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# Unconventional Oil and Gas Extraction in Ohio: Regulations, Production and Water Quality

Brittany Garman

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# UNCONVENTIONAL OIL AND GAS EXTRACTION IN OHIO: REGULATIONS, PRODUCTION AND WATER QUALITY

A Thesis

Submitted to the Bayer School of Natural and Environmental Science

Duquesne University

In partial fulfillment of the requirements for

the degree of Master of Science

By

Brittany Garman

May 2019

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Brittany Garman

2019

## UNCONVENTIONAL OIL AND GAS EXTRACTION IN OHIO: REGULATIONS, PRODUCTION AND WATER QUALITY

By

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Approved April 2, 2019

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#### ABSTRACT

## <span id="page-4-0"></span>UNCONVENTIONAL OIL AND GAS EXTRACTION IN OHIO: REGULATIONS, PRODUCTION AND WATER QUALITY

By

Brittany Garman

May 2019

Thesis supervised by Dr. Stolz

The Utica shale play is the main target for unconventional oil and gas extraction in Ohio. Over 2,000 wells have been drilled since the first in 2011. This rapid expansion has led to concerns over the availability of information and potential environmental impacts. An assessment of readily available data was done through an examination of the ODNR website for oil and gas regulations, permits, spud and completion reports, water usage and waste data, and complaints, as well as brine and de-icer application. Water quality testing of an exceptional warm water tributary in the Captina Creek watershed in Belmont County, Ohio indicated no lingering effects a year after the Schnegg well blowout. Lastly, the de-icing product AquaSalina $\circledR$  was analyzed. In addition to Na, Cl, Mg, and Ca, it was found to contain high concentrations of Br, Fe, Mn, As, Se, Sr, and Ba, in addition to  $^{226}$ Ra (600 pCi).

## DEDICATION

<span id="page-5-0"></span>I would like to dedicate this thesis to my family, friends, boyfriend, and peers for their constant support, guidance, and inspiration for the past two years as I worked towards a master's degree.

#### ACKNOWLEDGEMENT

<span id="page-6-0"></span>I would like to acknowledge and thank the Heinz Endowments, Colcom Foundation, and the Bayer School of Natural and Environmental Sciences for support. For choosing me to be a part of his lab and research and for the guidance through the completion of this thesis I would like to thank Dr. Stolz. I would also like to thank Dr. Porter and Dr. Bain for being members of my committee and for their guidance and suggestions throughout the writing process. An additional thank you to Dr. Bain is in order for conducting laboratory analysis on my samples. Thank you to Dr. Tetiana Cantlay for laboratory analysis, guidance on understanding my data, and suggestions for writing. You were extremely helpful throughout this process and I couldn't be more appreciative. Finally, I would like to acknowledge Dannielle Pratt for helping with collecting samples and providing suggestions while I wrote this thesis.



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#### **CHAPTER 1: BACKGROUND**

#### <span id="page-18-1"></span><span id="page-18-0"></span>1.1 Unconventional Shale Gas Formation

A productive extraction location of natural gas and oil in northeastern United States is through shale gas formations (Figure 1). These are considered "unconventional" reservoirs with low permeability due to the limited porosity of shale. This low permeability inhibits the natural flow that happens in a conventional well thus requiring horizontal drilling and mechanical stimulation with massive quantities of water and proppant otherwise known as high volume hydraulic fracturing (HVHF) or "fracking."



<span id="page-18-2"></span>**Figure 1.** Natural gas production by source in the U.S. (U.S. EIA, 2013)

Unconventional gas differs from conventional gas due the permeability and porosity of the host rock. Unconventional gas is trapped in low permeable rocks while conventional is

trapped in high permeable rocks (Figure 2). Examples of unconventional gases are tight gas sandstone, coalbed methane (CBM), methane hydrates, and biogenic gases (NETL, 2013). Since conventional gas is easier to access, vertical drilling is a common technique used. Unconventional gas requires horizontal drilling and HVHF.



Source: Adapted from United States Geological Survey factsheet 0113-01 (public domain)

<span id="page-19-0"></span>**Figure 2.** Natural gas reserves differing in location and geology (U.S. EIA, 2018)

Shale is a sedimentary rock that forms stratified layers of clay-sized particles. The small particles are carried by free-flowing water, such as a stream, and will settle on top of one another usually in deep ocean basins (NETL, 2013). Once compacted and buried, layers are held tightly together creating low permeability of fluids. All shale varies in natural fractures, liquid hydrocarbon reserves, and amount of organic matter (NETL, 2013). Figure 3 displays the lower

48 state shale plays in the United States.



<span id="page-20-0"></span>

Organic material that is trapped during the burial process will be transformed into thermogenic or biogenic methane or other volatile hydrocarbons. Thermogenic gases are formed abiotically due to elevated temperatures and pressures; organic material will become kerogen, then oil at 60-120 degrees Celsius, and finally natural gas once reached maximum temperature of 100-200 degrees Celsius (U.S. EIA, 2017). Thermogenic gases are known to contain valuable products such as methane, ethane, propane, butane, and pentane (Jackson et al., 2013). Biogenic gases are formed through methanogenesis to biotically transform organic material into trapped methane gas (Jackson et al., 2013).

#### <span id="page-21-0"></span>1.1.1 Unconventional Gas Demand

Natural gas supplies 22% of worldwide energy needs while one quarter is responsible for electricity generation (International Energy Agency, 2018). With over 750,000 oil and gas wells in 2016 producing approximately 27,485,517 million cubic feet of consumed natural gas in the U.S. alone, the demand for this resource is substantial (Figure 4) (U.S. EIA, 2018). Estimated by the EIA, 2016 U.S. production of 1,744 trillion cubic feet (TcF) natural gas can sustain the country for 90 years (U.S. EIA, 2018). With the known natural gas abundance and advanced extraction technology, the industrialized U.S. continues to exploit the resource for transportation, leisure, heating and cooking, and to fuel other necessities.



<span id="page-21-2"></span>**Figure 4.** U.S. natural gas consumption, dry production, and net imports in trillion cubic feet (U.S. EIA, 2017)

#### <span id="page-21-1"></span>1.1.2 Horizontal Drilling and Hydraulic Fracturing

Investments in unconventional shale gas exploration in the 1980s followed the shortages of conventional gas reserves in the 1970s in the U.S. (NETL, 2013). Horizontal drilling was one of the advanced technologies that was incorporated into vertical drilling. This directional drilling technique allowed the oil and gas industry to reduce their surface footprint by drilling multiple horizontal wells from a single surface location to reach target reservoirs (Cheremisinoff & Davletshin, 2015). Figure 5 depicts a fracking well pad in Ohio which consists of the rig, condensate tanks, storage tanks, impoundment reservoir, and other necessary holding containers for the process.



<span id="page-22-0"></span>**Figure 5.** Well pad set up in Ohio (Ohio EPA, 2017)

HVHF originated in the late 1940s, however the process used today was first developed in 1999 in the Barnett shale of Texas following the horizontal drilling investments in the 1980s (Cheremisinoff & Davletshin, 2015). Although expensive, HVHF production numbers have shown how efficient this technology is. One well in Ohio produced more than 1.5 billion cubic

feet of gas within just under 200 days of operation estimated at around \$3.3 million in value (Jackson et al., 2013).

Horizontal drilling involves drilling a vertical borehole thousands of feet into the earth passing through an aquifer and to shale rock formations (Cheremisinoff & Davletshin, 2015). Once the borehole has reached its designated vertical depth, termed the "kick-off" point at 900 to 3,000 meters, horizontal drilling begins (NETL, 2013). Steel and cement casings are installed around the borehole to prevent infiltration of fluids pumped in and out of the well (Molofsky et al., 2013). Vertical drilling requires a pad per conventional well however horizontal drilling only requires a pad per 6-8 unconventional wells (NETL, 2013).

Several million pounds of HVHF fluid, chemicals, and sands are pumped at substantial pressures to promote fracturing (Cheremisinoff & Davletshin, 2015). Fifteen-27 million liters of water and non-aqueous additives, utilized to increase oil and gas flow and retrieval, are utilized per well for fracturing and retrieval of resources (Burcat & Saunders, 2016). This mixture of fluid and solids vary depending on company preference and the geologic structure of the target site (U.S. Department of Energy, 2017). All fluids contain a mixture of water, sand, biocides, corrosion inhibitors, pH adjusters, surfactants, friction reducers, acids, gelling agents, and company and location specific additives (NETL, 2013).

In certain cases, explosives may be needed to further promote fracturing (Cheremisinoff & Davletshin, 2015). Perforation is necessary to create direct contact between the borehole and hydrocarbon reservoir. Jet-perforating guns are usually utilized to send explosive charges to create a hole between the cement casing and formation, thus producing the oil or gas (Cheremisinoff & Davletshin, 2015). Approximately 1 million pounds of pumped proppants, such as sand or silicon carbide, hold fractures open in the shale (Rozell & Reaven, 2012).

Natural gas and oil will be released from the fractures and pumped back to the surface with the "flowback" liquid that will be held in on-site storage tanks (NETL, 2013). Other necessary equipment for fracking includes storage tanks, pumping equipment, blending equipment, proppant transport equipment, monitoring and control equipment, valves, and hoses (Cheremisinoff & Davletshin, 2015). Figure 6 displays a diagram of the fracking process.



<span id="page-24-0"></span>**Figure 6.** Diagram of HVHF process (Healy, 2012).

#### <span id="page-25-0"></span>1.1.3 Transportation of Oil and Gas

The most effective and cost efficient method for transportation of natural resources in the oil and gas industry is through networks of pipelines that span across the United States. Pipeline routes take up almost half a million miles and vary in size from two to 60 inches in diameter (Kennedy, 1993). The need for efficient flow and expedient delivery of both resources was necessary once oil and gas demands increased. Both oil and gas can be transported simultaneously through pressurized pipes that allow gas then oil to reach the company's desired location (Baker, 1953).

#### <span id="page-25-1"></span>1.2 Federal Regulation of Hydraulic Fracturing

Multiple federal regulations apply to HVHF to control emissions, hazardous substances, water ways, and public health. The following nine acts all concern HVHF: Clean Air Act (CAA), Comprehensive Environmental Response, Compensation, and Liability Recovery Act (CERCLA), Clean Water Act (CWA), Emergency Planning and Community Right-to-Know Act (EPCRA), Endangered Species Act (ESA), National Environmental Policy Act (NEPA), Oil Pollution Act (OPA), Resource Conservation and Recovery Act (RCRA), and the Safe Drinking Water Act (SDWA) (Table 1).

<b>Federal Regulatory Act</b>	<b>Date of Enactment</b>
Clean Air Act (CAA)	1963
National Environmental Policy Act (NEPA)	1969
Clean Water Act (CWA)	1972
Endangered Species Act (ESA)	1973
Safe Drinking Water Act (SDWA)	1974
Resource Conservation and Recovery Act	1976
(RCRA)	
Comprehensive Environmental Response,	1980
Compensation, and Liability Recovery Act	
(CERCLA)	
<b>Emergency Planning and Community Right-</b>	1986
to-Know Act (EPCRA)	
Oil Pollution Act (OPA)	1989

<span id="page-26-0"></span>**Table 1.** Enactment dates of federal regulations concerning oil and gas

Under the CAA, all emissions that are released on both unconventional and conventional well sites must follow a set of requirements (U. S. Department of Energy, 2014). Compliance with pre-existing, current, and future air regulations are also controlled under this act. State and local agencies are put in charge of enforcing the compliance with the air regulations set by the federal EPA (U. S. Department of Energy, 2014). Enforcements under CERCLA pertain to HVHF if hazardous substances beside crude oil or natural gas are released into the environment in quantities that exceed designated limits (U. S. Department of Energy, 2014). Under the National Pollutant Discharge Elimination System (NPDES) required by the CWA, pollutant limits are set for produced waters in the oil and gas industry (U. S. Department of Energy, 2014). Permits are also required through the CWA for storm water with sedimentation that can cause a water quality violation (U. S. Department of Energy, 2014). Oil and gas facilities that store hazardous chemicals above threshold limits must report under the EPCRA and provide a material safety data sheet (MSDS) to local fire departments and officials (U. S. Department of Energy, 2014). Section 7 of the ESA applies to oil and gas activities if a proposed well pad could potentially "take" or affect a listed animal's habitat (U. S. Department of Energy, 2014).

Analyses of potential environmental impacts of oil and gas exploration and production are required by NEPA (U. S. Department of Energy, 2014). The OPA involves the oil and gas industry by regulating events and impacts that could happen after a spill such as preventative measures, reporting obligations, and response actions/planning (U. S. Department of Energy, 2014). The Solid Waste Disposal program proposed in Subtitle D of RCRA involves the actions to take to dispose of produced wastes from oil and gas activities such as drilling fluids and produced waters (U. S. Department of Energy, 2014). The final federal act that concerns HVHR is the SDWA. The Underground Injection Control (UIC) program presented under the SDWA was created to prevent injected waste from infiltrating into drinking water sources (U. S. Department of Energy, 2014). Fluids that contain diesel fuel are required to acquire a UIC permit while the entire program provides guidelines for "siting, construction, operation, closure, and financial responsibility" of deep injection wells (U. S. Department of Energy, 2014). In the U.S., 40 states are in charge of their own UIC program and can vary state-to-state (U. S. Department of Energy, 2014).

#### <span id="page-27-0"></span>1.2.1 Gaps in Federal Regulations

Gaps in federal regulations concerning water and HVHF pose potential increases in water contamination. More specifically, the five following acts do not govern all aspects of HVHF: SDWA, CWA, RCRA, CERCLA, and the EPCRA. Under the SDWA, all fluids besides diesel fuel that are involved in the hydraulic fracturing process do not require an UIC permit (U. S. Department of Energy, 2014). Additionally, under an exemption in the 2005 Energy Policy Act, HVHF processes are not regulated under the SDWA (Arthur et al., 2011). Federal storm water permits are also not required under the CWA for uncontaminated storm water at oil and gas

construction and operation sites (U. S. Department of Energy, 2014). Under RCRA, exploration and production wastes for the oil and gas industry are not considered and regulated as hazardous waste (U. S. Department of Energy, 2014). Authorized injections of HVHF fluids by state law for "production, enhanced recovery, or produced water" do not apply to liability and reporting provisions under CERCLA (U. S. Department of Energy, 2014). The final gap concerning water in federal regulations is under the EPCRA. Any released oil and gas chemicals are not required to be reported to the Toxics Release Inventory (TRI) by the operators (U. S. Department of Energy, 2014).

Gaps in federal regulations concerning emissions are also present for the oil and gas industry that can cause deleterious effects on public and environmental health. Under the CAA, emissions are not accounted collectively for the wells, equipment, compressors, and pump stations to determine if they are a major source (U. S. Department of Energy, 2014). Also under the same federal regulation, multiple common hydrocarbons released during HVHF are not included in the Risk Management Program process to determine if a facility should be regulated.

#### <span id="page-28-0"></span>1.3 History of Ohio's Oil and Gas

The first well drilled for petroleum in Ohio occurred in 1859 in Mecca township of Trumbull County (ODNR, 2014). Following the successful well, multiple wells were dug around Mecca township which led to an increase in prospectors (ODNR, 2014). A 20-year oil and gas boom in Ohio shortly followed and was responsible for the creation and survival of various Ohio counties such as Washington County and Licking County (ODNR, 2014). Today, cumulative Ohio is responsible for more than 1 billion barrels of oil and 9 TcF of natural gas (ODNR, 2014). The first well drilled in the Utica Shale play in Ohio was in 2011 with 2,391

wells following (Figure 7) (ODNR, 2014). Figure 8 depicts the wells drilled in the Marcellus shale.



OHIO DEPARTMENT OF NATURAL RESOURCES HORIZONTAL UTICA - PT PLEASANT WELL ACTIVITY IN OHIO

<span id="page-30-0"></span>**Figure 7.** Location, number, and status of horizontal wells in the Utica-Point Pleasant shale play in Ohio as of January 5, 2019 (ODNR, 2019).



OHIO DEPARTMENT OF NATURAL RESOURCES HORIZONTAL MARCELLUS WELL ACTIVITY IN OHIO

<span id="page-31-0"></span>**Figure 8.** Location, number, and status of horizontal wells in the Marcellus shale play in Ohio as of January 5, 2019 (ODNR, 2019).

#### <span id="page-32-0"></span>1.3.1 Transportation of Ohio's Natural Gas and Oil

Ohio is one of numerous states in northeastern U.S. that contains more than one interstate natural gas pipeline. The 2009 extension of the Rockies Express Pipeline (REX), also known as the largest cross-country pipeline in the U.S., stops in Clarington, Ohio (U.S. EIA, 2018). A second extension was built in August of 2015 allowing bidirectional delivery of natural gas to the Midwest from the east instead of the original sole delivery from the Rocky Mountains to the east (Waite, 2015). Ohio's natural gas is delivered to other states in the U.S. such as Kentucky, Indiana, and Michigan and have 24 natural gas storage fields that can hold up to 576 bcf (U.S. EIA, 2018).

Although Ohio's petroleum production is significantly lower than natural gas, this state consistently remains at the top of oil refining in the nation. The four refineries have a processing capacity of 583,000 barrels per day combined (U.S. EIA, 2018). Predominantly, this crude oil is retrieved through pipelines from Canada, North Dakota, the Appalachian Basin, and the Midcontinent region (U.S. EIA, 2018). All other oil in Ohio is retrieved from port facilities on Lake Erie (U.S. EIA, 2018).

#### <span id="page-32-1"></span>1.3.2 Utica Shale

During the Late Ordovician time around 445 million years ago, present-day Pennsylvania, Ohio, West Virginia, Maryland, and parts of New York were a semi-enclosed epicontinental sea (U.S. EIA, 2017). Eroded surfaces and fine layer sequences similar to moving currents indicated this area was a reoccurring storm point leading to the deposition of interbedding of limestone and shale (Figure 9) (King, 2010). The Utica Shale play's underlying joints and the formation of the Appalachian Basin eventually led to burial and formation (U.S.

EIA, 2017). Today, this play covers around 115,000 square miles, extending across Pennsylvania, New York, Ohio, and West Virginia (King, 2010).



**Figure 9.** Alternating layers of Utica shale and limestone in the Utica shale (National Energy Board, 2009)

<span id="page-33-0"></span>The Utica play is a sedimentary rock consisting of gray to black and brown calcareous shale that has a lower total organic carbon (TOC) than its underlying Point Pleasant Shale play (West Virginia Geological & Economic Survey, 2012). Amorphinite, a category of kerogen that has no distinct shape, is the major organic material found in this play suggesting high algal contents (U.S. EIA, 2017). The shale is indicative of large amounts of organic material, limited circulation that led to anoxia, and low energy conditions due to the shape of the basin (West Virginia Geological & Economic Survey, 2012). Figure 10 indicates depth of shale, fault lines, and the extent of the Utica shale play. Production wells are also included on this graph and are

most densely located where Ohio, Pennsylvania, and West Virginia meet. However, this figure demonstrates that predominantly most of the production wells of the Utica shale play are located along the eastern border of Ohio.



<span id="page-34-1"></span>**Figure 10.** Structure map of Utica Shale and production wells (U.S. EIA, 2017)

<span id="page-34-0"></span>1.4 Regulations of Hydraulic Fracturing in Ohio

Ohio Department of Natural Resources Division of Oil and Gas Resources Management (ODNR-DOGRM) and Ohio Environmental Protection Agency (Ohio EPA/OEPA) are in charge of the regulation of spacing, construction, location, design, and operation of wells under Chapter 1501 of the Ohio Administrative Code (OAC) and Chapter 1509 of the Ohio Revised Code (ORC) (Ohio EPA, 2017). Before a horizontal well is drilled, altered, or plugged, interested companies must acquire a permit-to-install and operate (PTIO) (Ohio EPA, 2017). Requirements such as fees, best management practices, and water sampling will vary between urban vs nonurban areas (Ohio EPA, 2017).

#### <span id="page-35-0"></span>1.4.1 Best Management Practices (BMPs)

In Ohio, all oil and gas operators must implement BMPs in urban areas and are recommended to utilize them in non-urban areas (Ohio EPA, 2017). Examples of BMPs utilized in this industry are wheel wash stations to prevent mud escaping the drill site, frequent inspections on site and taking necessary stabilizing actions such as mulching, and isolating drainage to prevent storm water run-off and sedimentation in on-site basins (Ohio EPA, 2017). Before construction of the horizontal well takes place, operators must submit a report for storm water hydraulics and a plan for erosion control (Ohio EPA, 2017). Injections for disposal or enhanced oil recovery are additional BMPs utilized in Ohio concerning produced waters.

#### <span id="page-35-1"></span>1.4.2 Well Pad Construction

During construction and operation, ODNR-DOGRM requires various reports concerning cementing, stimulation, and production (Ohio EPA, 2017). Companies must report the type and volume of injected and produced fluids while retaining a spill/clean-up plan in case of spills (Ohio EPA, 2017). All safety measures implied through ODNR-DOGRM must be complied throughout operation such as pipeline burial and construction specifications (Ohio EPA, 2017). ODNR-DOGRM requires reports of total gas and crude oil production but does not require separating dry gas from more valuable wet gas, containing butane, and ethane, which can lead to production number discrepancies (Shingler, 2012).
Site restoration is required after a well has been plugged in Ohio. All equipment involved in drilling must be removed. Activities to prevent sedimentation and erosion like seeding and terracing must then be conducted to all areas (urban and non-urban) (Ohio EPA, 2017). A surety bond is installed before construction to assist in financing and claims for damaged areas if a well owner fails to execute proper post-drilling site restoration (Ohio EPA, 2017).

ORC Chapter 1509.021 defines surface location requirements in urbanized and nonurbanized areas. The location of a new well is prohibited to be within 150 feet  $(\text{ft})/46$  meters (m) from an occupied parcel of land in an urbanized area unless there is consent from the owner for a distance under 150 ft/46 m (H.B. 153, No. 28, 129<sup>th</sup> General Assembly). However, the chief of the division of oil and gas will not approve a distance less than 100 ft/30 m between the parcel of land and the new well in urbanized areas (H.B. 153, No. 28, 129<sup>th</sup> General Assembly). For nonurbanized areas, a well shall not be within 100 ft/30 m of any occupied private parcel of land or building that is utilized as a "place of assembly, education, entertainment, lodging, trade, manufacture, repair, storage, or occupancy by the public" (H.B. 153, No. 28, 129<sup>th</sup> General Assembly). The private parcels and buildings do not apply to agricultural therefore there is no well distance requirement.

ORC 1509.021 also defines surface location requirements concerning waterways, roadways, and other wells. Surface wells are not allowed to be within 100 ft/30 m of one another unless permission is given by the chief of the division of oil and gas (H.B. 153, No. 28, 129<sup>th</sup> General Assembly). In addition to this distant limitation, new surface wells are prohibited to be within 50 ft/15 m a stream, pond, lake, and all bodies of water (H.B. 153, No. 28, 129<sup>th</sup> General Assembly). This limitation also applies to the necessary distance between a well and railroad

tracks, public streets, roads, and highways (H.B. 153, No. 28, 129<sup>th</sup> General Assembly). Less than 50 ft/15 m can be established for waterways and roadways with the approval of the chief if a reduced distance will lower impacts to the surrounding public and land (H.B. 153, No. 28, 129th General Assembly).

## 1.4.3 Emissions Permits

All units that emit air pollution must inquire a permit-to-install and operate (PTIO) from Ohio EPA's Division of Air Pollution Control (DAPC) before constructing emitting sources (Ohio EPA, 2017). Potential sources could be unpaved roadways, generators, leaks, engines, dehydration systems, and storage tanks (Ohio EPA, 2017). To be exempted from acquiring a PTIO under the OAC, industries must fall under three categories. "De minimis" exemption applies if the site emits less than ten pounds per day and less than 1 ton per year (Ohio EPA, 2017). Companies that fall under this exemption must still keep records but are not required to report to ODNR (Ohio EPA, 2017). Emissions sources that fall under an official list, such as small storage tanks and small boilers, are exempt under permanent exemptions (Ohio EPA, 2017). Permit-by-rule (PBR) involves small emissions sources and require a one-page notification to Ohio EPA without any permits (Ohio EPA, 2017).

General permits (GPs) have been modeled to improve Ohio EPA's efficiency in the air permit application process (Ohio EPA, 2017). GPs include commonly used equipment found at oil and gas well sites like storage tanks, flares, engines, and generators (Ohio EPA, 2017). They also include any emissions limits, restrictions, monitoring, and reporting standards that must be met before a GP is applied for (Ohio EPA, 2017). A GP can be discussed with Ohio EPA or local air agencies depending on the jurisdiction of target drill site (Ohio EPA, 2017).

1.4.4 Water Use

One well in Ohio requires between five to six million gallons of water that is retrieved from local streams, lakes, and other public water sources during hydraulic fracturing (Ohio EPA, 2017). Under Section 1521.16 of the ORC, companies that have the ability to withdraw more than 100,000 gallons a day/70 gallons per minute must register under ODNR's Division of Water Resources (ODNR-DWR) (Ohio EPA, 2017). Even if companies do not utilize this amount of water, they must still register.

If companies wish to connect their facilities to a public water supply, proper containment devices must be in accordance with Ohio EPA's requirements at the connection point to prevent backflow (Ohio EPA, 2017). The minimum requirement involves reduced-pressure backflow assembly at the connection point and approved air gap separations at the drill site (Figure 11) (Ohio EPA, 2017). If air gap separations are not utilized on the drill pad, one will be required at the connection point (Ohio EPA, 2017).



**Figure 11.** Air gap separator (A) and backflow assembly (D) (Ohio EPA, 2015)

In 2008, ORC's Section 1522.01 The Great Lakes-St Lawrence River Basin Water Resources Compact prohibits all increased or new diversions from the Lake Erie Basin (Ohio EPA, 2017). These diversions are defined as all "inter-basin transfers," despite the amount transferred and if unused amount will be returned (Ohio EPA, 2017). No permits are allowed to be issued through ODNR-DOGRM for the extraction of water in the 33 counties situated north of the Lake Erie-Ohio River drainage basin (Ohio EPA, 2017).

If projected drill sites will interfere with wetlands, streams, or other water systems, permits must be approved by the United States Army Corps of Engineers (USACE) under Section 401 of the Clean Water Act and Ohio EPA under Section 401 Water Quality Certification (WQC) (Ohio EPA, 2017). Depending on the scale of the impacts from the project, authorization may be necessary through Nationwide Permits (NWPs) issued by the USACE

(Ohio EPA, 2017). In March 2017, USACE's NWP 39 for "Commercial and Institutional Development" allows impacts on 0.5 acres of Category 1 and 2 wetlands and up to 300 linear feet of streams (Ohio EPA, 2017). A 401 WQC is required to impact a Category 3 wetland or more than 300 linear feet of streams (Ohio EPA, 2017). Isolated wetlands are regulated on a state level and require a wetland permit from Ohio EPA if impact is predicted (Ohio EPA, 2017).

Since 1983, the ODNR-DOGRM is in charge of conducting investigations concerning ground water contamination as a result of oil and gas activity (Ohio EPA, 2014). Pre-drilling water quality testing is recommended to be collected before any filtration or softener systems and analyzed by Ohio EPA drinking water certified laboratories. Results analyzed by Ohio EPA approved labs will have a less likely chance of being disregarded in legal situations (Ohio EPA, 2014). ODNR officials must investigate water supply complaints with 24 hours and then take appropriate actions following (Ohio EPA, 2014). Under Section 1509.22 of the ORC, ODNR has the authority to require an owner or operator of a well to replace water systems, both ground and surface water, of any parties that are disrupted by oil and gas activity (Ohio EPA, 2014).

## 1.4.5 Drill Cuttings

As of September 29, 2015, ODNR-DOGRM has sole authority to regulate waste substances produced in the oil and gas industry (Ohio EPA, 2017). Drill cuttings and drilling muds are not considered hazardous waste federally, however once in contact with contamination such as chemical additives Ohio considers it solid waste (Ohio EPA, 2017). ODNR sets the requirements operators must follow to store drill cuttings on site (Ohio EPA, 2017). Once ready for disposal, all solid waste must be sent to licensed solid waste landfills and handled accordingly (Ohio EPA, 2017). In general, two kinds of radioactive waste substances from oil

and gas are naturally occurring radioactive material (NORM) and technologically enhanced naturally occurring radioactive material (TENORM) (Ohio EPA, 2017). When NORM is altered it becomes TENORM and more radioactive (Ohio EPA, 2017). As of September 29, 2013, all parties involved in the disposal of these two substances must run the appropriate analytical tests following the Ohio Department of Health Bureau of Radiation Protection guidelines before acceptance at disposal facilities (Ohio EPA, 2017).

Drill cuttings may be reused off site with approval of Ohio EPA's Division of Material and Waste Management (DMWM) (Ohio EPA, 2017). TENORM drill cuttings are not approved for reuse (Ohio EPA, 2017). Remediate drill cuttings can be utilized for construction material, road aggregates, and mine reclamation.

# 1.4.6 Oil and Gas Fluids

ODNR-DOGRM regulates produced fluids from oil and gas operations. Brine produced from all drilling sites are prohibited from being directly discharged into waters of the state (Ohio EPA, 2017). Ohio prohibits disposal at publicly owned treatment works (POTWs) like municipal wastewater treatment plants (Ohio EPA, 2017). The designated way of disposal is through Class II injection wells where it will be reused in other drilling operations and other manners approved by ODNR (Ohio EPA, 2017). All brine not reused in drilling can be utilized to control ice or road surface dust (Ohio EPA, 2017).

Transporters of brine are overseen by ODNR as well (Ohio EPA, 2017). All companies involved in the transportation of drilling fluid must register through the ODNR-DOGRM (Ohio EPA, 2017). Each transporter is given an identification number, must have a surety bond and insurance, and maintain a daily log that will be reported to ODNR (Ohio EPA, 2017).

ODNR's Division of Oil and Gas Resources are in charge of protecting the groundwater reservoirs by regulating and monitoring the disposal of brine and other HVHF waste from drilling, stimulation, and production (ODNR, 2019). The Underground Injection (UIC) Program was approved by the EPA in 1983, thus granting ODNR full control (ODNR, 2019). UIC personnel are in charge of engineering, construction specifications, geological data, and issuing permits for all Class II wells that are utilized to inject fluids from HVHF into the ground for disposal or for secondary oil recovery (ODNR, 2019). Brine haulers, also a part of the UIC personnel, are in charge of spreading brine for dust and ice control in the state (ODNR, 2019).

Ohio has 226 active Class II Salt Water Disposal (SWD) wells as of January 9, 2019 (Figure 12) (Auch, 2019). The high volume of injection wells receives the HVHF liquid waste from wells in Ohio, Pennsylvania, and West Virginia (Auch, 2019). All Class II SWD wells are situated in close proximity to the unconventional wells along the eastern side of Ohio. Under OAC 1501:9-3, all owners of SWD wells must report annually quantities of saltwater hauled and locations of disposals by April 15<sup>th</sup>.



**Figure 12.** Location and production values of Class II SWD and unconventional wells until Quarter 3, 2018 in Ohio (Auch, 2019)

## 1.4.7 Prevention of Waste

In general, this state disposes up to 90% of HVHF fluids while 10% is recycled and utilized for oil recovery (Veil, 2015). In 2012, ODNR's Division of Oil and Gas indicated that out of 755,783 barrels/31,742,886 gallons, around 20% was utilized for road dust control and deicing while the remaining 80% was recycled for secondary gas exploration (ODNR, 2012). An additional activity that is conducted by Ohio's oil and gas industry is gas flaring. Under OAC 1509.20, burning gas in a succession of flares can occur to protect human and environmental health when there is "no economic market…for the escaping gas" (S.B. 165, No. 27, 128th General Assembly).

1.4.8 Spill Control

Under 40 Code of Federal Regulations (CFR) Part 112, companies that reach 1,320 gallons or more of aboveground stored oil are subject to Spill Prevention Control and Countermeasure (SPCC) Plan requirements (Ohio EPA, 2017). The two requirements are as follows: a written SPCC plan must be submitted and maintain proper secondary storage and proper transportation of stored oil (Ohio EPA, 2017). Under SPCC, containers that hold less than 55 gallons do not need to be calculated in total storage capacity (Ohio EPA, 2017).

ORC 3750.06 requires spills of petroleum products to be reported to local, state, and federal authorities if the petroleum creates a film on waterways and/or 25 gallons or more are released into the environment (Ohio EPA, 2017). However, if 25 or more gallons are spilled and contained on the owner's property, this does not need to be reported (Ohio EPA, 2017). ORC Chapter 1501:9-8 formed on August 9, 2015 requires notification within 30 minutes of a spill to ODNR, Local Emergency Planning Committee (LEPC), and the local fire department (Ohio EPA, 2017). Also, a written report must be submitted to ODNR within 30 days of the spill (Ohio EPA, 2017).

To inform the public of specific hazardous conditions industry operations have the EPCRA was created in 1986. All facilities that are subject to the Occupational Safety and Health Administration (OSHA) Hazard Communication Standard, that utilizes, creates, or accumulates hazardous chemicals or extremely hazardous substances (EHS), and that have to store all hazardous products in more than the threshold quantity (TQ) must abide by the EPCRA requirements (Ohio EPA, 2017). All EPCRA reports are submitted to the State Emergency Response Commission (SERC), the LEPC, and local fire departments and are compiled by ODNR-DOGRM under ORC Chapter 1501:9-8 (Ohio EPA, 2017).

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## 1.4.9 Brine

Under Section 1509.228 of ORC, requirements were established for the commercial sale of brine for deicing and snow removal. Brine will be available as a commodity if it is not from a well that was utilized to process or recycle "to remove free oil, dissolved volatile organic compounds, and other contaminants" defined under sections 1509.22 and 1509.227 (Sub. H. B., No. 393, 132<sup>nd</sup> Cong.). All "commodity" brine must not harm the safety of the public and the environment and additional documentation and approvals must be provided under Section 1509.228 before use. These include documentation and approval from the department of transportation for deicing, the northwest snowfighters qualified product list, and any necessary private certification entity (Sub. H. B., No. 393, 132<sup>nd</sup> Cong.). The chief in charge is allowed to take up to four samples annually of the commodity brine that is for sale (Sub. H. B., No. 393,  $132<sup>nd</sup>$  Cong.).

#### 1.5 AquaSalina

Although road salting is important for maintaining roadways and ensuring safety to drivers, it has been linked with soil and water degradation (Jungwirth, 2014). Approximately 20 million tons of salt is applied to roads across the U.S. which contains chlorides that are harmful to aquatic organisms and vegetation (Jungwirth, 2014). Due to this widespread use, chloride concentrations recorded above EPA's limits have been in ground and surface waters during winter maintenance throughout the U.S. (Fay et al., 2014).

A specific deicer manufactured in Cleveland and Mogadore, Ohio is AquaSalina®, a liquid deicer that is a combination of chlorides and mineral products. This deicer is composed of 10-11% calcium chloride (CaCl2), 7-8% sodium chloride (NaCl), 2-3% magnesium chloride

(MgCl<sub>2</sub>), and 1% potassium chloride (KCl) and can withstand temperatures as cold as  $-15^{\circ}F$ (Nature's Own Source, LLC., n.d.). In addition, this product contains a corrosion inhibitor that can reduce surrounding structural degradation (Nature's Own Source, LLC., n.d.). Pre-treating with AquaSalina® requires 8-10 gallons per lane mile and up to 20-40 gallons per lane mile for deicing (ODOT, 2019). This product includes on its label to use as directed and to not dilute (Figure 13).



**Figure 13.** AquaSalina<sup>®</sup> product label

## 1.6 Water Contamination Pathway

Water is the largest component in the HVHF process. In Eastern Ohio, nine counties have reported an average use of around 19 million gallons of freshwater withdrawn per site between 2010-2016 (Auch, 2018). Throughout the transition from conventional to unconventional exploration, a 770% increase in water usage per well occurred (Kondash et al., 2018). In 2018, Ohio's fracking industry has taken 90 million gallons of freshwater from local watersheds for production (Auch, 2018). The main issue that arises despite the substantial amount of water being withdrawn is only 73% of the water is accounted for by operators (Auch, 2018).

Physical petroleum leaking into water ways, infiltration of stray gases and fracturing chemicals into ground water, and storm water runoff from flow-back holding reservoirs are some of the main concerns with water contamination and HVHF operations. The leaks can be a result of improper reservoir pressures, casing failures such as corrosion or ruptures, and/or inadequate construction and maintenance of wells (Jackson et al., 2013). Once HVHF fluid is released directly into the environment it affects the land, waterways, public health, and organisms. If HVHF fluid is released through casing complications underground, it has the potential to contaminate ground water reservoirs. Both producing and abandoned wells have the potential to leak or cause a spill into the environment.

### 1.7 Barnesville, Ohio

Barnesville, Ohio in Belmont County is home to over 4,000 residents that rely on three reservoirs for drinking water (U.S. EPA, 2016). Slope Creek Reservoir (Barnesville Reservoir #3) is the secondary source of drinking water for the village while Barnesville Reservoir #1 is the first (U.S. EPA, 2016). Slope Creek Reservoir was created in 1964 to control flooding by damming Slope Creek north of Miller Run (U.S. EPA, 2016). Forty percent is used directly by treatment plants while the remaining 60% feeds into Reservoir #1 (U.S. EPA, 2016).

### 1.7.1 Leasing Water Rights in Barnesville

HVHF has become increasingly popular in Ohio since the Utica shale play was opened. This along with an abundance of water in Barnesville lead to several leases with large oil and gas corporations. These leases gave the permission for water extraction that will be used on well pads in the surrounding area. Due to this, many existing and operating wells surround Barnesville currently.

Barnesville signed a lease with Gulfport Energy Corporation in August of 2012 granting the unrestricted right to draw water from Slope Creek Reservoir for their HVHF wells of the Utica Shale nearby (Greenfield Advisors, 2015). This lease allotted Gulfport Energy Corporation to extract as much water as they wanted until it became an immediate threat to the health and safety of the area's residents and businesses. In 2014, this oil and gas company utilized 180 million gallons of water for the cost of 1 cent per gallon (Greenfield Advisors, 2015).

In August of 2012, Barnesville continued to sign a lease with another oil and gas corporation, Antero Resources (Marcellus Drilling News, 2012). This lease released 1,047 of village-owned acres to Antero Resources for drilling purposes in return for just under \$6 million for the city of Barnesville at a cost of \$5,700 per acre (Marcellus Drilling News, 2012). Antero Resources was also given the permission to utilize the water supply in Slope Creek Reservoir under an agreement in May 2013 (Greenfield Advisors, 2015). At \$3.75 per thousand gallons, this oil and gas company was allowed to draw up 2 million gallons per day from the Barnesville Reservoir (Greenfield Advisors, 2015).

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### 1.8 Captina Creek Watershed

Captina Creek Watershed extends into two counties in Ohio: Belmont and Monroe (Belmont Soil and Water Conservation District, 2014). However, it is predominantly located in Belmont County. Overall, 167.8 square miles, or 93.2%, of the watershed is situated within that county while the remaining 12.2 square miles, or 6.8%, are in Monroe (Figure 14) (Belmont Soil and Water Conservation District, 2014). Designated as part of the Central Ohio River Tributaries by Ohio EPA, six towns are included in this watershed (Belmont Soil and Water Conservation District, 2014). They are Barnesville, Beallsville, Bethesda, Jerusalem, Powhatan Point, and Wilson (Belmont Soil and Water Conservation District, 2014). Overall, approximately 11,138 people are located within this watershed (Belmont Soil and Water Conservation District, 2014).



**Figure 14.** Captina Creek Watershed (Belmont Soil and Water Conservation District, 2014)

## 1.8.1 Captina Creek Assessment

Captina Creek is considered a high-quality, warm water stream with headwater tributaries that can support cold water fish and macroinvertebrates. Ohio EPA listed the main stretch of Captina Creek, between mile 0.8 to 25.42, as an "Outstanding State Water" while categorizing most of the tributaries as "Superior High Quality Water" (Belmont Soil and Water Conservation District, 2014). Due to its impressive biodiversity and exceptional water quality, the EPA have also categorized this watershed as an "Aquatic Resource of National Importance" (Belmont Soil and Water Conservation District, 2014).

Twenty-seven sites in this watershed were analyzed by the Ohio EPA for general water chemistry, Index of Biotic Integrity (IBI) through fish assemblage sampling, Invertebrate Community Index (ICI), and Stream Habitat Qualitative Habitat Evaluation Index (QHEI) to determine overall quality between 2008 and 2009. The Stream Habitat QHEI combines "substrate type, embeddedness within streams, and stream geomorphology characteristics" into one number (Belmont Soil and Water Conservation District, 2014). Appendix B determines sampling sites and river mile while Appendix C displays IBI, ICI, and Stream Habitat QHEI scores and exceedances of the EPA's National Recommended Water Quality Criteria for freshwater aquatic life with measured values.

Focusing on Appendix B, 20 sites were Exceptional Warmwater Habitat (EWH) and 6 sites were Warmwater Habitat (WWH) based off of the biocriteria (Appendix D) and 2009 IBI scores (Ohio EPA, 2010). Sample site 26 did not reach IBI criteria and had the lowest score of 31. For ICI, 12 sites were EWH and one site was WWH. The Ohio EPA narratively scored the remaining 14 sites in their report. From this, seven were deemed Exceptional (E), five were Very Good (VG), and 2 were Good (G) (Ohio EPA, 2010). QHEI scores from 2009 concluded out of the 27 sites, 14 were exceptional, 12 were good, and one was fair (Ohio EPA, 2010). Water chemistry parameters reported determined six sites either reached or exceeded maximum contaminant criteria set by the EPA for TDS, dissolved oxygen, copper, or temperature. This historical data concludes Captina Creek Watershed overall as healthy with exceptional fish, macroinvertebrate, and QHEI indexes.

Captina Creek's stream health quality can also be distinguished by other sensitive, pollution-intolerant species that inhabit the stretch of the watershed. In this case, the watershed has been documented to provide the correct water quality limits for the sensitive Eastern

Hellbender (Belmont Soil and Water Conservation District, 2014). External gills and sensitive, permeable skin have led to the determination of the Eastern Hellbender as an indicator species. The presences of these individuals in a reach of a stream conclude high water quality, cool temperatures, high dissolved oxygen, and low turbidity. Captina Creek is one of the two watersheds in the state where successful reproduction of Eastern Hellbender populations has occurred (Belmont Soil and Water Conservation District, 2014).

## 1.8.2 Pollutants affecting Captina Creek

Despite being a high-quality stream, Captina Creek has multiple outside, anthropogenic factors that can and have influenced its quality. Throughout these actions, key qualities of the stream that can be impacted include nutrient levels, turbidity and total suspended solids (TSS) (Belmont Soil and Water Conservation District, 2014). Recreational human activity, such as allterrain vehicles (ATV), are prevalent along the stretch the of watershed and can contribute excess sedimentation (Belmont Soil and Water Conservation District, 2014). Other activities that contribute to sedimentation include construction, logging, and gravel extraction (Belmont Soil and Water Conservation District, 2014).

Direct impacts to the water quality of a stream include agriculture within the Captina Creek watershed. Free access of streams to livestock increase the amount of animal waste contributed to the stream (Belmont Soil and Water Conservation District, 2014). This increases the nutrient levels thus promoting eutrophication, or the increase of algal blooms that restrict oxygen levels to biotic organisms in the streams. The release of sewage from outdated or inadequate home sewage systems also contributes to nutrient loading and areas of low dissolved oxygen throughout the stream due to eutrophication (Belmont Soil and Water Conservation

District, 2014). Additionally, road brining and deicing that occurs during winter in Ohio degrades soil and water chemistry.

Mining for coal and minerals near the watershed also impacts the streams' health (Figure 15). Two active coal mines are located in the middle of the watershed and there are documented releases of coal slurry and blackwater into the stream (Belmont Soil and Water Conservation District, 2014). This can increase organic and metal contaminants which decrease biodiversity and overall water quality in this watershed (Belmont Soil and Water Conservation District, 2014).



**Figure 15.** Strip Mines within Captina Creek Watershed (Belmont Soil and Water Conservation District, 2014)

## 1.8.3 Blowout at Powhatan Point

On February 15, 2018, a blowout occurred in Belmont County, Ohio at the XTO Energy Schnegg well pad. The cause of the blowout was uncontrolled venting of the natural gas from one well out of four on the pad (U.S. EPA, 2018). Table 2 and 3 indicate the potentially hazardous substances and preliminary lists of chemicals reported by XTO Energy pre-blowout that could have been released into the environment. Cat Run tributary was estimated to receive 5,000 gallons initially and 100 million cubic feet per day of natural gas, produced water, and brine from this blowout (U.S. EPA, 2018). This tributary continues to Captina Creek which flows into the Ohio River, containing several endangered and threatened native species. VOCs and condensates were reported to be discharged from this incident as well (U.S. EPA, 2018). Due to sustained natural gas leaking from the wellhead, consistent flares occurred on site (Figure 16).

**Table 2.** Estimated volumes of potentially hazardous substances characterized by CERCLA



**Table 3.** Preliminary list of chemicals on well pad reported by XTO Energy (U.S. EPA, 2018)





**Figure 16.** XTO Energy Schnegg well pad blowout that occurred on February 15, 2018 (Ohio State Highway Patrol, 2018).

Air monitoring was set in motion by the EPA and conducted by OEPA within a 1-mile radius of the blowout. EPA determined air samples collected a day after the blowout did not exceed regulatory air quality limits (U.S. EPA, 2018). Water quality sampling was initiated by the EPA and conducted by OEPA as well. Additionally, a Natural Resources consultation was conducted with the U.S. Fish and Wildlife Services to address the impact on ecological sensitive species, such as Eastern Hellbenders, Cryptobranchus alleganiensis alleganiensis, and long-eared bats, Plecotus auratus, on February 20, 2018 (U.S. EPA, 2018).

On the day of the blow out, 94 residents in 36 homes within a 1-mile radius of the pad were under mandatory evacuation (U.S. EPA, 2018). Unified Command implemented the residential re-occupancy plan on February 19, 2018, returning 30 residents to their homes that lived within 0.5-1 mile of the well pad (U.S. EPA, 2018). Twelve additionally properties were cleared this day, but were not reoccupied (U.S. EPA, 2018). The remaining six houses that were within a 0.5 mile radius of the well pad were not permitted to return to their homes (U.S. EPA, 2018).

#### **CHAPTER 2: SPECIFIC AIMS AND HYPOTHESIS**

#### 2.1 Specific Aims

The purpose of this study was to determine long term effects on the Captina Creek watershed in Powhatan Point, Ohio due to a Utica well blowout. In addition, this study focused on regulations concerning the oil and gas industry in Ohio with particular attention to the environment's and public's health. The specific aims that guided this study were as follows:

- 1) Review of Ohio regulations for the oil and gas industry. These regulations concern drilling operations, production operations, waste brine disposal, underground injections, and drilling rules.
- 2) Review of current production and waste numbers for Ohio's oil and gas industry in the Utica and Marcellus shale plays.
- 3) Assess the water quality in the Captina Creek Watershed upstream and downstream of the Powhatan Schnegg pad to determine if there were lingering effects.
- 4) Analyze the AquaSalina® deicer for its chemical makeup and radioactivity.

#### 2.2 Hypotheses

- 1) Contamination of the Captina Creek watershed can be determined by comparing past and present water quality data. Mass ratios of specific analytes can further support putative sources of contamination.
- 2) An extensive report of regulations concerning Ohio's oil and gas industry can be concluded from information provided by governmental officials that are in charge of enforcing compliance with these guidelines.

## 2.3 Experimental Design

#### 2.3.1 Production and Waste Reports

Information concerning production data are retrieved and compiled from ODNR Division of Oil and Gas (http://oilandgas.ohiodnr.gov/production). Analysis involved displaying yearly production numbers based on past reports. Information concerning waste data were retrieved from ODNR's Oil and Gas Well Database (http://oilandgas.ohiodnr.gov/well-information/oilgas-well-database) and cross referenced with FracTracker Alliance's, the 501(c)3 non-profit organization, collection of Class II Salt Water Disposal wells

(https://www.fractracker.org/2019/01/diminishing-returns-in-ohio/). Analysis involved displaying data concerning each well and the multiple active Class II Salt Water Disposal wells throughout Ohio.

## 2.3.2 Ohio Surface Water Sampling

Sites were predetermined before sampling in October 2018 to ensure little to no disturbances to the public. All sites were within 2.5 miles away from the well pad. One sampling site was located up stream while the remaining four were downstream. All samples were analyzed for general water chemistry, cations, and anions.

Samples were plotted in OriginLab 2018 software to determine geochemical ratios. All ratios were compared to abandoned mine drainage (AMD), conventional, and unconventional drilling to determine if samples were impacted.

### 2.3.3 AquaSalina<sup>®</sup> Sampling

AquaSalina® was acquired commercially at a Lowe's in the deicing section. Once acquired, this product was analyzed for general cations and anions. This sample was also plotted on OriginLab 2018 software and compared to AMD, conventional, and unconventional drilling to determine if this sample was impacted.

# 2.3.4 Ohio Regulations

All Ohio oil and gas regulations were determined form the OAC and ORC located on ODNR's public website. Additional regulations of concern were found through other regulatory agencies such as the EPA. All were compiled to make a complete, comprehensive list of Ohio's regulations concerning the oil and gas industry.

### **CHAPTER 3: MATERIALS AND METHODS**

## 3.1 Surface Water Acquisition

GPS coordinates were taken at each sampling site through a GPSmap 62s GARMIN, Olathe, Kansas. After, a 1-liter sample was collected from the bank of the stream in an autoclaved 1-liter French glass bottle to ensure sterility (Figure 17). An additional sample was collected in a 50 mL French glass jar with 7 drops of 10 M nitric acid (HNO<sub>3</sub>). This preacidified sample ensured metal preservation. Both samples were stored in a portable cooler on ice during transportation and stocked in the 4°C in Dr. John Stolz's laboratory. Once at the lab, each sample got their own master sheet (MS) number for proper identification.



**Figure 17.** Field equipment utilized for sampling trips

#### 3.2 Chemical Analysis of Samples

#### 3.2.1 YSI Multi Meter Analysis

Before sampling, a Xylem YSI Professional Plus Multi Meter, Yellow Springs, Ohio was checked to ensure full battery, efficient operation, and up-to-date calibration. The equipment was calibrated every two weeks or ten samples for quality control practices. Each calibration method followed the user manual's instructions. The pH was calibrated utilizing standard buffer solutions of pH 4.0, 7.0, and 10.0. Dissolved oxygen was calibrated utilizing deionized water to 1,000 mg/L. Specific conductance was calibrated utilizing 1,000 μS/cm standard solution provided by the company. Both temperature and pressure were factory calibrated.

Once at the sampling site, the YSI Professional Plus Multi Meter analyzed general water chemistry including pH, temperature (°C), specific conductance (μS/cm), conductivity (μS/cm), pressure (mmHg), and dissolved oxygen (mg/L and %). All probes of the YSI Multi Meter were submerged into the designated water samples until the values stabilized. All chemical parameters were recorded. Once conductivity was acquired, it was converted in to total dissolved solids (TDS) (mg/L) in a spreadsheet to contribute to the general water chemistry the YSI can retrieve on site.

## 3.2.2 Anion Analysis via Ion Chromatography (IC)

EPA Method 300.1 was the method utilized in Stolz laboratory to measure anions in samples. Suspended solids and transition metals were filtered out of the samples with a 0.45 μm polyethersulfone (PES) membrane filter and a Dionex OnGuard IIM filter. Dionex polyvials were filled with 3 mL of the filtered sample and capped. All samples that were above the specific conductance range of the IC of 1,500 μS/cm were filtered, diluted, and capped.

Ion Chromatography was completed utilizing a Dionex ICS-1100 Ion Chromatography System, Sunnyvale, California, equipped with a UV/VIS detector and a conductivity cell. Both an IonPac AS22A Carbonate Eluent Anion-Exchange Column (2 x 250, 6.5 μm particle diameter) and an IonPac AG22 Guard Column (2 x 50 mm) were utilized with a Dionex ASRS-300 anion self-regenerating suppressor to separate anions. Data collection and processing and instrumental control were accessed through Thermo Scientific Dionex Chromeleon 7 Chromatography Data System. Target anions and their minimum detection limits (MDLs) analyzed by the IC are displayed in Table 4.

**Table 4.** Minimum detection limits (MDLs) and target anion analyzed by the IC (Cantlay et, al., 2019a)

<b>Anion</b>	<b>Minimum Detection Limit (mg/L)</b>
Fluoride (F)	0.035
Chloride (Cl)	0.01
Nitrite $(NO2)$	0.02
Nitrate $(NO3)$	0.045
Bromide (Br)	0.05
Phosphate $(PO4)$	0.05
Sulfate $(SO4)$	0.05

Multiple dilutions were conducted for the AquaSalina® sample to ensure accurate results. For the IC the following dilutions were made and ran during analysis: 1:200, 1:500, and 1:1,000. The results from the dilutions were compared to pre-existing calibration curves. All results that fell outside of the calibration curves were disregarded and results within the calibration curves of each analyte were averaged and then recorded as the final result for the 7 anions.

3.2.3 Cation Analysis via Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

EPA Method 200.8 and ICP-MS were utilized for cation analysis. A Perkin-Elmer NexION 300x ICP-MS system and a Perkin Elmer auto-sampler equipped with NexION 300x ICP-MS software, Waltham, Massachusetts, performed this analysis at the University of Pittsburgh.

Preparation of samples involved filtration through a 0.45 μm PES filter followed by dilution with sub-boiled 2% nitric acid, beryllium, germanium, and thallium internal standards to promote consistency in measurements. Five-point calibration standards and blanks with internal standards were ran prior to and after sample analysis. Instrumental drift was checked by running every seventh sample twice. Target cations and their MDLs analyzed by the ICP-MS are displayed in Table 5.

<b>Cation</b>	Minimum Detection Limit (µg/L)
Lithium (Li)	0.008
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
$\overline{\text{Chromium}}$ (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
$\overline{R}$ ubidium (Rb)	0.002
Strontium (Sr)	0.100
Molybdenum (Mo)	0.096
Silver $(Ag)$	0.080
$\overline{\text{C}}$ admium (Cd)	0.021
$T$ in $(Sn)$	0.243
Antimony (Sb)	0.024
Barium (Ba)	0.521
Tungsten (W)	0.004
Lead (Pb)	0.28
Mercury (Hg)	0.066
Uranium (U)	0.030

**Table 5.** MDLs and target cation analyzed by the ICP-MS (Cantlay et al., 2019b)

Several dilutions were conducted for the AquaSalina® sample to ensure accurate results. For the ICP-MS the following dilutions were made and ran during analysis: 1:10, 1:100, 1:500, 1:1,000, and 1:10,000. The results from the dilutions were compared to pre-existing calibration curves. All results that fell outside of the calibration curves were disregarded and results within

the calibration curves of each analyte were averaged and then recorded as the final result for the 32 cations.

#### 3.3 Radioactivity via Broad Energy Germanium Detector

A broad energy germanium detector, Canberra BE3825, San Ramon, California, was utilized to measure radioactivity of AquaSalina®. After an equilibration period of at least a month, Marinelli beakers were used. <sup>226</sup>Ra activities were determined from the <sup>214</sup>Bi (609) kiloelectrons [keV]) and <sup>214</sup>Pb (259 keV, 351 keV) energies to prevent uranium interferences. <sup>228</sup>Ra measurements were achieved by using the <sup>228</sup>Ac daughter activity (911) keV).

## 3.4 Data Analysis

All samples were labeled with their MS number and logged in a book that remains in the lab. This data was inputted on a GoogleDocs spreadsheet shared exclusively with the members of Dr. John Stolz's lab.

#### 3.4.1 Drinking Water Standards

All results were compared to EPA Primary and Secondary Drinking Water Standards to gauge overall water quality. Table 6 and 7 indicate the Maximum Contaminant Levels (MCLs) in mg/L of all analytes and water quality parameters analyzed by the YSI Multi Meter, IC, and ICP-MS. All Primary and Secondary Standards are not included in the tables because they were not analyzed in this study.

<b>Primary Drinking Water Standard</b>	$MCL$ (mg/L)
Antimony (Sb)	0.006
Arsenic (As)	0.010
Barium (Ba)	2.0
Cadmium (Cd)	0.005
Chromium (Cr)	0.1
Copper (Cu)	1.3
Fluoride (F)	4.0
Lead $(Pb)$	0.015
Mercury (Hg)	0.002
Nitrate $(NO3)$	10.0
Nitrite $(NO2)$	1.0
Selenium (Se)	0.05
Uranium (U)	0.03

**Table 6.** U.S. EPA's Primary Drinking Water Standards MCLs (U.S. EPA, 2018, March 22)

**Table 7.** U.S. EPA's Secondary Drinking Water Standards MCLs (U.S. EPA, 2017)

<b>Secondary Drinking Water Standard</b>	$MCL$ (mg/L)
Aluminum (Al)	$0.05 - 0.20$
Chloride (Cl)	250
Copper (Cu)	1.0
Fluoride (F)	2.0
Iron $(Fe)$	0.3
Manganese (Mn)	0.05
pH	$6.5 - 8.5$
Silver $(Ag)$	0.10
Sulfate $(SO4)$	250
<b>Total Dissolved Solids (TDS)</b>	500
$\text{Zinc}(\text{Zn})$	5

# 3.4.2 National Recommended Water Quality Criteria

All results were compared to the National Recommended Water Quality Criteria for aquatic life in freshwater set by the EPA. Tables 8 indicates the acute and chronic limits concerning the analytes that were analyzed with the YSI, IC, and ICP-MS. All criterion that were hardness-based were not included since hardness was not measured in this study. Criterion Maximum Concentration (CMC) define the highest concentration freshwater aquatic life can be

exposed to acutely without causing adverse effects. Criterion Continuous Concentration (CCC) are defined as the highest concentration that can occur in a body of water continuously and not pose a risk to aquatic life.

<b>Pollutant</b>		Acute Freshwater CMC (mg/L)   Chronic Freshwater CCC (mg/L)
Arsenic (As)	0.34	0.15
Chloride	860	230
Iron $(Fe)$	-	
pH	-	$6.5 - 9$

**Table 8.** National Recommended Water Quality Criteria for freshwater aquatic life (U.S. EPA, 2018)

## 3.4.2.1 Dilution Calculations

Diluted concentrations for the arsenic, chloride, and iron were calculated for the following scenario: all of the recommended amount for pre-treatment (8-10 gallons/30-38 liters per lane mile) and deicing (30-40 gallons/113-151 liters per lane mile) for AquaSalina® ran off into a 0.5 mile stretch of a first order stream in Cat Run in the Captina Creek Watershed. The total time frame considered for the calculations was 120 days, the average of a winter season in northeastern U.S. The frequencies of application considered were once every 5, 10, 20, 30, and 40 days. Therefore, the amount of applications considered in this time frame were 24, 12, 6, 4, and 3.

Information concerning the 0.5 mile stretch of Cat Run was retrieved from USGS Stream Stats (https://streamstats.usgs.gov/ss/) (Figure 18). Average harmonic stream flow calculated was  $0.0169$  ft<sup>3</sup>/s/0.126 gallons/s. Stream flow was then converted to volume per day (1460)  $ft^3$ /day/10,886 gallons/day).



**Figure 18.** Segment of Cat Run utilized for dilution calculation (USGS, 2019).

After stream flow for one day was calculated, diluted concentrations of arsenic, chloride, iron, and nickel were retrieved by incorporating recommended pre-treatment volumes (8-10 gallons/30-38 liters) and deicing volumes (30-40 gallons/113-151 liters) in the dilution calculation  $(C_1V_1 = C_2V_2)$ . Example calculation for the diluted concentration of arsenic from mixing 8 gallons of AquaSalina® with this segment of Cat Run based on its flow per day is as follows:

$$
C_1V_1 = C_2V_2
$$
  
(6.98 $\frac{mg}{L}$ )(30 L) = (C<sub>2</sub>)(41238 L)  
 $C_2 = 0.0051 \frac{mg}{L}$  arsenic per day

From this concentration, both pre-treatment and deicing dilutions were retrieved by multiplying the respective frequency within the 120-day time period. These are as follows: 24 for 5-day-frequency, 12 for 10-day-frequency, 6 for 20-day-frequency, 4 for 30-day-frequency, 3 for 40-day-frequency. The two values retrieved for each frequency were averaged and represented graphically with the EPA's freshwater aquatic CMC and CCC to determine if concentrations would exceed acute or chronic values in this scenario.

## 3.4.3 Mass Ratios

Mass ratios were created with OriginLab 2018 software for all surface water samples. Ions that are in drilling wastewater influenced waters, such as Cl, Na, Mg, Ca, Br, Sr, and Ba, were used to compare surface water samples. Produced waters and flowback from shale gas extraction are related to Na, Ca, and Cl contaminants in surface and groundwaters (Brantley et al., 2014). However, these elements are naturally found in waters and can sometimes be misleading. The most distinct "fingerprint" of HVHF activity affecting surface water is connected to Sr, Ba, and Br (Brantley et al., 2014). The produced water, oil brine, flowback, and impoundment samples used to compare to ratios were acquired from western Pennsylvania oil and gas activity. All surface water samples were compared to abandoned mine drainage (AMD) ratios as well.

The following ratios were graphed in OriginLab for surface water samples: Mg/Li vs. SO4/Cl and SO4/Cl vs. Mg/Na. Ratios that included bromide were not graphed because all water samples had below detectable limits bromide concentrations. The following mass ratios were graphed in OrginLab for the AquaSalina® sample: Mg/Li vs. SO4/Cl, SO4/Cl vs. Mg/Na, Ba/Cl vs. Br/SO4, Mg/Li to Br, and Cl/Br to Cl. As mentioned above, impoundment, produced fluids,

unconventional, conventional, and AMD data for the six ratios were included in each graph. All information was retrieved from data collected by Dr. John Stolz's lab or from outside sources that reported their data for approved institutional access. All graphs that contain circles distinguishing conventional, unconventional, and AMD samples were created through an ANOVA statistical analysis and presented with a 99% confidence interval.

### 3.4.4 Ohio Regulations

The ODNR Division of Oil and Gas Resources website was utilized to compile all information concerning oil and gas industry regulations (http://oilandgas.ohiodnr.gov/lawsregulations/oil-gas-law-summary). Other outside governmental resources, such as the EPA, were utilized as well. Information reported concerned drilling, safety, and environmental and public health regulations. This information was presented in the results sections when applicable.

## 3.4.5 Geospatial Analysis

All geospatial analysis was conducted using geographical information system (GIS) software, ERSI ArcMap 10.5.1. A map of the surface water samples was created by utilizing the coordinate points retrieved in the field. The Schnegg well pad that was the focus of this study was included on this map to reference distance. All shapefiles were provided by ODNR Division of Oil and Gas Resources online Oil and Gas Well Locator interactive map.
#### 3.4.6 Production Data and Water Usage

Production data for conventional and unconventional wells in Ohio was analyzed and combined to report total amounts between the years 2011 and 2017. Production data from 2018 was not included since the reporting date for this year does not occur until March 31, 2019, therefore it was not complete. All data was reported per year and collaboratively retrieved from ODNR Division of Oil and Gas Resources website under the well production section (http://oilandgas.ohiodnr.gov/production).

Water usage data was acquired from ODNR's Oil and Gas Well Database (http://oilandgas.ohiodnr.gov/well-information/oil-gas-well-database) between January 11, 2013 and December 23, 2015 to display usage of water in 207 registered wells in Belmont County, Ohio.

#### **CHAPTER 4: RESULTS**

4.1 Oil and Gas Drilling Development in Ohio

Unconventional drilling development in Ohio in the Utica-Pleasant Point shale play increased dramatically after the first well drilled in 2011. After 2012, Ohio unconventional drilling companies continued to expand their resource exploration into the Marcellus shale play that extends over the eastern half of the state. However, Ohio drills most predominantly in the Utica shale play. As of January 5, 2019, ODNR reported that the ratio between Utica wells and Marcellus wells are around 312:1 (ODNR, 2019).

#### 4.1.1 Current Unconventional and Conventional Activity

Before a company can drill a new well, drill an existing well, plug a well, convert a well, or any other modification, they must be approved of a permit by the chief of the division of the Oil and Gas Resources Management at ODNR according to the ORC 1509.05 (ODNR, 2011). Between 2011 and January 5, 2019, ODNR has approved over 5,000 permits and the state of Ohio currently has 4,051 operating unconventional and conventional drilling wells in the Marcellus and Utica-Pleasant Point shale plays (ODNR, 2019). Figure 19 demonstrates the rapid development of oil and gas well pads and roads in Ohio within two years.



**Figure 19.** Before (October 8, 2013) and after (October 4, 2015) of oil and gas development in Belmont County, Ohio (Google Earth, 2018)

As of January 5, 2019, there were 17 rigs, 2,498 drilled wells, and 2,968 permits for shale

activity in the Utica-Pleasant Point shale play (ODNR, 2019). In the Marcellus shale play, there

are 0 rigs, 40 drilled wells, and 63 permits concerning shale development and activity (ODNR, 2019). Ohio still currently conducts conventional drilling across the state. Conventional oil and gas statistics in Ohio include 12 rigs, 1,513 drilled wells, and 2,196 permits (ODNR, 2019).

#### 4.1.2 Oil and Gas Reserves in Ohio

Ohio contains some of the countries' largest natural gas reserves which leads to high unconventional drilling activity. The EIA reported that between 2016 and 2017, Ohio had approximately 28,000 billion cubic feet (BCF) in proven reserves and an approximately 10,000 BCF increase in change of proven reserves, thus resulting in an overall 40% change in proven reserves (U.S. EIA, 2018). With 11.1 Tcf of total natural gas proved reserves in 2017, Ohio ranked 5th with West Virginia in the country (U.S. EIA, 2018).

Ohio did not lead in the country for oil production and proved reserves in 2017, however the state still produced a large amount. Published proved reserves of crude oil on December 31, 2016 was 167 million barrels (U.S. EIA, 2018). After adjustments, sale, acquisitions, and other revisions, proved reserves the follow year on December 31 was 189 million barrels (U.S. EIA, 2018). Overall, this determined a 13% increase in crude oil reserves in the state of Ohio. Table 9 displays the changes in reserves and overall estimated production in Ohio in 2017.

<b>Reason for Change</b>	<b>Changes in Reserves during 2017</b>	<b>Changes in Reserves</b>		
	(million barrels)	during 2017 (million		
		gallons)		
Adjustments	40	1,680		
<b>Revision Increases</b>	69	2,898		
<b>Revision Decreases</b>	69	2,898		
Sales	24	1,008		
Acquisitions		294		
Extensions & Discoveries	18	756		
<b>Estimated Production</b>	19	298		

**Table 9.** Changes in oil reserves in Ohio (U. S. EIA, 2017)

#### 4.1.3 Oil, Gas, and Brine Production

Under ORC Section 1509.11, Ohio law requires all owners and operators of wells that are capable to produce oil or gas to annually report production data of oil, gas, and brine on each well to the Division of Oil and Gas Resources by March 31 for the preceding calendar year (ODNR, 2011). However, domestic well owners are exempt from ORC Section 1509.11 and are not required to report production statements (ODNR, 2011). Under the Sub. House Bill 59 (Sub. H.B. 59), effective September 29, 2013, all operators of horizontal oil and gas wells located in Ohio were required to submit quarterly production data instead of annually (ODNR, 2013). In hopes of increasing the accuracy and efficiency of oil and gas reporting in Ohio, four times a year a report for every well is required. Well operator or owners are given 45 days after the end of the quarter to turn in production data to the ODNR. Since all information is provided by the well owner and operators, the Division includes a disclaimer on the production section of the website that they "can neither guarantee the accuracy of the information, nor guarantee that the information set forth herein reflects all of the production of oil and gas" that has occurred that reporting year (ODNR, 2019).

All production data has been compiled concerning only unconventional production between 2011 and December 2017. Data has not been compiled for 2018 by the ODNR, therefore it was left out of the study since it was not a complete report and representation of the reporting year. All information is located on ODNR Division of Oil and Gas Resources website under the well production section. Quarterly horizontal shale production between 2013-2017 and combined production reports for both unconventional and conventional between 1984-2017 are available for download for free to the public.

Oil, gas, brine, and total number of days of productions are provided for unconventional drilling between 2011-2012 (Table 10). This is separated from 2013-2017 because 2011-2012 reported unconventional production data from Utica shale while 2013-2017 reported production data from both Utica and Marcellus shale plays (Table 11). Table 10 contains days of production while Table 11 does not because of the implementation of Sub H.B. 59 in 2013 that required quarterly over annual reports. In oil and gas industry, amounts of oil and brine are recorded in barrels while gas is recorded in MCF (thousand cubic feet). Under Ohio oil and gas law, LNG, or "dry" gas, and natural gas liquids (NGL), or "wet" gas, do not need to be reported separately. Therefore, all gas is reported as one production number quarterly per well by the owner/operator. Production data for oil and brine were also converted into gallons  $(1 \text{ barrel} = 42 \text{ gallons})$ .



**Table 10.** Annual oil, gas, and brine results from 2011-2012 Utica horizontal drilling in Ohio. Data from ODNR.

Year	<b>Oil (Barrels)</b>	<b>Gas (MCF)</b>	<b>Brine (Barrels)</b>
2013	3,677,734	100,119,054	2,663,397
2014	11,001,117	453,053,944	7,463,308
2015	23,129,760	956,161,655	13,717,621
2016	18,015,346	1,388,656,313	15,836,645
2017	16,535,808	1,725,495,877	20,278,911
Sum	72,359,765	4,623,486,843	59,959,882
Sum (gallons)	3,039,110,130		2,518,315,044

**Table 11.** Annual oil, gas, and brine results from 2013-2017 Utica and Marcellus horizontal drilling in Ohio. Data from ODNR.

Table 12 combines all unconventional drilling data from Utica-Pleasant Point and

Marcellus shale play reported to the ODNR Division of Oil and Gas Resources. All barrels were

converted to gallons in Table 12 for perspective.

**Table 12.** Total oil, gas, and brine results from 2011-2017 Utica and Marcellus horizontal drilling in Ohio. Data from ODNR.

	Oil (Barrels)	Gas (MCF)	<b>Brine</b>
			(Barrels)
Sum (2011-	73,041,965	4,638,879,659	60,717,571
2017)			
Sum (2011-	3,067,762,530		2,550,137,982
2017 in			
gallons)			

Based off of Table 12, in Ohio the ratio in gallons concerning oil to brine is 1.2:1. The ratio in gallons for natural gas to brine is 7,480:1. When excluding natural gas, from this data one gallon of oil is said to produce one gallon of brine between 2011-2017. When excluding oil production within this time frame an estimated 7,480 gallons of natural gas will produce one gallon of brine. In comparison, natural gas extraction in Ohio creates less HVHF waste than oil extraction when analyzing production data in the Marcellus and Utica shale between 2011 and 2017.

Figures 20 and 21 show the number of producing oil and gas wells and the amount of oil or gas they produced yearly. All wells that failed to produce oil or gas were omitted from the data set collaborated for the figures. Both graphs demonstrate that oil and gas wells continued to increase in number between the time frame. Oil production increased between 2011-2015 then decreased by 5 million barrels/210 gallons and an additional 2 million/84 gallons in 2017 (Figure 20). Natural gas production also increased between the time frame (Figure 21).



**Figure 20.** The number of producing unconventional oil wells (left y axis) and their total production of oil in barrels (right y-axis) over time in Ohio. Data from ODNR.



**Figure 21.** The number of producing unconventional natural gas wells (left y axis) and their total production of natural gas in MCF (right y-axis) over time in Ohio. Data from ODNR.

#### 4.1.4 Production Declines Over Time Per Well

Although the overall trend of gas and oil production in Ohio is increasing, constant gas and oil exploration and drilling is necessary since the productivity of wells decline dramatically over time. The increase in exploration and drilling result in an increase in resource demand, water usage, waste production, and potential environmental harm.

The same data from the ODNR concerning production from 2011-2017 was utilized in this section for all 370 Belmont County wells. Two separate graphs were created for oil and gas productivity for 267 wells. Wells that were permitted to start production in 2017 were not included in Figures 22 and 23 because 2018 production data was not collected for this analysis thus no trend would occur.

Figure 22 demonstrates the 105 wells drilled between 2012-2016 that produced oil between 2012-2017 in Belmont County, Ohio. Production year 0 indicates the year the well was permitted to start production. Yearly oil productivity data correlates with Figure 20 with an overall increase in total oil production between 2011-2015 followed by a decline in 2016. Overall, after one year of production, the 105 oil producing wells drilled between 2012-2016 in Belmont County started to decrease.



**Figure 22.** Total production of unconventional oil wells in Belmont County, Ohio drilled in the same year over time. Data from ODNR.

Figure 23 demonstrates the 263 gas producing wells drilled between 2012-2016 in Belmont County. Similar to Figure 22, production year 0 indicates the year the wells were permitted to start gas production. Figure 23 correlates with Figure 21 by displaying an overall increase in natural gas production in Ohio wells. Similar to oil, after one year the 263 natural gas producing wells in Belmont County started to decrease in productivity.



**Figure 23.** Total production of unconventional natural gas wells in Belmont County, Ohio drilled in the same year over time. Data from ODNR.

## 4.1.5 Water Usage

According to analysis conducted by FracTracker Alliance, Utica well lateral lengths are increasing by 9.1-15.6% per year (Auch, 2018). Annual water usage data per well lateral was compiled for 207 Belmont County wells between January 11, 2013 and December 23, 2015. These dates span between reporting Quarter 1 of 2013 to reporting Quarter 4 of 2015. The highest amount of water utilized between this time frame was 27,566,784 gallons in Quarter 4, 2015. The lowest amount of water utilized in this time frame was 359,259 gallons in the same Quarter and year. A 65% increase in water usage per lateral occurred between 2013 and 2014 followed by an 8% decrease between 2014 and 2015 (Figure 24).



**Figure 24.** Average gallons of water utilized between 2013 to 2015 in 207 wells located in Belmont County, Ohio. Data from ODNR.

### 4.1.6 HVHF Waste

Disposal rates were acquired from ODNR's website by utilizing the API number reported in FracTracker's data set of Class II SWD wells in Ohio. To acquire data, the API number was put into the ODNR's Oil and Gas Well Database. Volume in, volume out that was determined to be recycled, and total volumes of HVHF fluids are available in this database (Table 13). Ohio's 226 active Class II SWD wells received 200,555,813 barrels/8,423,344,175 gallons between 2010-2018.

**Table 13.** Volume in, volume out, and total sum of HVHF fluid in Ohio's Class II SWD wells. Data from ODNR.

	<b>Volume In</b>	<b>Volume Out</b>	<b>Total</b>
<b>Barrels</b>	103,960,045	96,595,768	200, 555, 813
<b>Gallons</b>	4,366,321,903	4,057,022,272	8,423,344,175

Concerning the 226 active Class II SWD wells and Table 13, there is a 1.4:1 ratio concerning brine injected and brine recycled. ODNR reports that throughout their UIC program concerning the Class II SWD wells, 98% of the "volume out" is utilized for secondary oil recovery while 2% is utilized for road dust and ice control (ODNR, 2019). Therefore, 3.9 billion gallons of volume out was utilized for secondary oil recovery while 81 million gallons was utilized for road deicing and dust control in the state.

An additional comparison concerns Table 11 and Table 12. Although the production and waste data sets have different time frames, it demonstrates that Ohio is not responsible for the majority of the injected brine in the Class II SWD wells (Table 12). An estimated 2.5 billion gallons of brine from Ohio out of 8.4 billion gallons of brine total was injected into the wells. Ohio was estimated to have contributed 30% of the brine in the active SWD wells while the remaining 70%, or 5.9 billion gallons, came from Pennsylvania and West Virginia wells.

## 4.2 Surface Water Analysis

Five surface water samples were collected in October 2018 for this study in Captina Creek and Cat Run, a tributary of Captina Creek, in Powhatan Point, Ohio (Figure 25). The well pad explosion that occurred in February of 2018 in Powhatan Point was located near sample Cat Run #2. Geospatial analysis involved creating a map and determining the exact distances from each site to the well pad explosion site. Production numbers from ODNR Division of Oil and Gas were also reported for the four wells located on this well pad. Finally, all samples were analyzed in the field with the YSI Multi Meter and analyzed in the laboratory using IC and ICP-MS.

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## 4.2.1 Geospatial Analysis



# Sampling Locations Near Powhatan Point, Ohio Well Pad Blow Out

**Figure 25.** Location of five surface water samples in Captina Creek and Cat Run (Captina Creek #1, Captina Creek #2, Cat Run #1, Cat Run #2, and Cat Run #3) near the Schnegg Well Pad (Well No. 3H, 5H, 7H, and 9H)

All samples were under 2.5 miles of the well pad explosion site that occurred on February 15, 2018 in Powhatan Point, Ohio. The furthest sample was Cross Creek #1, the sample closest to Captina Creeks mouth that meets the Ohio River. The closest surface water sample was collected at Cat Run #2. Refer to Table 14 for distances between the Schnegg Pad and the five sampling sites in miles and meters.

<b>Sample</b>	<b>Distance from Well Pad</b>	<b>Distance from Well Pad</b>		
	(miles)	(meters)		
Captina Creek #1	2.3	3,630		
Captina Creek #2	1.5	2,380		
Cat Run $#1$		1,700		
Cat Run #2	0.004	6.4		
Cat Run $#3$	0.3	492		

**Table 14.** Distance in miles and meters of sampling sites to Schnegg well pad explosion site

## 4.2.2 Water Chemistry

All samples were analyzed utilizing the YSI, IC, and ICP-MS to conduct complete water

quality analysis (Table 15).









All samples exceeded one SMCL, iron. The highest concentration of iron was at Captina Creek #1 at 0.78 mg/L while the lowest concentration was Cat Run #2 at 0.36 mg/L. Captina Creek #2 also exceeded an additional SMCL, manganese, with a concentration of 0.059 mg/L. Overall from the small sample set, 100% exceeded one SMCL while 20% exceeded more than one SMCL. Additionally, from this sample set 0% of the samples exceeded any MCLs.

**Table 16.** Water chemistry results of surface water samples at Cat Run and Captina Creek and EPA CCC and CMC exceedances (U.S. EPA, 2018)

<b>Sample</b>	Captina	Captina	Cat	Cat	Cat	<b>EPA</b>	<b>EPA</b>	<b>Samples</b>
	Creek $#1$	Creek #2	Run#1	$Run$ #2	Run#3	CCC	<b>CMC</b>	<b>Exceeding</b>
								<b>CCC</b> or
								<b>CMC</b>
$pH^*$	7.7	7.7	7.9	8.0	8		$6.5 - 9$	$\theta$
<b>Chloride</b>	17.8	18.5	8.9	6.1	5.2	860	230	$\overline{0}$
(mg/L)								
Fe	0.8	0.6	0.5	0.4	0.5			$\boldsymbol{0}$
(mg/L)								
As	< 0.001	0.001	bdl	bdl	bdl	0.34	0.15	$\boldsymbol{0}$
(mg/L)								

After analysis of the surface water samples, no CCC or CMC set by the EPA were exceeded (Table 16).

## 4.2.3 Production Numbers

The Schnegg well pad contains four wells, Well No. 3H, 5H, 7H, and 9H, that have produced, or are producing, oil and brine since 2015. Schnegg Unit C, Well No. 5H produced the most oil and brine. Schnegg Unit B, Well No. 9H produced the least in both. However, reporting commenced in Quarter 4, 2017, a short period of time before the February blowout,

thus potentially halting operations and production. Schnegg Unit C, Well No. 7H produced the

second least amount of oil and brine. Overall, the four wells combined produced 11,080,241

MCF of gas and 113,008 barrels/4,746,336 gallons of brine between Quarter 2, 2015 and Quarter

3, 2018 (Table 17) (ODNR, 2018).

**Table 17.** Brine and oil production data for Schnegg well pad in Powhatan Point, Ohio between Quarter 2, 2015 and Quarter 3, 2018. Data from ODNR.



#### 4.3 AquaSalina<sup>®</sup> Chemistry

AquaSalina® was acquired commercially from a Lowe's and analyzed in the laboratory using IC and ICP-MS. Nature's Own Source, LLC., the creator company of the deicer, presents on their website the chemical composition to the public. The total chloride salt blend in this commercial product is 26.4% effective (Nature's Own Source, LLC., 2013). The company also

reported on the chemical composition of the total chloride salt blend as follows: 9.0% CaCl2,

2.5% MgCl2, 1% KCl, and 11.0% NaCl (Nature's Own Source, LLC., 2013).



Table 18. IC and ICP-MS results of AquaSalina® and EPA (S)MCLs exceedances

\*SMCL – Secondary Drinking Water Standards, "-" indicates no (S)MCL

After analysis, AquaSalina® exceeded seven MCLs (Table 18). Those are as follows: Al, Cr, Cu, As, Se, Ba, and Pb. This product also exceeded three SMCLs which were chloride, Mn, and Fe. Therefore, this product exceeded 10 (S)MCLs and was in compliance with the remaining 9 (S)MCLs (Figure 26).



**Figure 26.** Percent differences in chemical exceedances and compliances with EPA (S)MCLs concerning AquaSalina® results

AquaSalina® was compared to the EPA's National Recommended Water Quality

Criteria for freshwater (Table 19). After analysis, chloride and arsenic exceeded the EPA's CCC

and CMC for aquatic life. Additionally, iron exceeded the CMC.

**Table 19.** AquaSalina® results compared to EPA's CCC and CMC (U.S. EPA, 2018)



#### 4.3.1 Radioactivity

After analysis AquaSalina® was concluded to be radioactive. <sup>228</sup>Ra was calculated to be 600 picocurie/L (pCi).

#### 4.3 Concentration Ratios

Concentration ratios were created and analyzed utilizing OriginLab 2018 to determine if any of the water samples had a relationship with conventional oil brine, impoundment water, flowback, produced water, or AMD. All water quality data was collected by Dr. Stolz's lab or outside, accredited researchers.

#### 4.3.1 Surface Water Samples Ratios

The following ratio was analyzed for the surface water samples: Mg/Li, mass ratio to SO4/Cl, mass ratio (Figure 27). Flowback, impoundment water, and conventional oil were collected previous to this study. Mine drainage ratios were provided by Cravotta, 2007, conventional oil ratios from both Ohio and Pennsylvania were from USGS and Dresel et al., 2010, and unconventional data was from Hayes, 2009. The water samples (WS), designated by blue stars on the graphs, were not located in a spot that determined impact from conventional, unconventional, or AMD. However, the closest ratios the WS were located by was AMD.



**Figure 27.** Mg/Li to SO4/Cl OriginLab graph of five surface water samples compared to conventional oil brine, unconventional oil, impoundment water, flowback, produced water, and AMD (Cantlay et al., 2019c)

The second ratio that was analyzed for the surface water samples was SO4/Cl, mass ratio to Mg/Na, mass ratio (Figure 28). Flowback, impoundment, and conventional oil ratios were collected previous to this study. All of the outside resources are the same for this analysis with the addition of conventional ratios from Warner et al., 2012 and unconventional ratios from PA DEP and Hayes, 2009. WS, designated by blue stars again, are grouped within the AMD ratios provided by Cravotta, 2007. Both graphs and analysis determine that the water samples are located in close proximity to AMD ratios.



**Figure 28.** SO4/Cl to Mg/Na OriginLab graph of five surface water samples compared to conventional oil brine, unconventional oil, impoundment water, flowback, produced water, and AMD (Cantlay et al., 2019c)

## 4.3.2 AquaSalina® Ratios

The first graph created for AquaSalina® was Mg/Li, mass ratio to SO4/Cl, mass ratio (Figure 29). Similar to the surface water sample OriginLab graphs, flowback, impoundment water, and conventional oil were provided previous of this study. Mine drainage data was retrieved from Cravotta, 2007, conventional samples were retrieved from USGS and Dresel et. al, 2010, and unconventional samples were retrieved from USGS and Hayes, 2009. The

AquaSalina $\circledR$  sample is represented by a blue star. For this specific relationship between mass ratios, this sample was located in the grouping of unconventional oil samples.



**Figure 29.** Mg/Li to SO4/Cl OriginLab graph of AquaSalina® compared to conventional oil brine, unconventional oil, impoundment water, flowback, produced water, and AMD (Cantlay et al., 2019c)

The following ratios were analyzed in the second graph for AquaSalina®:  $SO_4/Cl$ , mass ratio to Mg/Na, mass ratio (Figure 30). Flowback, impoundment, and mine drainage data were retrieved previous of this study. Unconventional data for ratios were retrieved from the USGS, PA DEP, and Hayes, 2009. Dresel et al., 2010, USGS, and Warner et al., 2012 ratios were utilized for conventional data in the graph. The same symbol was utilized for the AquaSalina® sample as the proceeding graph. In this relationship, the sample was located in the designated area for ground water and brines, closest to unconventional and conventional ratios.



**Figure 30.** SO4/Cl to Mg/Na OriginLab graph of AquaSalina<sup>®</sup> compared to conventional oil brine, unconventional oil, impoundment water, flowback, produced water, and AMD (Cantlay et al., 2019c)

Mg/Li, mass ratio to Br, parts per million (ppm) was created by utilizing flowback, impoundment water, and mine drainage data collected previous of this study (Figure 31). Mine drainage ratios were reported from Carvotta, 2007, unconventional data was collected from Akob et al., 2015, Rowan et al., 2015, USGS, and the PA DEP, and conventional ratios were retrieved from Dresel et al., 2010 and the USGS. AquaSalina® is represented by a blue star. Although

this sample didn't fall into any of the circles that dictated mine drainage, conventional, or unconventional impacted, it was closest to the unconventional ratios.



Figure 31. Mg/Li to Br OriginLab graph of AquaSalina<sup>®</sup> compared to conventional oil brine, unconventional oil, impoundment water, flowback, produced water, and AMD (Cantlay et al., 2019c)

Ba/Cl, mass ratio to Br/SO4, mass ratio was an additional graph created for analysis (Figure 32). All data utilized for the last four graphs for flowback, impoundment water, and mine drainage were collected previous of this study. Mine drainage ratios were retrieved from Brantley et al., 2014 and Cravotta, 2007, conventional ratios were retrieved also from Brantley et al., 2014, the USGS, Dresel, 2010, and Warner et al., 2013, and unconventional ratios were

retrieved from the USGS, the PA DEP, and Hayes, 2009. AquaSalina® is represented by a blue star and is located in the oil and gas brines location near conventional ratios.



**Figure 32.** Ba/Cl to Br/SO4 OriginLab graph of AquaSalina® compared to conventional oil brine, unconventional oil, impoundment water, flowback, produced water, and AMD (Cantlay et. al., 2019c)

The final graph created was Cl/Br, mass ratio to Cl, mass ratio (Figure 33). Dilute groundwater/halite, dilute groundwater/seawater, flowback, impoundment, and conventional oil and gas data were collected previous of this study for comparison. AquaSalina® is represented by a blue star on the graph and is located near the flowback data collected from unconventional oil and gas.



**Figure 33.** Cl/Br to Cl OriginLab graph of AquaSalina® compared to unconventional flowback (FB) and impoundment (IMP), conventional oil and gas (Conv), dilute groundwater/halite, and dilute groundwater/seawater ratios (Cantlay et al., 2019c).

#### 4.4 Dilution Analysis

All dilution graphs included concentrations of the analyte after recommended volumes of AquaSalina® were mixed with the volume of a 0.5 segment of Cat Run in the Captina Creek Watershed. The assumption for this analysis was all AquaSalina® applied to a  $0.5$  mile two-lane road ran off into the stream. Additionally, the EPA's CMC and CCC for freshwater aquatic life based on the Recommended Water Quality Criteria were included in each graph to display if any analytes exceeded them within the 120-day time frame.

The first graph created focused on diluted arsenic concentrations in Cat Run after this scenario occurred (Figure 3). All diluted concentrations concerning pre-treatment averages did not exceed CMC nor CCC set by the EPA. However, two frequencies exceeded the CCC and one frequency exceeded the CMC for deicing averages. When AquaSalina® was applied every 5 days, it exceeded both acute and chronic EPA limits. Additionally, when application of this product occurred every 10 days it exceeded chronic exposure limits.



Figure 34. Diluted concentrations of arsenic in a 0.5 mile stretch of Cat Run when AquaSalina® is applied at different frequencies for both pre-treatment and deicing purposes within a winter season in Ohio (U.S. EPA, 2018)

Figure 35 demonstrates the dilution concentrations of chloride in the stream. Concerning the EPA's CCC, all frequencies for both pre-treatment and deicing exceeded. Within 120 days, the two frequencies that exceeded the CMC for chloride concentration are 5 and 10 days concerning the pre-treatment averages. For deicing averages, all frequencies were above the CMC for chloride concentrations in freshwater streams.



**Figure 35.** Diluted concentrations of chloride in a 0.5 mile stretch of Cat Run when AquaSalina $\circledR$  is applied at different frequencies for both pre-treatment and deicing purposes within a winter season in Ohio (U.S. EPA, 2018)

Diluted concentrations of iron are presented in Figure 36. For this analyte there is no CMC (Table 8). Therefore, the only maximum limit included on the graph was CCC. For both pre-treatment and deicing at all frequencies the CCC was exceeded.



**Figure 36.** Diluted concentrations of iron in a 0.5 mile stretch of Cat Run when AquaSalina® is applied at different frequencies for both pre-treatment and deicing purposes within a winter season in Ohio (U.S. EPA, 2018)

#### **CHAPTER 5: DISCUSSION**

#### 5.1 Ohio Oil and Gas

Information concerning Ohio's oil and gas activity was readily found on ODNR's Oil and Gas Resources website that is always available to the public. This website provided important information about this industry concerning emergency response, shale activity, oil and gas well locator and databases, production totals, laws and regulations, chemical information, employment, and an extensive FAQ for the general public.

## 5.1.1 Ohio Production Numbers

All information concerning production numbers of Ohio's shale and gas industry was easily accessible on the Well Production section of ODNR's Oil and Gas Division Resources website. All production data between 1984 to 3<sup>rd</sup> Quarter, 2018 was located in a "Production" Archive" in the form of a downloadable excel sheet (Figure 37). All excel sheets included the production year, quarter, well operator and/or owner name, county, permit number, township of well, the well name and/or well number, amount of oil in barrels, amount of gas in MCF, amount of brine in barrels, and days in production. Additional information is provided for specific wells such as the date of first production.



**Figure 37.** Production data available on ODNR's Division of Oil and Gas Resources Website

The discrepancy in Ohio production numbers is the owner and/or operator of the well are reporting the data to the ODNR. ODNR is only in charge of compiling and presenting the data to the public. This could result in miscalculations conducted by ODNR in production of oil, gas, and brine by each well. Another important factor that can lead to a continuing of discrepancy in the data is the separation between wet and dry gas. In Ohio, total gas, a combination of dry and wet gas, is required to be reported. However, distinguishing the amount produced between the two is beneficial to ensure accurate extraction data and promote more comprehensive predictions in gas availability and price.

Oil, gas, and brine production data between 2011-2017 was retrieved from ODNR's website (Table 10, 11, and 12). Between 2011-2015, oil production increased and peaked in 2015. A 5-million-gallon decrease followed in 2016 and then an additional 2 million gallons in 2017. A continuous increase in production for natural gas is the trend in Ohio between 2011 and 2017. However, Figure 20 and 21 demonstrated that regardless of increasing or decreasing

trends, the number of oil and gas wells increased within this time frame. Figures 22 and 23 demonstrated 267 Belmont County oil and gas wells drilled between 2012-2016 started to decline in productivity after one year of operation. Total production when disregarding natural gas production was 1.2:1 oil to brine ratio. When disregarding oil production, the ratio for natural gas to brine was 7,480:1. Therefore, natural gas production in Ohio produced less brine than oil production.

## 5.1.2 Water and Disposal Rates

Water utilized and disposal rates were not as readily accessible as production numbers on ODNR's website. All information retrieved for this study was acquired through ODNR's Oil and Gas Database and cross referenced with data from FracTracker Alliance, a 501(c)3 nonprofit organization that focuses on data for air, water, and waste, economics, HVHF fluids, and other releases in the environment. Disposal volumes were publicly available for 2010 to Quarter 3, 2018 for all Class II SWD injection wells for download. Due to this easily accessible link over navigating ODNR's website, FracTracker Alliance was the better option.

Trends in water and disposal rates reflect the trends that were produced from analyzing production data. With the increase in wells over time in Ohio, both waste and disposal rates increase as well. Continuing to consume oil and gas will cause not only production to increase over time, but also water consumption and discharge fluids.

### 5.1.3 Comparison to Pennsylvania Oil and Gas

Ohio and Pennsylvania's Oil and Gas industries both varied in accessibility and availability concerning permitting, completion reports, production and waste numbers, and other

important information (Table 20). Ohio's interactive map that contains the oil and gas database was more direct and had all information on one page while Pennsylvania's contain subheadings that increased structure, but also potentially increased the difficulty of the user. Pennsylvania exceeded Ohio in accessibility of waste and complaints. The Department of Environmental Protection's (DEP) website had links for the two aspects of oil and gas that ODNR's website lacked. Although the information is on ODNR's website, it required opening individual reports for the well or getting in contact with an ODNR official. However, overall Ohio and Pennsylvania's oil and gas department websites both were easy to navigate and had important information on the main page or within no more than two links.

	Ohio	Pennsylvania
<b>Permits</b>	<b>ODNR's Oil and Gas</b>	DEP PA Oil and Gas
	Database $\rightarrow$ Click on desired	Mapping $\rightarrow$ Click on desired
	well and look at information	well and look at information
	for permits	for permits
<b>Spud Data</b>	ODNR's Division of Oil and	DEP's Oil and Gas Reports
	Gas Resources home page $\rightarrow$	→ "Spud Data Report"
	"Well information" $\rightarrow$ "Oil &	
	Gas Well Database" $\rightarrow$ Input	
	specific API number of well	
	to determine the spud date	
	OR "Well information" $\rightarrow$	
	"Oil & Gas Well Locator" $\rightarrow$	
	toggle until desired well is	
	found, select, and read spud	
	report	
<b>Completion Report</b>	<b>ODNR's Oil and Gas</b>	DEP's PA Oil and Gas
	Database $\rightarrow$ Click on desired	Mapping $\rightarrow$ Click on desired
	well $\rightarrow$ "Completion Report"	well $\rightarrow$ Look through each
	link	production report
<b>Waste Numbers</b>	<b>ODNR's Oil and Gas</b>	DEP's Oil and Gas Reports
	Database $\rightarrow$ Click on desired	$\rightarrow$ "Oil and Gas Production"
	well $\rightarrow$ Completion Report or	and Waste Reports"
	<b>Well Survey Report</b>	
<b>Complaints</b>	<b>ODNR's Division of Oil and</b>	DEP's Oil and Gas Reports
	Gas Resources home page $\rightarrow$	$\rightarrow$ "Water Supply Resolved"
	"Public Records Request" $\rightarrow$	Complaints"
	Email and get a response	<b>OR</b>
	within 24 hours	DEP's Right-to-Know
		Procedure $\rightarrow$ File a Request
		& Submit

**Table 20.** Locations for information concerning oil and gas on Ohio and Pennsylvania's websites

Table 21 displays number of total complaints between 2014-2018. Complaints for Pennsylvania were acquired through the DEP while complaints for Ohio were acquired through an ODNR official upon request. Both data sets exclude public records requests and focus strictly on total complaints. Additionally, Ohio's complaints in Table 21 define how many were logged, not total complaints that were made within that year. Pennsylvania complaints start to decrease
after 2015 while Ohio's stay consistent between 2016-2018. On average, Pennsylvania

complaints are three times larger.

**Table 21.** Total complaints between 2014-2018 for Pennsylvania and Ohio (DEP, 2019 & ODNR, 2019).

Year	<b>Ohio complaints</b>	Pennsylvania complaints
2014	302	837
2015	286	965
2016	259	763
2017	253	711
2018	258	

## 5.2 Powhatan Point Surface Water Samples

Initially, this study was going to follow the pattern of Stolz's lab that requires public participation of home owners who provide access for the researchers to sample their well water supplies. However, after months of networking and presenting this opportunity to the wellwater-community in Belmont County, Ohio, no interested parties came forth. Around this time, a well pad explosion occurred in February 2018 at Powhatan Point, Ohio. A local tributary that runs parallel to the well pad, Cat Run, was estimated to receive 5,000 gallons of HVHF fluids initially and 100 million cubic feet per day during the attempt to contain the explosion and fix the blowout (U.S. EPA, 2018). The focus of this study was then switched from well water to surface water quality to determine any impacts on this local stream.

## 5.2.1 Surface Water Analysis

All surface water samples exceeded one EPA Secondary Drinking Water Standards, iron. Iron concentrations and distance from the well pad were almost directly related. As iron concentration increased, distance from the well pad increased as well except Cat Run #2 and #3. Therefore ranked highest iron concentration to lowest, the samples were as follows: Captina

Creek #1, Captina Creek #2, Cat Run #1, Cat Run #3, Cat Run #2. This increase in concentration could be due to flow of the tributary into Captina Creek. From start to end, Cat Run will be increasingly impacted by surrounding geological and anthropogenic activities, thus resulting in a higher concentration of a specific anion or cation. Additionally, a second Secondary Drinking Water Standard exceeded was manganese at Captina Creek #2. However, historical data concerning this watershed did not indicate exceedances of iron nor manganese in 2009. Secondary Drinking Water Standards are not federally enforceable because they cause "aesthetic, cosmetic, or technical effects" that create tastes or odors, undesirable but not harmful effects to the body, and potential disruptions in water treatment systems (U.S. EPA, 2017). Increased concentrations of manganese and iron are related to abandoned mine drainage, which is prevalent in this watershed's history.

Similar to the historical data collected in 2009 by Ohio EPA, all surface water samples did not exceed CCC or CMCs set by the EPA for National Recommended Water Quality Criteria for freshwater aquatic life. Although the criteria are not enforceable by law, they demonstrate critical maximum values for acute and chronic exposure of pollutants over time. Due to all samples remaining below the maximum values, Cat Run and Captina Creek should not affect the vitality of the aquatic life present.

# 5.2.2 Surface Water Ratios

All results did not contain bromide, thus the concentration ratios created on OriginLab to determine if the samples were contaminated were Mg/Li to SO4/Cl and SO4/Cl to Mg/Na. All surface water samples near the Powhatan Point blowout were located near the mine drainage samples. Therefore, all samples were determined to be most impacted by this source of water

pollution. Additionally, six months after the blow out, all water samples did not demonstrate chemically or graphically to be impacted by the unconventional gas that leaked into the stream in February of 2018.

# 5.3 AquaSalina<sup>®</sup> Sample

This product was retrieved from a Lowe's store in the deicing section, courtesy of L. Harper, and shipped via UPS to Pittsburgh. AquaSalina® is an Ohio-produced corrosion inhibitor that is also applied to the roads during the winter to ensure road safety.

# 5.3.1 AquaSalina<sup>®</sup> Analysis

After IC and ICP-MS analysis of AquaSalina®, six Primary Drinking Water Standards and three Secondary Drinking Water Standards were exceeded. Ten total (S)MCLs were exceeded out of 19 total (S)MCLs set forth by the EPA. Due to the addition of CaCl<sub>2</sub>, MgCl<sub>2</sub>, and NaCl to AquaSalina® by the creator, these four analytes were expected to be extremely high after analysis. Although chloride is the only one that has an EPA limit, all four analytes had high concentrations between 2,280 to 162,000 mg/L (Table 18).

The remaining analytes exceeded were as follows: Al, Mn, Fe, Cr, Cu, As, Se, Ba, Pb. The negatives impacts are numerous and can be biomagnified in the environment once combined with one another. All analytes found in the deicer are linked with one or more of the following impacts on human health: increase cancer risk, respiratory diseases, cardiovascular diseases, paralysis, and death. Additionally, NaCl, that is added by the manufacture to the product, can increase the mobilization of metals, such as copper and lead, and increase the concentrations that can occur in bodies of water, groundwater, and in human and animal tissue (Tromp et al., 2012).

All CCC and CMCs set by the EPA for the National Recommended Aquatic Life Criteria were exceeded for AquaSalina®. However, run off that occurs from this product would not contain the same concentrations that were presented in this study. This would only happen if direct disposal of AquaSalina® in a given body of freshwater occured. Since roadways are one of the main impervious surfaces that cause runoff and where this product is being applied to in Ohio, the concentration of the run off should remain below the CCC and CMCs to prevent any interruptions to freshwater aquatic life.

After radioactivity analysis, AquaSalina® was determined to be radioactive as  $600$  pCi/L of <sup>223</sup>Ra. At small amounts, <sup>223</sup>Ra can have detrimental effects to human health. Medical treatments utilizing regulated minimal amounts of  $^{223}$ Ra can directly affect the soft tissues, such as the kidney and spleen, and deplete osteocytes and osteoblasts in bones (Vaidyanathan et al., 2012). AquaSalina® does not have regulations concerning radioactivity or exposure limits and could potentially cause harm to public and environment's health due to multiple applications on Ohio roads in the winter.

## 5.3.2 Mass Ratio Analysis of AquaSalina

The road deicer is labeled as "natural saltwater solution" retrieved from ancient seas (Nature's Own Source, LLC., 2013). Therefore, graphs were created in OriginLab to determine if it is impacted or related to ratios concerning impoundment water, conventional drilling, unconventional drilling, and/or AMD. The following ratios were included in the OriginLab analysis: Mg/Li to SO4/Cl, SO4/Cl to Mg/Na, Mg/Li to Br, Ba/Cl to Br/SO4, and Cl/Br to Cl. All samples were located in close proximity to unconventional ratios provided by outside research

and Dr. Stolz's lab. All samples were determined to be impacted or closely related to the composition of unconventional drilling ratios.

## **CHAPTER 6: SUMMARY AND FUTURE DIRECTION**

Data reported from the EIA between 2017 and 2018 ranked Ohio as the  $5<sup>th</sup>$  state in proven natural gas reserves in the United States. Over 11 Tcf in 2017 demonstrated how this area has contributed to the HVHF industry and the extraction of natural gas products. Although oil did not match with the natural gas reserves, Ohio still extracted 189 million barrels of oil in the same year. Production data retrieved from ODNR between 2011 and 2017 in both Utica and Marcellus shale plays reflected the ranked state. During this time frame, Ohio produced over 73,000,000 barrels/3,000,000,000 gallons of oil and over 4,000,000,000 MCF of natural gas. All extractions of resources were achieved through 17 rigs, over 2,000 wells, and over 2,000 permits in the state of Ohio.

To achieve the mass quantities of natural gas and oil, drilling is prevalent in Ohio due to the short producing lifetime of a singular well. Although one well can contribute to multiple horizontal wells to reach the shale play, Belmont County wells between 2012-2016 decreased in productivity after one year for both unconventional oil and gas extraction.

With high production numbers and short lifespans of Ohio wells, excessive water and waste are utilized and produced. Data retrieved from wells revealed increasing amounts for water used over time, with highest reported amounts being over 8,000,000 gallons. To manage the waste produced by shale extraction, Ohio implemented 226 active Class II SWD injection wells. Data retrieved for HVHF waste management indicated a 51% increase per year in cumulative disposal rate, thus resulting in an average of over 24,000 million barrels per well, per year.

Following the well pad blow out in February of 2018, thousands of gallons of HVHF fluids, proppants, oil, and natural gas leaked into a tributary of a high quality, warm water

watershed in Belmont County, Ohio. After analysis that followed in October of 2018 to determine if the stream was still impacted, two (S)MCLs were exceeded in the six sampling sites. Additionally, OriginLab graphing analysis determined that most of the samples shared similar positions with AMD data. This concluded that predominantly the surface water samples were impacted by local mines that are included in this area's history. However, future analysis should continue that involves chemical water analysis and OriginLab graphing analysis to determine if the results change. Additionally, fish and macroinvertebrate sampling should take precedence in Captina Creek Watershed, specifically Cat Run, since the Ohio EPA, ODNR, nor Ohio Fish and Wildlife Services have conducted a post-blowout biological test. Although the Ohio Fish and Wildlife Services conducted a Natural Resources consultation on February 17, 2018, it did not include fish assemblage tests nor a macroinvertebrate collection.

AquaSalina® IC and ICP-MS results determined exceedance of ten out of 19 total (S)MCLs. The company advertises this product as ancient seawater and reports the addition of the following compounds:  $CaCl<sub>2</sub>$ , MgCl<sub>2</sub>, NaCl, and KCl. All four were expected to exceed EPA Drinking Water Standards. OriginLab analysis indicated the ratios from this product were closely related to unconventional ratios. Further analysis should be conducted on road salting and brining to ensure biomagnification is not occurring in the aquatic organisms that are directly impacted by run off. Additionally, ground water sampling should occur to ensure the quality is safe for public consumption and the environment in general when this deicer is utilized. Both of these actions should occur during a low flow time of the year, preferably in the summer months, to determine differences in water chemistry. This can then be compared to the samples taken during this study since sampling occurred during a high flow time.

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# Appendix A: XTO Energy Schnegg Well Pad Information





DNR 5606 (Rev. 6/10)



#### **Ohio Well Completions Report**

**QUEENSTON** 

**BOBLEIBIOL** 

POINT PLEASANT

8270

10146

API Well Number: 34013207690000 Well Name: SCHNEGG UNIT C Well No. 5H Owner. XTO ENERGY INC. Permit Issued:  $10/16/2015$ Status: PR County: BELMONT Township: **YORK** Lot: Section: Tract: Quadrangle: POWHATAN POINT Measured: 518' NL & 1121' WL OF SEC 19 Twp. Qtr. Zone S Surface Coord X: 2459911 Y: 683098 Bot Hole Coord X: 2464824 Y: 679818 Lat 39.86407 Long 80 86157  $\ensuremath{\mathrm{LTD}}$  $\mathbf{GL}$ 697 DF  $\mathbf{K}\mathbf{B}$ 16998 DTD 16998 PB Depth Acres 425.981 Date Commenced: 05/30/2014 Date Completed: Date PB Date Abandoned TD Formation POINT PLEASANT FORMATION Prod. Form. POINT PLEASANT FORMATION Class POOL  $MCFG$  IP AT IP Natural MCFG Initial Rock Pressure  $\operatorname{Perforations}$ Stimulations Logging Co. **RTAF**  $\rm Log$  Types Tool DIA CLASS SACKS CLASS2 SACKS2 Comment PIPE TOP BOT COND 0  $\overline{70}$  $30$  $\overline{\mathbf{H}}$  $\overline{\mathfrak{o}}$ 2110  $13.3$ 1456  $\overline{12^*}$  $\overline{\mathbf{0}}$ 8965 9.62 1818 PROD 0 16974 5.5 2509  $SURF$  0 414 18.6 482 **FORMATION TOP BOTTOM REMARKS KEENER SAND** 1170 **BIG INJUN SAND** 1240 **BEREA SANDSTONE** 1770 **MARCELLUS SHALE** 5640 **BIG LIME** 5700 **ORISKANY** 5802 **LOCKPORT DOLOMITE 7320** 





#### **Ohio Well Completions Report**

API Well Number: 34013210960000 Well Name: SCHNEGG UNIT C Well No. 7H Owner. XTO ENERGY INC. Permit Issued:  $09/07/2016$ Status: PR County: BELMONT Township: YORK Section: Lot: Tract: Measured: 525'NL & 1108'WL OF SEC 19 Twp. Qtr. Quadrangle: POWHATAN POINT Zone S Surface Coord X: 2459898 Y: 683091 Bot Hole Coord X: 2466256 Y: 680106 Lat 39.86406 Long 80 86161  $\mathbf{GL}$ 697 DF  $\mathbf{K}\mathbf{B}$  $\ensuremath{\mathrm{LTD}}$ 18499 DTD  $18556$  PB Depth Acres 426.533 Date Commenced: 03/20/2017 Date Completed: Date PB Date Abandoned TD Formation POINT PLEASANT FORMATION Prod. Form. Class EW  $MCFG$  IP AT IP Natural MCFG Initial Rock Pressure  $\operatorname{Perforations}$ Stimulations Logging Co. **RTAF**  $\rm Log$  Types Tool PIPE TOP BOT DIA CLASS SACKS CLASS2 SACKS2 Comment COND 0  $100$  $30$  $\overline{c}$  $310$  $\overline{\mathbf{H}}$  $\overline{\mathfrak{o}}$  $13.3$  CJ 2030 1460  $\overline{12}$  $\mathbf{0}$ 8564  $9.62$  CJ 680  $\overline{cJ}$ 595 PROD 0  $\overline{cJ}$ 2250 18529 5.5  ${\bf C} {\bf J}$ 490  $SURF$  0 331 18.6 CJ 725 **FORMATION BOTTOM REMARKS TOP BEREA SANDSTONE** 1700 **MARCELLUS SHALE** 5403 5460 **BIG LIME** 5460 **ORISKANY** 5662 **BASS ISLANDS** 6093 **SALINA GROUP** 6222 **LOCKPORT DOLOMITE** 7141 7452 PACKER SHELL 7732 7800 **CLINTON SAND** 7800 **QUEENSTON** 8016 **UTICA SHALE** 9653 **POINT PLEASANT** 10301





#### **Ohio Well Completions Report**

API Well Number: 34013210970000 Well Name: SCHNEGG UNIT B Well No. 9H XTO ENERGY INC. Permit Issued:  $09/09/2016$ Status: PR Owner. County: BELMONT Township: YORK Section: Lot: Tract: Measured: 532'NL & 1096'WL OF SEC 19 Twp. Qtr. Quadrangle: POWHATAN POINT Zone S Surface Coord X: 2459884 Y: 683084 Bot Hole Coord X: 2462753 Y: 678636 Lat 39.86404 Long 80.86166  $\mathbf{GL}$ 697 DF  $\mathbf{K}\mathbf{B}$  $\ensuremath{\mathrm{LTD}}$ 16875 DTD 16900 PB Depth Acres 355.447 Date Commenced: 03/23/2017 Date Completed: Date PB Date Abandoned TD Formation POINT PLEASANT FORMATION Prod. Form. Class EW  $MCFG$  IP AT IP Natural MCFG Initial Rock Pressure  $\operatorname{Perforations}$ Stimulations Logging Co. **RTAF**  $\rm Log$  Types Tool DIA CLASS SACKS CLASS2 SACKS2 Comment PIPE TOP BOT COND 0  $100$  $30$  $310$  $\overline{\mathbf{H}}$  $\overline{\mathfrak{o}}$  $13.3$  CJ 2055 1460  $\overline{12}$  $\mathbf{0}$ 8645  $9.62$  CJ 680  $\overline{cJ}$ 595 PROD 0  $\overline{cJ}$ 16831 5.5  ${\bf C} {\bf J}$ 485 1865  $SURF$  0 313 18.6 CJ 725 **FORMATION BOTTOM REMARKS TOP BEREA SANDSTONE** 1706 **RHINESTREET SHALE** 4685 **MARCELLUS SHALE** 5405 5463 **BIG LIME** 5463 **ORISKANY** 5660 **BASS ISLANDS** 6090 **SALINA GROUP** 6212 **LOCKPORT DOLOMITE** 7126 7438 PACKER SHELL 7728 7792 **CLINTON SAND** 7792 **OUEENSTON** 8044 **UTICA SHALE** 9643 9777 POINT PLEASANT 9777





<b>Site Number</b>	<b>Name</b>	<b>River Mile</b>	
1	Captina Creek	23.12	
$\overline{2}$	Captina Creek	22.10	
$\overline{3}$	Captina Creek	20.90	
$\overline{4}$	Captina Creek	20.54	
5	Captina Creek	17.60	
6	Captina Creek	16.00	
$\overline{7}$	Captina Creek	11.70	
8	Captina Creek	6.71	
9	Captina Creek	3.33	
10	North Fork Captina Creek	6.65	
11	North Fork Captina Creek	3.94	
12	North Fork Captina Creek	0.43	
13	South Fork Captina Creek	9.48	
14	South Fork Captina Creek	2.97	
15	South Fork Captina Creek	0.10	
16	<b>Bend Fork</b>	8.35	
17	<b>Bend Fork</b>	3.59	
18	<b>Bend Fork</b>	0.26	
19	Joy Fork	0.30	
20	Jakes Run	0.10	
21	Pea Vine Creek	0.15	
$\overline{22}$	Crabapple Creek	0.46	
23	Piney Creek	0.02	
24	Casey Run	0.75	
25	Long Run	0.04	
26	Cat Run	3.30	
27	Cat Run	0.25	

Appendix B: Captina Creek Watershed Sampling sites 2008-2009 (Ohio EPA, 2010).

Appendix C: IBI, ICI, Stream Habitat, and water quality exceedances of EPA's Recommended Water Quality Criteria for freshwater aquatic life in Captina Creek Watershed 2009 Sampling (Ohio EPA, 2010).

<b>Site</b>	<b>Sampling</b>	<b>IBI</b>	ICI	<b>Stream</b>	Water
	<b>Type</b>			Habitat	Quality
					<b>Exceedances</b>
					(mg/L)
$\mathbf{1}$	Wading	56	56	84.0	None
$\overline{2}$	Wading	52	$\overline{E^*}$	67.0	TDS (1,520,
					$1,810, \&$
					$2,320$ mg/L)
$\overline{3}$	Wading	57	48	69.5	TDS (1,630)
					mg/L)
$\overline{4}$	Wading	56	$E^*$	72.5	None
$\overline{5}$	Wading	52	48	92.0	Temp
					$(30.04^{\circ}C)$
6	Wading	49	52	70.5	None
$\overline{7}$	Wading	52	42	67.5	Copper $(0.03)$
					mg/L)
$8\,$	Wading	56	50	70.5	None
$\overline{9}$	Wading	$\overline{56}$	$\overline{52}$	75.0	None
$10\,$	Headwater	46	$G***$	71.0	None
11	Wading	53	52	66.0	None
12	Wading	46	54	59.0	None
13	Headwater	54	$\sqrt{G^{**}}$	72.5	None
14	Wading	41	50	67.5	None
15	Wading	52	52	60.5	None
$\overline{16}$	Headwater	50	$E^*$	56.5	None
$17\,$	Headwater	57	50	86.0	None
18	Wading	52	52	83.0	None
19	Headwater	44	$\overline{E^*}$	71.0	None
20	Headwater	54	$\overline{\text{VG}^{**}}$	65.0	None
21	Headwater	54	$E^*$	73.0	None
$\overline{22}$	Headwater	58	$\overline{E^*}$	75.0	None
23	Headwater	56	$G***$	79.5	TDS (2,050,
					1,730, 2,470,
					$1,690 \text{ mg/L}$
24	Headwater	44	$E^*$	60.0	D.O. (4.36)
					mg/L)
25	Headwater	50	$VG**$	92.0	None
26	Headwater	31	$VG**$	86.0	None
27	Headwater	58	$VG^{**}$	83.0	None

\*E=Exceptional, \*\*VG=Very Good, \*\*\*G=Good

Appendix D: Biocriteria for Western Allegheny Plateau (WAP) for Biological Indexes (Ohio Epa, 2010).



