ND
MS661	CC1	12/17/15	11.77	ND	ND	ND	ND	ND
MS667	CC1	1/6/16	2.69	ND	ND	ND	ND	ND
MS675	CC1	1/14/16	3.67	0.02	ND	ND	ND	ND
MS691	CC1	1/28/16	2.57	ND	ND	ND	ND	ND
MS703	CC1	2/11/16	4.67	0.01	ND	ND	ND	ND
MS719	CC1	2/26/16	2.89	ND	ND	ND	ND	ND
MS733	CC1	3/17/16	1.99	ND	ND	ND	ND	ND
MS752	CC1	4/6/16	4.82	ND	ND	ND	ND	ND
MS768	CC1	4/20/16	4.17	ND	ND	ND	ND	ND
MS775	CC1	5/4/16	9.13	ND	ND	ND	ND	ND

APPENDIX P: SURFACE WATER GAS CHROMATOGRAPHY DATA

					h	g/L		
Sample	Description	Analysis Date	Methane	Ethane	Ethene	Propane	Propylene	Butane
MS463	CC2	5/29/15	0.53	ND	ND	ND	ND	ND
MS471	CC2	6/10/15	2.98	ND	ND	ND	ND	ND
MS486	CC2	6/22/15	0.6	ND	ND	ND	ND	ND
MS493	CC2	7/6/15	0.53	ND	ND	ND	ND	ND
MS517	CC2	7/23/15	0.44	ND	ND	ND	ND	ND
MS521	CC2	7/30/15	5.63	ND	ND	ND	ND	ND
MS537	CC2	8/20/15	6.45	ND	ND	ND	ND	ND
MS553	CC2	9/1/15	7.63	ND	ND	ND	ND	ND
MS571	CC2	9/11/15	12.61	ND	ND	ND	ND	ND
MS582	CC2	10/1/15	7.83	ND	ND	ND	ND	ND
MS596	CC2	10/8/15	0.76	ND	ND	ND	ND	ND
MS623	CC2	10/22/15	2.25	ND	ND	ND	ND	ND
MS635	CC2	11/5/15	0.51	ND	ND	ND	ND	ND
MS646	CC2	11/19/15	0.73	ND	ND	ND	ND	ND
MS660	CC2	12/8/15	ND	ND	ND	ND	ND	ND
MS665	CC2	12/17/15	ND	ND	ND	ND	ND	ND
MS671	CC2	1/6/16	ND	ND	ND	ND	ND	ND
MS679	CC2	1/14/16	ND	ND	ND	ND	ND	ND
MS697	CC2	1/28/16	ND	ND	ND	ND	ND	ND
MS707	CC2	2/11/16	ND	ND	ND	ND	ND	ND
MS724	CC2	2/26/16	0.65	ND	ND	ND	ND	ND
MS738	CC2	3/17/16	0.27	ND	ND	ND	ND	ND
MS756	CC2	4/6/16	0.26	ND	ND	ND	ND	ND
MS773	CC2	4/20/16	ND	ND	ND	ND	ND	ND
MS780	CC2	5/4/16	0.51	ND	ND	ND	ND	ND

			μg/L					
Sample	Description	Analysis Date	Methane	Ethane	Ethene	Propane	Propylene	Butane
MS461	SA	5/29/15	6.49	ND	ND	ND	ND	ND
MS470	SA	6/10/15	6.54	ND	ND	ND	ND	ND
MS484	SA	6/22/15	2.58	ND	ND	ND	ND	ND
MS492	SA	7/6/15	4.03	ND	ND	ND	ND	ND
MS514	SA	7/23/15	5.53	ND	ND	ND	ND	ND
MS523	SA	7/30/15	14.02	ND	ND	ND	ND	ND
MS536	SA	8/20/15	10.58	ND	ND	ND	ND	ND
MS552	SA	9/1/15	11.34	ND	ND	ND	ND	ND
MS576	SA	9/11/15	554.08	ND	0.04	0.02	ND	ND
MS588	SA	10/1/15	10.37	ND	ND	ND	ND	ND
MS601	SA	10/8/15	5.09	ND	ND	ND	ND	ND
MS622	SA	10/22/15	11.57	ND	ND	ND	ND	ND
MS640	SA	11/5/15	5.14	ND	ND	ND	ND	ND
MS645	SA	11/19/15	5.31	ND	ND	ND	ND	ND
MS658	SA	12/8/15	3.05	ND	ND	ND	ND	ND
MS664	SA	12/17/15	6.71	ND	ND	ND	ND	ND
MS670	SA	1/6/16	2.13	ND	ND	ND	ND	ND
MS678	SA	1/14/16	3.18	ND	ND	ND	ND	ND
MS694	SA	1/28/16	2.19	ND	ND	ND	ND	ND
MS706	SA	2/11/16	2.26	ND	ND	ND	ND	ND
MS720	SA	2/26/16	0.95	ND	ND	ND	ND	ND
MS736	SA	3/17/16	1.22	ND	ND	ND	ND	ND
MS755	SA	4/6/16	3.16	ND	ND	ND	ND	ND
MS771	SA	4/20/16	3.50	ND	ND	ND	ND	ND
MS778	SA	5/4/16	4.89	ND	ND	ND	ND	ND

					há	g/L		
Sample	Description	Analysis Date	Methane	Ethane	Ethene	Propane	Propylene	Butane
MS462	SB	5/29/15	ND	ND	ND	ND	ND	ND
MS469	SB	6/10/15	0.32	ND	ND	ND	ND	ND
MS482	SB	6/22/15	0.6	ND	ND	ND	ND	ND
MS491	SB	7/6/15	0.36	ND	ND	ND	ND	ND
MS512	SB	7/23/15	ND	ND	ND	ND	ND	ND
MS522	SB	7/30/15	0.37	ND	ND	ND	ND	ND
MS535	SB	8/20/15	ND	ND	ND	ND	ND	ND
MS551	SB	9/1/15	ND	ND	ND	ND	ND	ND
MS575	SB	9/11/15	ND	ND	ND	ND	ND	ND
MS587	SB	10/1/15	ND	ND	ND	ND	ND	ND
MS600	SB	10/8/15	0.72	ND	ND	ND	ND	ND
MS621	SB	10/22/15	0.96	ND	ND	ND	ND	ND
MS639	SB	11/5/15	1.53	ND	ND	ND	ND	ND
MS644	SB	11/19/15	0.59	ND	ND	ND	ND	ND
MS657	SB	12/8/15	1.63	ND	ND	ND	ND	ND
MS663	SB	12/17/15	1.72	ND	ND	ND	ND	ND
MS669	SB	1/6/16	2.72	ND	ND	ND	ND	ND
MS677	SB	1/14/16	2.45	ND	ND	ND	ND	ND
MS693	SB	1/28/16	2.32	ND	ND	ND	ND	ND
MS705	SB	2/11/16	2.82	ND	ND	ND	ND	ND
MS722	SB	2/26/16	3.42	ND	ND	ND	ND	ND
MS735	SB	3/17/16	3.16	ND	ND	ND	ND	ND
MS754	SB	4/6/16	2.18	ND	ND	ND	ND	ND
MS770	SB	4/20/16	1.85	ND	ND	ND	ND	ND
MS777	SB	5/4/16	2.19	ND	ND	ND	ND	ND

			μg/L							
Sample	Description	Analysis Date	Methane	Ethane	Ethene	Propane	Propylene	Butane		
N/A	SC	5/29/15	N/A	N/A	N/A	N/A	N/A	N/A		
MS472	SC	6/10/15	4.47	ND	ND	ND	ND	ND		
MS485	SC	6/22/15	2.61	ND	ND	ND	ND	ND		
MS495	SC	7/6/15	4.92	ND	ND	ND	ND	ND		
MS518	SC	7/23/15	3.98	ND	ND	ND	ND	ND		
MS524	SC	7/30/15	3.24	ND	ND	ND	ND	ND		
MS538	SC	8/20/15	0.92	ND	ND	ND	ND	ND		
MS554	SC	9/1/15	8.92	ND	ND	ND	ND	ND		
MS572	SC	9/11/15	4.00	ND	ND	ND	ND	ND		
MS584	SC	10/1/15	20.87	ND	ND	ND	ND	ND		
MS597	SC	10/8/15	13.78	ND	ND	ND	ND	ND		
MS624	SC	10/22/15	30.85	ND	ND	ND	ND	ND		
MS636	SC	11/5/15	31.39	ND	ND	ND	ND	ND		
MS647	SC	11/19/15	15.85	ND	ND	ND	ND	ND		
MS659	SC	12/8/15	15.79	ND	ND	ND	ND	ND		
MS666	SC	12/17/15	20.89	ND	ND	ND	ND	ND		
MS672	SC	1/6/16	7.43	ND	ND	ND	ND	ND		
MS680	SC	1/14/16	9.90	ND	ND	ND	ND	ND		
MS695	SC	1/28/16	7.27	ND	ND	ND	ND	ND		
MS708	SC	2/11/16	13.38	ND	ND	ND	ND	ND		
MS723	SC	2/26/16	8.04	ND	ND	ND	ND	ND		
MS737	SC	3/17/16	3.96	ND	ND	ND	ND	ND		
MS757	SC	4/6/16	18.16	ND	ND	ND	ND	ND		
MS772	SC	4/20/16	90.13	0.03	ND	ND	ND	ND		
MS779	SC	5/4/16	91.33	ND	ND	ND	ND	ND		
			μg/L							
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Sample	Description	Analysis Date	Methane	Ethane	Ethene	Propane	Propylene	Butane		
N/A	SD	5/29/15	N/A	N/A	N/A	N/A	N/A	N/A		
N/A	SD	6/10/15	N/A	N/A	N/A	N/A	N/A	N/A		
MS483	SD	6/22/15	0.57	ND	ND	ND	ND	ND		
MS490	SD	7/6/15	0.54	ND	ND	ND	ND	ND		
MS510	SD	7/23/15	0.7	ND	ND	ND	ND	ND		
MS520	SD	7/30/15	1.11	ND	ND	ND	ND	ND		
MS534	SD	8/20/15	0.48	ND	ND	ND	ND	ND		
MS550	SD	9/1/15	1.34	ND	ND	ND	ND	ND		
MS574	SD	9/11/15	0.84	ND	ND	ND	ND	ND		
MS586	SD	10/1/15	2.37	ND	ND	ND	ND	ND		
MS599	SD	10/8/15	1.12	ND	ND	ND	ND	ND		
MS620	SD	10/22/15	1.82	ND	ND	ND	ND	ND		
MS638	SD	11/5/15	1.24	ND	ND	ND	ND	ND		
MS643	SD	11/19/15	1.05	ND	ND	ND	ND	ND		
MS656	SD	12/8/15	0.81	ND	ND	ND	ND	ND		
MS662	SD	12/17/15	0.72	ND	ND	ND	ND	ND		
MS668	SD	1/6/16	0.57	ND	ND	ND	ND	ND		
MS676	SD	1/14/16	ND	ND	ND	ND	ND	ND		
MS692	SD	1/28/16	0.47	ND	ND	ND	ND	ND		
MS704	SD	2/11/16	0.35	ND	ND	ND	ND	ND		
MS721	SD	2/26/16	0.40	ND	ND	ND	ND	ND		
MS734	SD	3/17/16	0.57	ND	ND	ND	ND	ND		
MS753	SD	4/6/16	0.33	ND	ND	ND	ND	ND		
MS769	SD	4/20/16	0.31	ND	ND	ND	ND	ND		
MS776	SD	5/4/16	0.40	ND	ND	ND	ND	ND		

APPENDIX Q: WELL WATER DATA

Sample	Name	Date	Temp. (°C)	DO (%)	DO (mg/L)	рН	Pressure (mmHg)	Conductivity (µS)	Specific Cond. (µS/cm)	TDS (mg/L)
CC1	WW	8/10/13	20.0	13.95	1.26	7.66	736.3	790.0	716.0	513.5
CC2	WW	8/10/13	14.4	76.85	7.77	6.99	734.5	852.5	675.5	554.1
CC3	WW	8/10/13	19.1	19.75	1.81	7.15	735.5	509.3	439.6	331.0
CC4	WW	8/10/13	14.65	25.2	2.56	7.03	735.6	639.0	514.5	415.4
CC5	WW	8/10/13	14.2	16.75	1.58	7.34	736.2	694.5	553.5	451.4
CC6	WW	8/10/13	15.55	32.2	3.17	6.44	736.2	574.1	471.2	373.1
CC7	WW	8/10/13	14.2	21.9	2.19	6.85	736.2	512.2	408.9	332.9
CC8	WW	8/10/13	13.8	12.7	1.31	7.05	735.8	458.4	360.8	298.0
MS252	WW	1/3/14	10.40	15.40	1.72	6.91	742.0	673.0	486.9	437.5
MS291	WW	3/20/14	6.3	65.45	8.09	7.18	728.9	675.3	433.7	438.9
MS292	WW	3/20/14	8.7	63.1	7.36	7.14	731.0	335.2	231.1	217.8
MS583	WW	9/25/15	15.45	66.35	6.60	6.87	738.0	904.0	739.0	587.6
MS682	WW	1/13/16	12.55	8.70	0.92	7.24	733.2	467.9	357.0	304.1
MS681	WW	1/13/16	10.95	61.50	6.80	6.96	732.9	534.7	390.0	347.6
MS698	WW	1/27/16	12.60	40.75	4.34	7.19	737.3	409.7	312.2	266.3
MS699	WW	1/27/16	11.15	42.35	4.45	7.15	737.8	544.7	396.0	354.1
MS725	WW	2/24/16	11.30	44.35	4.80	8.44	715.9	815.5	604.0	530.1
MS726	WW	2/24/16	13.75	18.38	1.90	7.03	713.2	413.9	325.5	269.0

Sample	Name	Date	Fluoride (mg/L)	Chloride (mg/L)	Nitrite (mg/L)	Bromide (mg/L)	Nitrate (mg/L)	Phosphate (mg/L)	Sulfate (mg/L)
CC1	WW	8/10/13	0.41	45.95	bdl	bdl	2.45	bdl	21.52
CC2	WW	8/10/13	0.06	77.83	bdl	bdl	4.10	bdl	62.24
CC3	WW	8/10/13	0.11	23.79	bdl	bdl	4.64	bdl	27.46
CC4	WW	8/10/13	0.12	20.01	bdl	bdl	5.40	bdl	50.89
CC5	WW	8/10/13	0.22	43.18	bdl	bdl	3.76	bdl	37.18
CC6	WW	8/10/13	0.06	87.37	bdl	bdl	8.55	bdl	44.11
CC7	WW	8/10/13	0.07	25.24	bdl	bdl	1.35	bdl	49.59
CC8	WW	8/10/13	0.06	4.43	bdl	bdl	4.95	bdl	56.06
MS252	WW	1/3/14	bdl	32.37	bdl	bdl	0.54	bdl	17.00
MS291	WW	3/20/14	bdl	3.13	bdl	bdl	19.27	bdl	127.85
MS292	WW	3/20/14	bdl	3.97	bdl	bdl	1.14	bdl	43.19
MS583	WW	9/25/15	bdl	135.94	bdl	bdl	2.94	bdl	44.99
MS682	WW	1/13/16	0.15	2.20	bdl	bdl	0.89	bdl	36.29
MS681	WW	1/13/16	0.07	33.40	bdl	bdl	6.83	bdl	25.45
MS698	WW	1/27/16	0.08	3.72	bdl	bdl	9.35	bdl	39.12
MS699	WW	1/27/16	0.11	3.93	bdl	bdl	8.89	bdl	69.05
MS725	WW	2/24/16	0.59	23.08	bdl	bdl	0.54	bdl	4.32
MS726	WW	2/24/16	0.20	0.93	bdl	bdl	0.34	bdl	25.78

				mg/L										
Sample	Name	Date	Li	В	Na	Mg	Al	Si	Р	K	Са	Ti	V	Cr
CC1	WW	8/10/13	0.023	0.221	153.90	3.25	bdl	5.08	0.04	0.88	11.90	bdl	bdl	0.002
CC2	WW	8/10/13	0.009	0.006	19.40	15.66	bdl	4.99	bdl	0.94	110.62	bdl	bdl	0.002
CC3	WW	8/10/13	0.017	0.066	31.12	16.20	bdl	5.60	bdl	1.91	63.96	bdl	bdl	0.002
CC4	WW	8/10/13	0.012	0.015	16.05	13.36	bdl	4.03	bdl	1.09	87.76	bdl	bdl	0.002
CC5	WW	8/10/13	0.019	0.108	63.30	13.90	bdl	6.51	bdl	1.46	48.90	bdl	bdl	0.002
CC6	WW	8/10/13	0.005	0.009	28.88	9.90	bdl	4.78	bdl	1.11	53.10	bdl	bdl	0.001
CC7	WW	8/10/13	0.015	bdl	8.80	9.38	bdl	4.58	bdl	0.93	68.07	bdl	bdl	0.000
CC8	WW	8/10/13	0.009	bdl	3.98	7.68	bdl	3.60	bdl	0.69	70.71	bdl	bdl	0.001
MS252	WW	1/3/14	0.022	0.263	115.75	5.26	0.041	5.64	0.10	0.83	16.77	0.002	bdl	0.002
MS291	WW	3/20/14	0.015	0.164	5.41	9.34	0.082	3.46	0.17	4.37	83.09	0.002	bdl	0.001
MS292	WW	3/20/14	0.009	0.065	5.25	10.32	0.006	3.64	0.11	0.64	31.33	0.001	bdl	bdl
MS583	WW	9/25/15	0.009	0.014	35.31	19.42	bdl	5.66	0.01	1.28	135.35	0.001	<0.001	0.002
MS682	WW	1/13/16	0.016	0.009	5.81	11.90	0.018	4.48	bdl	0.77	77.41	bdl	<0.001	bdl
MS681	WW	1/13/16	0.006	0.052	14.50	6.46	0.041	4.47	bdl	0.57	88.25	bdl	<0.001	bdl
MS698	WW	1/27/16	0.013	0.037	11.44	11.32	0.050	5.44	bdl	0.83	61.11	<0.001	<0.001	bdl
MS699	WW	1/27/16	0.011	0.038	13.33	16.19	0.043	4.16	bdl	2.31	85.01	bdl	<0.001	bdl
MS725	WW	2/24/16	0.039	0.274	315.20	0.96	0.027	4.60	bdl	0.50	1.28	bdl	<0.001	bdl
MS726	WW	2/24/16	0.030	0.066	25.45	15.02	0.017	8.86	bdl	1.72	54.68	bdl	<0.001	bdl

								mg/L					
Sample	Name	Date	Mn	Fe	Со	Ni	Cu	Zn	As	Se	Rb	Sr	Мо
CC1	WW	8/10/13	0.07	0.05	0.0001	0.000	0.006	0.00	bdl	bdl	0.001	0.23	0.0001
CC2	WW	8/10/13	0.00	0.42	0.0002	0.002	0.004	0.01	bdl	bdl	0.001	0.56	0.0001
CC3	WW	8/10/13	0.04	0.25	0.0001	0.001	0.036	0.00	bdl	<0.001	0.001	1.13	0.0005
CC4	WW	8/10/13	0.00	0.33	0.0001	0.001	0.005	0.00	bdl	bdl	0.001	0.42	0.0002
CC5	WW	8/10/13	0.06	0.18	0.0001	0.001	0.010	0.01	bdl	bdl	0.001	1.04	0.0006
CC6	WW	8/10/13	0.01	0.19	0.0002	0.002	0.023	0.01	bdl	bdl	<0.001	0.27	0.0001
CC7	WW	8/10/13	0.43	0.31	0.0004	0.002	0.001	0.57	bdl	0.001	0.001	0.36	0.0006
CC8	WW	8/10/13	0.01	0.27	0.0002	0.002	0.004	0.01	bdl	bdl	<0.001	0.25	0.0002
MS252	WW	1/3/14	0.28	1.27	0.0001	0.003	0.024	0.44	bdl	bdl	0.001	0.21	0.0002
MS291	WW	3/20/14	0.01	1.72	0.0007	0.006	0.024	0.03	bdl	0.001	0.003	0.33	0.0010
MS292	WW	3/20/14	0.01	0.71	0.0004	0.003	0.052	0.01	bdl	bdl	<0.001	0.25	0.0002
MS583	WW	9/25/15	0.01	0.89	0.0003	0.007	0.003	0.01	bdl	0.001	0.001	0.54	0.0003
MS682	WW	1/13/16	0.06	0.22	0.0002	0.002	0.004	0.01	0.001	0.001	0.001	0.32	0.0003
MS681	WW	1/13/16	<0.01	0.26	0.0002	0.003	0.034	0.02	<0.001	<0.001	0.001	0.31	0.0003
MS698	WW	1/27/16	<0.01	0.19	0.0002	0.002	0.011	0.01	bdl	0.001	0.001	0.25	0.0003
MS699	WW	1/27/16	0.01	0.26	0.0002	0.004	0.005	0.05	bdl	bdl	0.002	0.60	0.0007
MS725	WW	2/24/16	<0.01	bdl	<0.000 1	0.001	0.011	0.01	<0.001	bdl	0.001	0.12	0.0003
MS726	WW	2/24/16	0.71	0.42	0.0003	0.002	0.002	0.01	0.001	<0.001	0.002	0.95	0.0004

			mg/L									
Sample	Name	Date	Ag	Cd	Sn	Sb	Ва	W	Pb	U		
CC1	WW	8/10/13	bdl	<0.0001	<0.0001	<0.0001	0.0003	<0.0001	<0.0001	<0.0001		
CC2	WW	8/10/13	bdl	<0.0001	<0.0001	bdl	0.0001	<0.0001	<0.0001	bdl		
CC3	WW	8/10/13	bdl	<0.0001	0.000	<0.0001	0.0001	0.0009	<0.0001	<0.0001		
CC4	WW	8/10/13	bdl	bdl	bdl	<0.0001	0.0001	<0.0001	bdl	<0.0001		
CC5	WW	8/10/13	bdl	<0.0001	<0.0001	<0.0001	0.0001	bdl	<0.0001	<0.0001		
CC6	WW	8/10/13	bdl	<0.0001	<0.0001	<0.0001	0.0001	<0.0001	<0.0001	<0.0001		
CC7	WW	8/10/13	bdl	<0.0001	bdl	<0.0001	0.0001	<0.0001	<0.0001	<0.0001		
CC8	WW	8/10/13	bdl	0.0002	<0.0001	<0.0001	0.0002	<0.0001	0.0002	<0.0001		
MS252	WW	1/3/14	0.0002	bdl	0.001	bdl	bdl	0.0003	bdl	bdl		
MS291	WW	3/20/14	0.0035	0.0000	<0.001	0.0001	bdl	0.0005	0.0000	0.0001		
MS292	WW	3/20/14	0.0034	0.0000	<0.001	0.0002	bdl	0.0001	0.0000	0.0002		
MS583	WW	9/25/15	bdl	<0.0001	0.001	0.0004	0.0003	0.0007	<0.0001	0.0004		
MS682	WW	1/13/16	<0.0001	<0.0001	0.002	0.0001	0.0001	0.0001	<0.0001	0.0001		
MS681	WW	1/13/16	bdl	<0.0001	0.002	0.0001	0.0001	0.0005	<0.0001	0.0001		
MS698	WW	1/27/16	bdl	<0.0001	0.004	0.0001	<0.0001	0.0005	<0.0001	0.0001		
MS699	WW	1/27/16	bdl	<0.0001	0.004	0.0001	<0.0001	0.0021	<0.0001	0.0001		
MS725	WW	2/24/16	bdl	0.0002	0.003	0.0024	<0.0001	0.0003	0.0002	0.0024		
MS726	WW	2/24/16	0.0001	0.0002	0.002	0.0015	<0.0001	0.0004	0.0002	0.0015		

		_	μg/L							
Sample	Description	Analysis Date	Methane	Ethane	Ethene	Propane	Propylene	Butane		
CC1	WW	8/19/13	3007.14	0.21	ND	0.02	0.02	ND		
CC2	WW	8/19/13	ND	ND	ND	ND	ND	ND		
CC3	WW	8/19/13	0.65	ND	ND	ND	ND	ND		
CC4	WW	8/19/13	ND	ND	ND	ND	ND	ND		
CC5	WW	8/19/13	26.49	ND	ND	ND	0.02	ND		
CC6	WW	8/19/13	ND	ND	ND	ND	ND	ND		
CC7	WW	8/19/13	4.61	0.02	ND	ND	ND	ND		
CC8	WW	8/19/13	ND	ND	ND	ND	ND	ND		
MS252	WW	N/A	N/A	N/A	N/A	N/A	N/A	N/A		
MS291	WW	3/26/14	ND	ND	ND	ND	ND	ND		
MS292	WW	3/26/14	ND	ND	ND	ND	ND	ND		
MS583	WW	10/1/15	ND	ND	ND	ND	ND	ND		
MS682	WW	1/14/16	ND	ND	ND	ND	ND	ND		
MS681	WW	1/14/16	ND	ND	ND	ND	ND	ND		
MS698	WW	1/28/216	ND	ND	ND	ND	ND	ND		
MS699	WW	1/28/16	1300.98	0.51	ND	ND	ND	ND		
MS725	WW	2/26/16	1.89	0.01	ND	ND	ND	ND		
MS726	WW	2/26/16	26.62	0.01	0.09	ND	0.02	ND		

APPENDIX R: SURFACE WATER GAS CHROMATOGRAPHY DATA

API-Permit	Well #	Source 1	Vol. 1 (L)	Source 2	Vol. 2 (L)	Recycled (L)	Source 3	Vol. 3 (L)	Total Base Fluids Used
125-22830	06H	N/A	N/A	N/A	N/A	N/A	N/A	12,575,787	12,575,787
125-22861	07H	N/A	N/A	N/A	N/A	N/A	N/A	21,106,455	21,106,455
125-22793	08H	N/A	N/A	N/A	N/A	N/A	N/A	12,343,806	12,343,806
125-22668	9H-A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
125-23165	14H	N/A	N/A	N/A	N/A	N/A	N/A	11,667,738	11,667,738
125-23182	15H	N/A	N/A	N/A	N/A	N/A	N/A	12,365,589	12,365,589
125-23300	16H	N/A	N/A	N/A	N/A	N/A	N/A	12,759,432	12,759,432
125-24743	17H	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
125-24744	18H	(a)	15,333,999	<i>(b)</i>	15,077	4,161,199	(C)	8,744	19,519,020
125-24754	19H	(a)	15,040,509	(b)	15,077	4,161,199	(C)	8,744	19,225,530
125-23859	25H	N/A	N/A	N/A	N/A	N/A	N/A	14,697,642	14,697,642
125-26980	41H	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
125-26928	42H	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
125-26981	43H	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
125-26982	44H	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
125-24745	45H	(a)	18,009,754	(b)	15,077	4,161,199	(C)	8,744	N/A
125-24746	46H	(a)	13,627,431	<i>(b)</i>	15,077	4,161,199	(C)	8,744	17,812,451
125-24747	47H	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
125-24720	48H	(a)	16,329,085	N/A	N/A	6,728,468	(d)	8,744	23,066,297
125-24721	49H	(a)	16,290,928	N/A	N/A	6,728,468	(d)	8,744	23,028,140
125-24722	50H	(a)	17,544,225	N/A	N/A	6,728,468	(d)	8,744	24,281,437
125-24723	51H	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
125-24724	52H	(a)	17,405,270	N/A	N/A	6,728,468	(d)	8,744	24,142,482
125-24725	53H	(a)	15,901,894	N/A	N/A	4,457,214	(d)	8,744	20,367,853

APPENDIX S: WATER USE FOR HYDRAULIC FRACTURING IN CCCP