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A Study of Chloride Levels in Pine Creek, Allegheny County, PA

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A STUDY OF CHLORIDE LEVELS IN PINE CREEK, ALLEGHENY COUNTY, PA

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By

Selina Prettner

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ABSTRACT

A STUDY OF CHLORIDE LEVELS IN PINE CREEK, ALLEGHENY COUNTY, PA

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Dissertation supervised by Dr. Brady Porter

Pine Creek is a 22.8-mile long tributary to the Allegheny River draining over 67 square miles of northern Allegheny County, PA. The main stem runs along Route 8 and receives extensive runoff from road salt from deicing. A site near Etna, PA sampled biweekly in 2013 consistently showed elevated conductivity that correlated with increased chloride levels. Winter road deicing runoff produced acute chloride concentrations up to 678 mg/L. Chloride fluctuated in the summer and autumn months but did not exceed the USEPA Secondary Drinking Water Standard (250 mg/L) or the aquatic life criterion for chronic concentrations (230 mg/L). Sampling throughout Pine Creek failed to identify point sources but chronic chloride contamination throughout the watershed, including the headwaters. Seasonal chemical parameters of surface and groundwater their associations with fish surveys of the watershed were examined. The results suggest deicing is a main contributor to chloride in the Pine Creek watershed.

DEDICATION

I would like to dedicate this thesis to my family, friends, and pets who kept me focused and grounded when I needed it most. Thank you for all of your words of encouragement and belief in me.

ACKNOWLEDGEMENT

I would like to thank Linnea Manley, Dr. Tetiana Cantlay, Dr. Joseph Bain, and Dr. John Stolz for their previous work in collecting well water and surface water data within the Pine Creek Watershed. Thanks to Lou Reynolds from EPA Region 3 for all of his help in coordinating data collection and guidance. Thanks to Mike Koryak for his guidance and knowledge on the system. A big thank you to all of the Stream Field Biology students who aided in data collection: Abbie Ellert, Brittany Garman, Dan Robinson, Josh Steenbock, Kathleen Glancey, Kevin Quevedo, Natalie Campbell, and Zach Steffensmeier. Many thanks to Dr. Porter, Dr. Dakin, Dr. Stolz, and Dr. Kahler for their help and guidance throughout this research.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

3RQ- Three Rivers QUEST

AMD- Acid or Abandoned Mine Drainage

AWS- Wildlife water supply

B- Boating

CWF- Cold water fishes

E- Esthetics

EASI- Environmental Alliance for Senior Involvement

EPA- Environmental Protection Agency

F- Fishing

FSN- Fixed Station Network

IRS- Irrigation water supply

IWS- Industrial water supply

LD50- Lethal Dose that kills 50% of the sample population

LWS- livestock water supply

MCL- Maximum Contaminant Level

NAEC- North Area Environmental Council

NPDES- National Pollutant Discharge Elimination System

NPS- Non-point source

PA DEP- Pennsylvania Department of Environmental Protection

PASDA- Pennsylvania Spatial Data Access

PaSEC- Pennsylvania Senior Environment Corps

PennDOT- Pennsylvania Department of Transportation

POTWs- Publicly Owned Treatment Works

Ppm- parts per million

PWS- Potable water supply

SDWA- Safe Drinking Water Act

SDWS- Secondary Drinking Water Standards

SPC- Specific Conductance

TDS- Total Dissolved Solids

TMDL- Total Maximum Daily Load

TSF- Trout stocked fishes

USDA-United States Department of Agriculture

US EPA- United States Environmental Protection Agency

USGS-United States Geologic Survey

WCS- Water contact sports

WWF- Warm water fishes

CHAPTER 1: BACKGROUND

1.1 Pine Creek Watershed

1.1.1 Watershed Characteristics

Pine Creek is a 22.8-mile tributary located in Allegheny County, PA, draining over 67.3 square miles of land that flows from reaches of Franklin Park Borough, Marshall Township, Pine Township, and Richland Township. It forms confluence with the lower part of the Allegheny River at Etna in Shaler Township (Pennsylvania Environmental Council & North Area Environmental Council, 2005). The watershed spans across 14 municipalities (Bradford Woods Borough, Etna Borough, Franklin Park Borough, Fox Chapel Borough, Hampton Township, Indiana Township, Marshall Township, McCandless Township, O'Hara Township, Pine Township, Richland Township, Ross Township, Shaler Township, and Sharpsburg Borough).

Several major roads run through the Pine Creek watershed (Figure 2) including I-76 in the northern portion, otherwise known as the Pennsylvania Turnpike. Other roads include I-79 and Route 19 both on the western side of the watershed, and PA State Route 8 runs about 10.15 miles within the Pine Creek watershed and crosses the stream about 10 times along this length (Mackin, 2010; "StreamStats," 2019). These major roads make up one portion of the impervious surfaces in the Pine Creek watershed as well as being sources for road salting events and potential road salt runoff into Pine Creek. Furthermore, Figure 3 shows the types of soils in the Pine Creek watershed. The watershed is mostly composed of soils that are considered well-draining soils that act as the opposite of those impervious surfaces. These soils more easily allow the water to infiltrate the groundwater. While the watershed is comprised of a large amount of deciduous forest, it is also comprised of a large area of impervious surfaces which prevent infiltration from occurring in the soil (Figure 4). Table 1 displays the land coverage numerically by percentage land cover from 2001 and 2011

Table 1. Land cover percentages for Pine Creek Watershed from 2001 to 2011.

Land Cover	2001 % Land Cover (Bacteria TMDLs to Address the Recreation Use Impairment in the Pine Creek Watershed Allegheny County, Pennsylvania, 2013)	2011 % Land Cover ("Data | Multi-Resolution Land Characteristics (MRLC) Consortium," 2016)
Open Water	0.22	0.17
Developed, Open Space	30.42	30.91
Developed, Low Intensity	19.84	20.28
Developed, Medium Intensity	4.10	5.33
Developed, High Intensity	1.70	1.88
Barren Land (Rock/Sand/Clay)	0.01	0.11
Deciduous Forest	39.87	38.09
Evergreen Forest	0.38	0.36
Mixed Forest	0.22	0.19
Grassland/ Herbaceous	0.53	0.44
Pasture/ Hay	1.57	1.32
Cultivated Crops	1.10	0.88
Woody Wetlands	0.03	0.02
Emergent Herbaceous Wetlands	0.01	0.02

("Data | Multi-Resolution Land Characteristics (MRLC) Consortium," 2016) dataset to compare the changes in land cover of the watershed over time. The most significant categories for this watershed are deciduous forest (38.09%), followed by open space developed land (30.91%), and low developed land (20.28). Overall, the watershed is comprised of 58.51% developed surfaces and 41.49% undeveloped surfaces. This increased when compared to 2001 when it was 56.07% undeveloped surfaces and 43.93% developed surfaces. Neighboring watersheds to Pine Creek are Deer Creek and Squaw Run (Figure 5). Comparing land coverage and soil types in these watersheds could shed light on differences in runoff volumes based upon any differing land types.

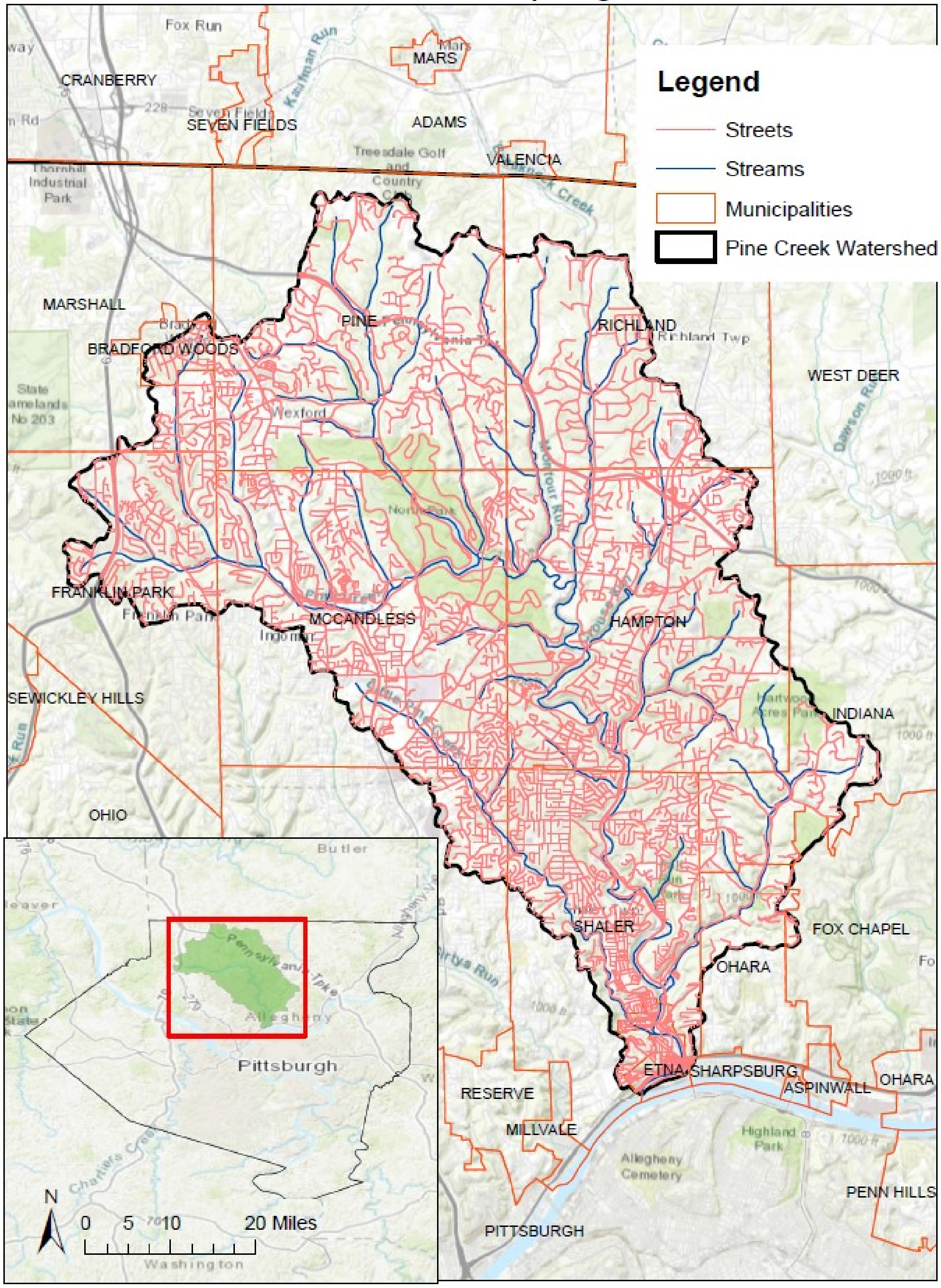


Figure 1. Map of the Pine Creek watershed with the streets and sampling sites (PASDA).

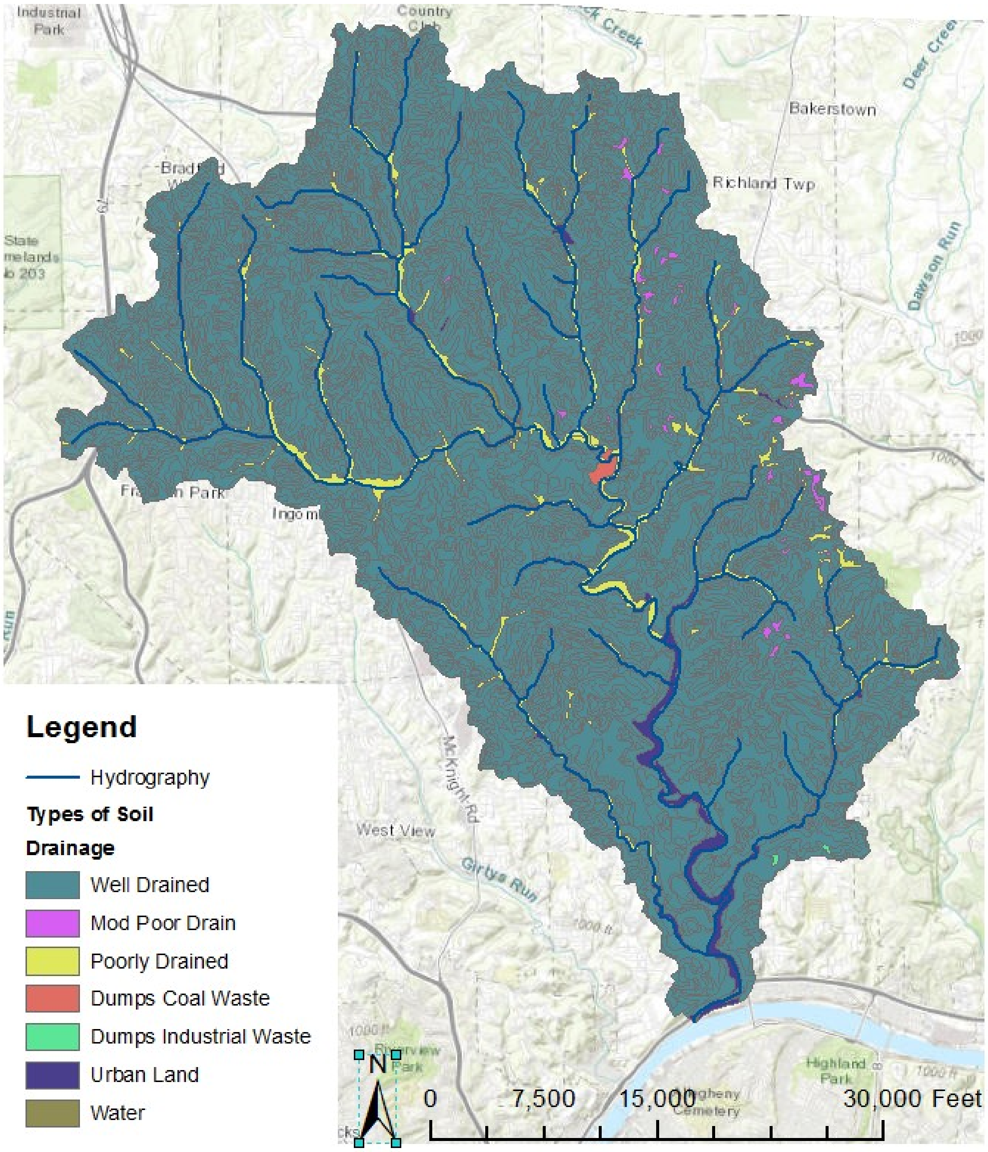


Figure 2. Map of the Pine Creek watershed soil drainage abilities (ESRI, PASDA, USDA).

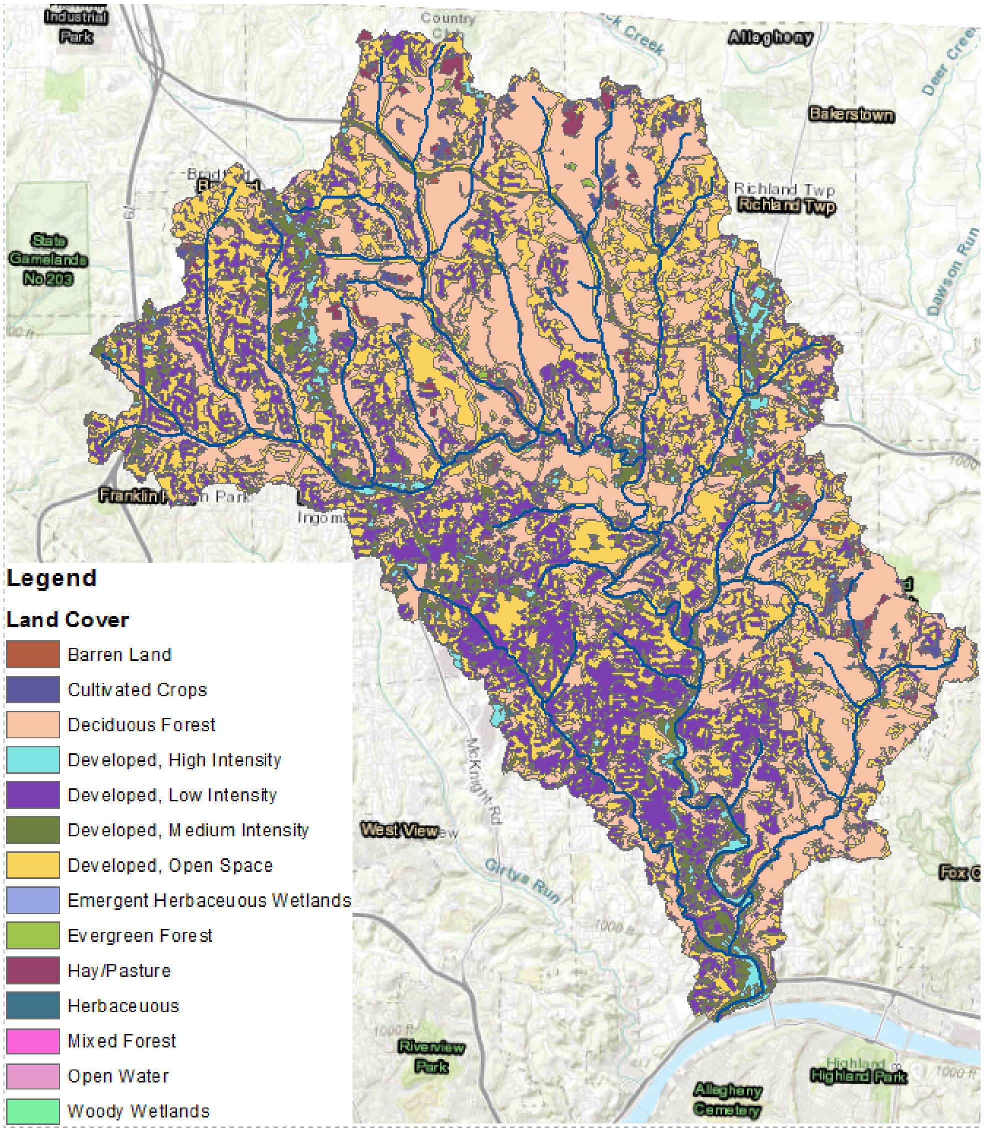


Figure 3. Map of the Pine Creek watershed land cover (ESRI, PASDA, USDA).

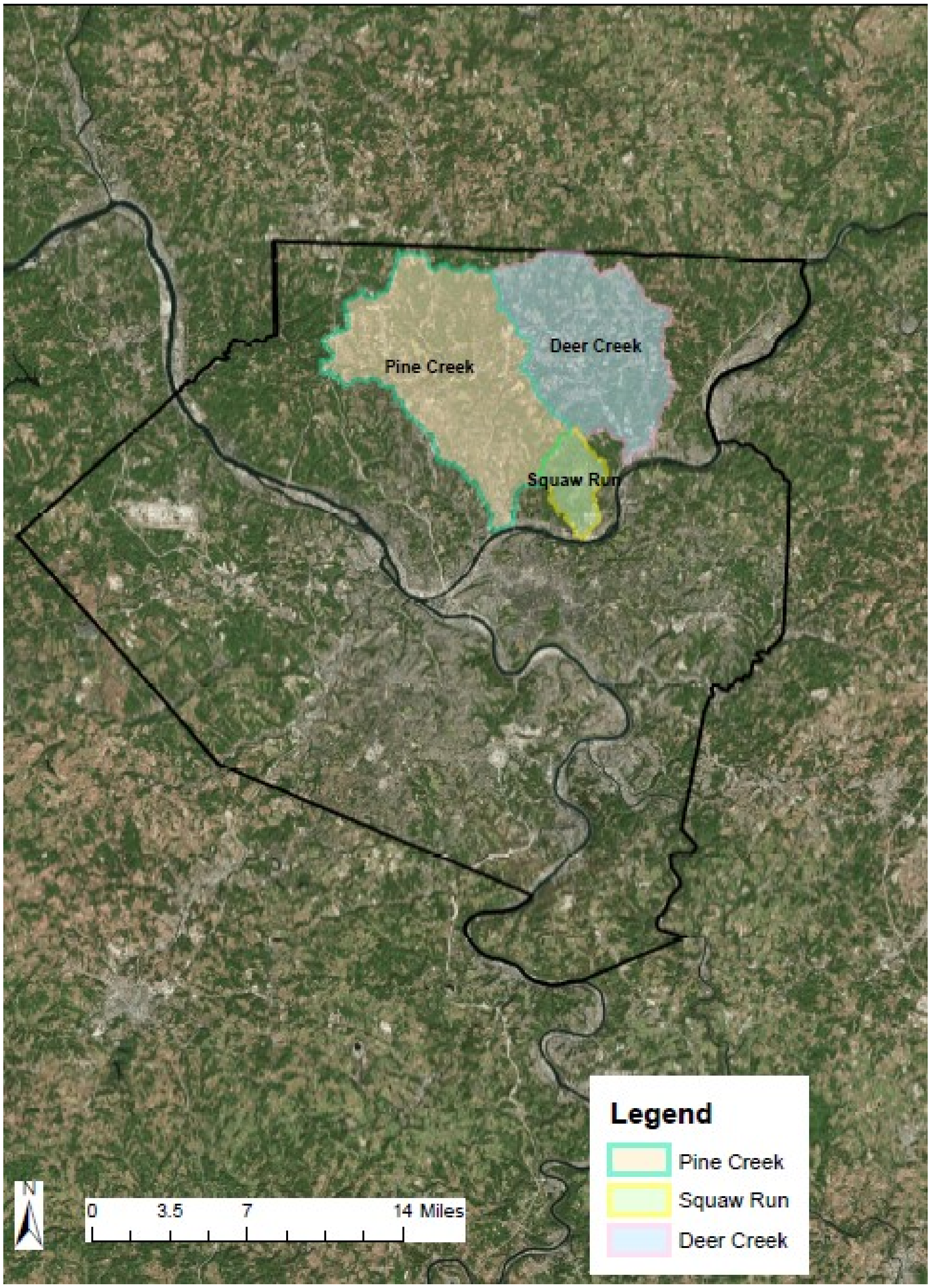


Figure 4. Map of the Pine Creek watershed and neighboring Deer Creek and Squaw Run (ESRI, PASDA, USDA).

North Park Lake is part of the Pine Creek watershed, located in McCandless township. The surrounding forested area has become urbanized, and soils have been disturbed. This has created issues for the lake. Sediments and nutrients have been released, causing eutrophication of the lake. They have also aided in excess algae growth as well as the diminishing depth of the original lake (Mackin, 2010). Remediation of the lake occurred from 2009-2012 under the direction of the United States Army Corps of Engineers (USACE). This project removed sediment and algae from the bottom of the lake to expand the lake to what it once was before. During this dredging project, many efforts were made to improve the area and provide structures to prevent further sedimentation as well as structures to support aquatic species. However, this project also had a negative effect on Pine Creek downstream of this project. Sediment disturbed from the lake flowed downstream in Pine Creek in areas that support trout fishing. This fishing was ruined for years to come due to this new pollution (Hayes, 2012). Furthermore, as of a 2016 PA DEP report, the Pine Creek watershed is considered to be impaired, listed as a category 5 requiring Total Maximum Daily Loads (TMDLs) on the 303d impaired surface waters list (PA DEP, 2016b, 2016a). The 303d list helps to identify bodies of water that do not meet their designated uses therefore considering them to be impaired or threatened. (US EPA, 2015c). Pine Creek's designated uses are cold water fishes (CWF), warm water fishes (WWF), trout stocked fishes (TSF), potable water supply (PWS), industrial water supply (IWS), livestock water supply (LWS), wildlife water supply (AWS), irrigation water supply (IRS), boating (B), fishing (F), water contact sports (WC), aesthetics (E). If all of these designations are not met, it is considered to be impaired leading to potentially setting total maximum daily loads (TMDLs) on pollution entering the stream (*Bacteria TMDLs to Address the Recreation Use Impairment in the Pine*

Creek Watershed Allegheny County, Pennsylvania, 2013; PA DEP, 2013; Pennsylvania Environmental Council & North Area Environmental Council, 2005).

1.1.2 Geology of Watershed

Pine Creek is situated in the Pittsburgh low plateau region of the Appalachian Plateaus. The rock types in this region include shale, siltstone, sandstone, limestone, and coal (DCNR, 2018). Pine Creek specifically is underlain by the Allegheny Formation, Casselman Formation, Glenshaw Formation, and Monongahela Group. The Allegheny Formation is made of layers of sandstone, shale, limestone, clay, and coal. The Casselman Formation is made of shale, siltstone, sandstone, red beds, impure limestone, and non-persistent coal. The Glenshaw Formation is made of shale, sandstone, red beds, thin limestone, and coal. The Monongahela Group is made of limestone, shale, sandstone, and coal (Mackin, 2010). Figure 6 shows a cross section of the geology for a specific section of Pine Creek, North Park Lake which is situated in the red bed, limestone, and sandstone layers.

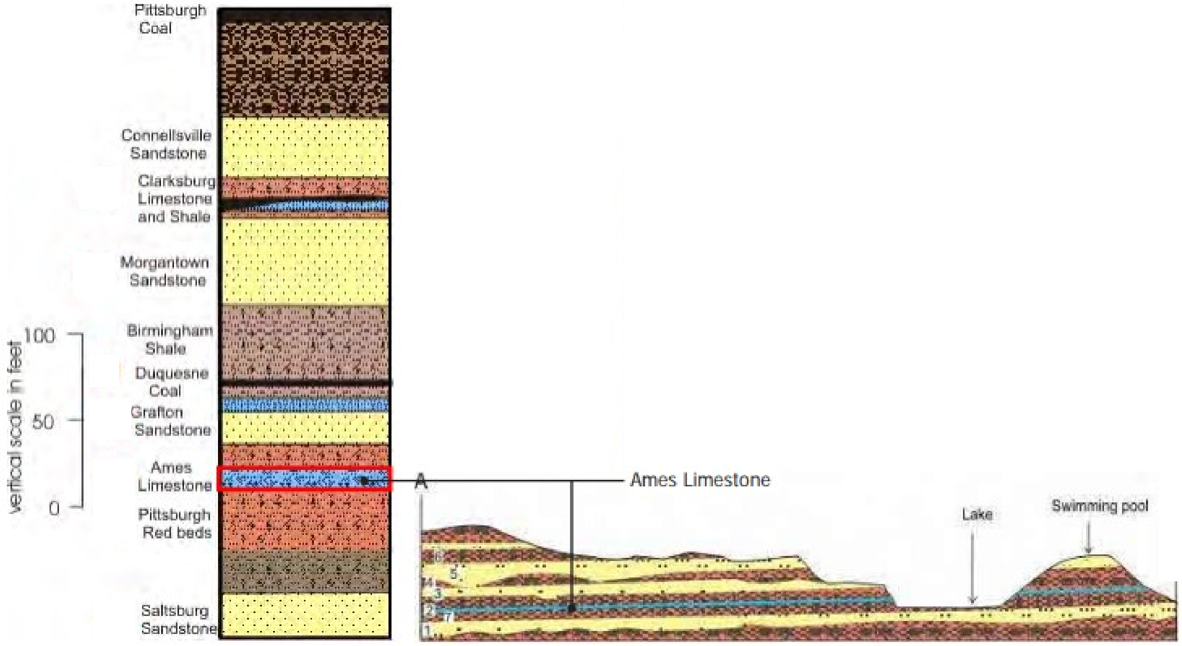


Figure 5. Geological layers of North Park Lake *(*North Park Lake Area Master Plan | Allegheny County Parks Foundation*, 2012)*.

1.1.3 Sources of Pollution

Since Pine Creek is designated as a category 5 water requiring TMDLs to be set from the 303d list, several TMDLs were listed for the watershed (Figure 7) as detailed in Table 2. Sources of pollution include road runoff, abandoned mine drainage, urban runoff and storm sewers, land development, small residential runoff, and on-site wastewater. These identified sources have led to siltation, increased metals, increased nutrient levels, and issues with low dissolved oxygen (PA DEP, 2016a).

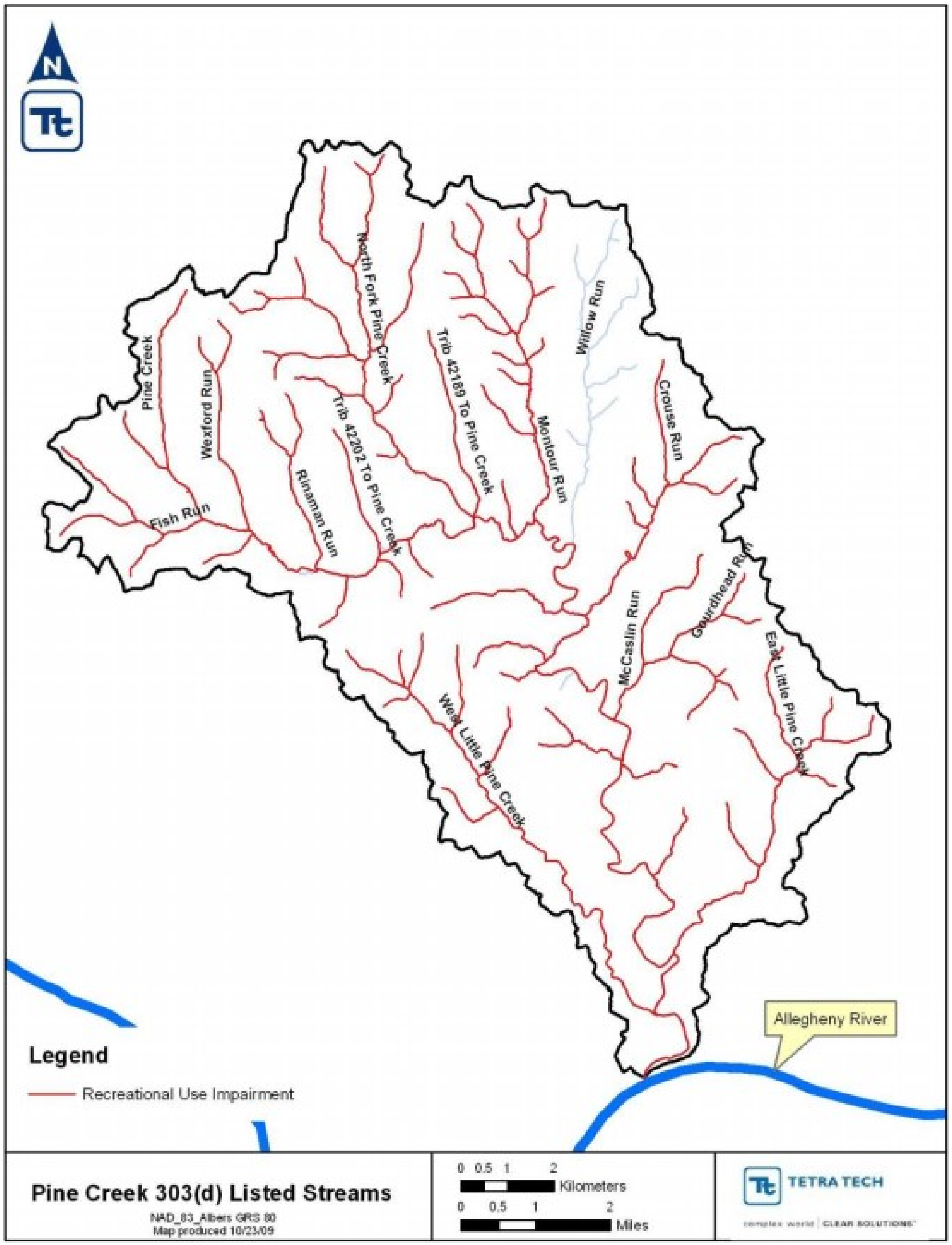


Figure 6. Impaired waters of Pine Creek listed on 303d list for recreational use (Bacteria TMDLs to Address the Recreation Use Impairment in the Pine Creek Watershed Allegheny County, Pennsylvania*, 2013)*.

Table 2. Pine Creek 303d list identifying streams requiring TMDLs for certain pollutant sources, causes, dates of 303d listing, and dates that the TMDLs are in effect *(DEP, 2016)*

Stream Name	Use Assessed	Miles	Source	Cause	Date Listed	TMDL Target Date
North Branch South Fork Pine Creek	Aquatic Life	2.22	Bank/Habitat Modifications Road Runoff	Siltation	2012	2025
South Fork Pine Creek Unnamed To	Aquatic Life	0.57	Abandoned Mine Drainage	Metals	2004	2017
South Fork Pine Creek Unnamed To	Aquatic Life	0.58	Abandoned Mine Drainage	Metals	2004	2017
Little Pine Creek Unnamed To	Aquatic Life	1.07	Urban Runoff/ Storm Sewers	Nutrients	2002	2015
Pine Creek	Aquatic Life	24.09	Land Development Small Residential Runoff	Siltation Nutrients	2002	2015
Pine Creek Unnamed Of	Aquatic Life	0.5	Urban Runoff/ Storm Sewers	Nutrients	2002	2015
Pine Creek Unnamed To	Aquatic Life	0.83	Land Development Urban Runoff/ Storm Sewers	Siltation Nutrients	2002	2015
Pine Creek Unnamed To	Aquatic Life	1.04	Land Development Small Residential Runoff	Siltation Nutrients	2002	2015
Pine Creek Unnamed To	Aquatic Life	1.4	Urban Runoff/ Storm Sewers	Nutrients	2002	2015
Pine Creek Unnamed To	Aquatic Life	0.9	On site wastewater Urban Runoff/ Storm Sewers	Organic Enrichment/ Low D.O. Nutrients	2002	2015
Pine Creek Unnamed To	Aquatic Life	1.1	On site wastewater Urban Runoff/ Storm Sewers	Organic Enrichment/ Low D.O. Nutrients	2002	2015

1.2 Three Rivers QUEST

1.2.1 Program Background

Three Rivers QUEST (3RQ) is a collaborative program focused on water quality monitoring of the Allegheny River, Monongahela River, Ohio River, and their tributaries. The program is overseen by the West Virginia Water Research Institute and involves several groups including Duquesne University, Wheeling Jesuit, and Redhorse Environmental who take monthly water samples from multiple sites and sends them to PACE Analytical for water chemistry analyses. (“3 Rivers QUEST,” 2012). Results are then stored on a shared database for all groups to access.

1.2.2 Sampling Study Area

Western Pennsylvania as well as parts of Ohio and West Virginia are separated into four major river basins: Northern Allegheny, Southern Allegheny, Upper Ohio, and Monongahela (“3 Rivers QUEST,” 2012). These basins can be seen in Figure 1 along with their sub basins. Pine Creek is part of the Lower Allegheny sub basin of the Allegheny River and served as a sampling site for 3RQ samplers from Duquesne University from January 2013 to January 2014, collecting biweekly samples. During this time, it was a site to gather baseline data for the watershed since the Pine Creek Watershed Coalition was no longer routinely monitoring Pine Creek (Dakin, 2019). Pine Creek experienced elevated chlorides when compared to the surrounding watersheds that were sampled. Once a year of baseline data was collected, it was then removed as a 3RQ site to appropriate funds to obtain baselines of other watersheds (Dakin, 2019). In 2018, 3RQ monthly sampling of Pine Creek resumed at the original Grant Street site as well as targeted sampling of four other sites in the Pine Creek drainage to collect pre-winter and winter data.

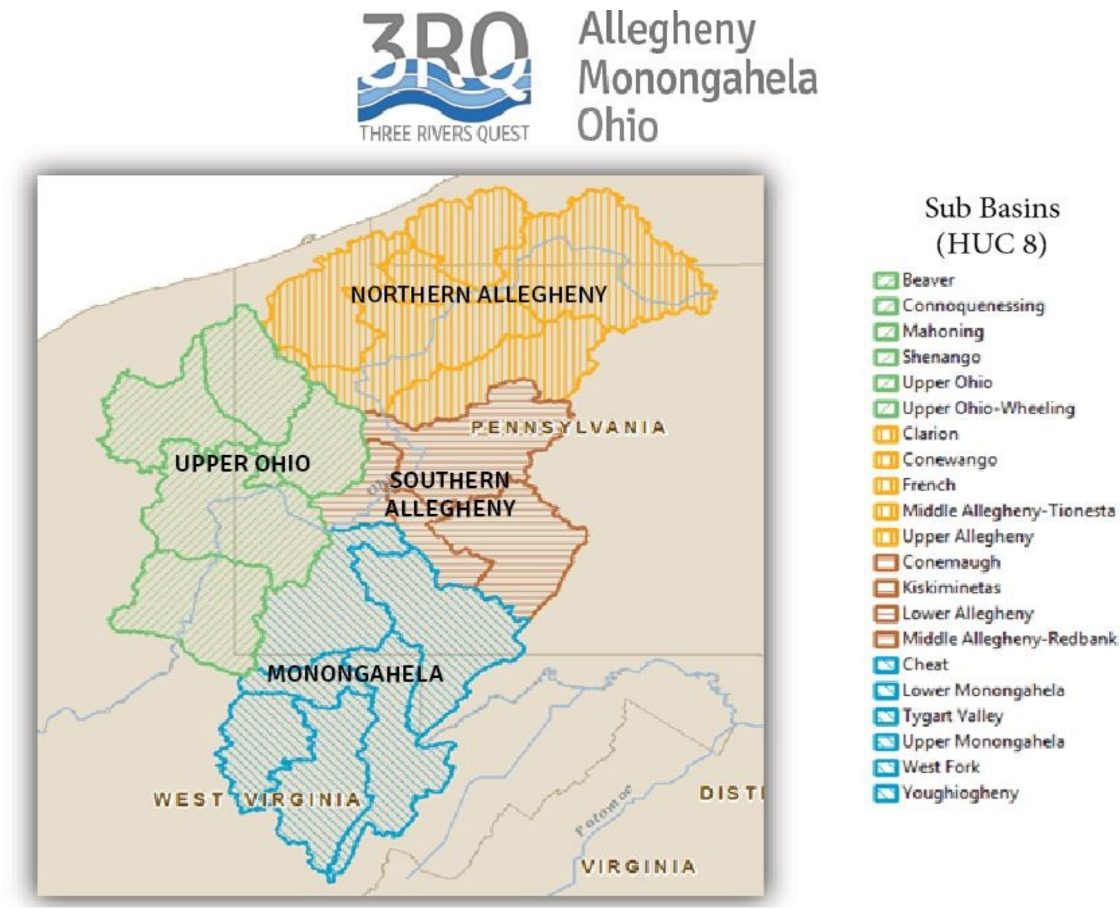


Figure 7. Map of the study area of 3RQ ("3 Rivers QUEST," 2012)

1.3 Salt and Chlorides

1.3.1 Background

There are two routes for chlorides to enter the environment, either anthropogenically or naturally. Anthropogenic sources include road salting, agricultural runoff, wastewater treatment plant effluents, industrial plants discharges, and activities from drilling oil and gas wells (US EPA, 1988). Chlorides in water are not enforceable, however, the United States Environmental Protection Agency (US EPA) has set forth secondary maximum contaminant levels (SMCLs) for chlorides at 250 mg/L. These SMCLs are in place for aesthetic purposes; higher chloride levels can be detected in drinking water by odor and taste. Chlorides can also lead to issues with corrosion of pipes which can also add a metallic flavor to the water and potentially lead to larger issues with water quality (US EPA, 2015a). Since this SMCL is in regards to drinking water, it applies at the intake of water treatment plants to most accurately represent the conditions (SW PA Water Resource Commission & PA DEP, 2013). The US EPA also created an aquatic life criteria table to suggest the highest concentration of chemicals in water that elicit no danger to the inhabiting species or degrade the environment. The maximum acute chloride concentration for aquatic life is 860 mg/L, while the continuous chronic chloride concentration is 230 mg/L. (US EPA, 2015b). Acute conditions were defined as being a period between 24 to 48 hours while chronic conditions vary based upon the species and can be anywhere from 24 to 90 days.

1.3.2 Chloride Movement

Chloride ions hold a negative charge and remain dissolved in water more easily. It does not readily precipitate out as it has a high solubility (100 g/L at 20°C) and there are limited ways to increase chloride concentrations in surface waters such as evaporation, times of low flow, and road deicing. Salt water has a higher density than fresh water, suggesting that road salt runoff can create a stratified saline layer in nearby ponds and lakes that cannot dilute and disperse chlorides through mixing flows. This impacts chemical and biological characteristics of the water (Novotny, Murphy, & Stefan, 2007).

Road salting can alter soil chemistry and ion exchange between sodium and calcium and magnesium. This can also aid in the movement of hydronium ions as well as metals such as zinc and cadmium (Löfgren, 2001). Top soil is exposed not only to salt, but also to evaporation that can concentrate the salinity. This creates a more saline environment and allows for a suitable environment for halophilic bacteria (Elshahed et al., 2004). Elevated chlorides in the soil can also have an effect on the bacterial metabolism by inhibiting nitrification (Groffman, Gold, &

Howard, 1995). Nitrification is an important, aerobic, two-step process that bacteria utilize. They take ammonia and convert it to nitrite which can then be oxidized into nitrate (EPA, 2002). Inhibiting the bacteria's ability to oxidize ammonia hinders the removal process of nitrogen in the water.

1.4 Potential Sources of Chlorides in the Pine Creek Drainage

1.4.1 Road Salting

Chlorides enter the environment through several routes, including processes related to road salting during winter storm events. There are several types of deicers used to treat roads. The most popular is referred to as chloride salt which includes sodium chloride, magnesium chloride, and calcium chloride. Calcium chloride and magnesium chloride both originate from natural brines. Sodium chloride is most commonly used to salt the roads and comes from mining operations as well as natural brines (National Cooperative Highway Research Program, Transportation Research Board, & National Academies of Sciences, Engineering, and Medicine, 2007). Proper storage of these resources is crucial to prevent leaching and loss of product. Salt can leach from storage containers, flowing into and contaminating surface water, groundwater, and soils. Best management practices suggest keeping storage sites away from water sources on impervious surfaces that can be covered and protected from runoff due to precipitation(SW PA Water Resource Commission & PA DEP, 2013). Additionally, treatment can runoff from road applications as well as from snow sites which melt and the salt leaches out (Howard & Haynes, 1993) (Marsalek as cited in (Salt Institute, 2019a).

The goal of road salt application during winter storms is to maintain safe roads for drivers. Pennsylvania Department of Transportation (PennDOT) alone has spread 950 thousand tons of salt on Pennsylvania roads during the 2018-2019 winter (PennDOT, 2019). Roads can be pre-treated or treated during the storm, depending on the severity and conditions. Pre-treatment includes spraying a brine on the roads, which is most effective if rain does not precede snow to wash the treatment off (PennDOT, 2019; Salt Institute, 2019b). This method is more efficient, requiring one-third to one-quarter of the salt of regular salt applications. During a storm, trucks plow the roads and spread salt to minimize snow and ice buildup (PennDOT, 2019). The most common type of salt used is sodium chloride, otherwise referred to as rock salt (Salt Institute, 2019b). It is a cheaper than calcium chloride or magnesium chloride (around $60 a ton) treatment that is easy to obtain, making it a popular choice for road salting (CM IT Solutions of Wexford, 2014). Abrasives, such as sand, can be combined with salts to allow tires to more easily grip the road, however it is not an ideal choice if other options are viable. It is a short-term fix to allow car tires to gain traction with the road, but it does not treat the snow or ice (SW PA Water Resource Commission & PA DEP, 2013). Salt can be pre-wetted with a brine for faster interactions resulting in the snow melting. This also aids in preventing salt loss during the process of spreading. As dry salt is applied to the roads, it bounces further from the intended area, however, pre-wetting prevents this from happening, allowing for more optimal treatment (Salt Institute, 2019b; SW PA Water Resource Commission & PA DEP, 2013). Figure 8 shows the varying conditions in which physical forms of salt can change based upon temperature and concentrations. If road salting does not result in road conditions within the “melting occurs” region, refreezing or crystallization can occur, causing hazardous driving conditions.

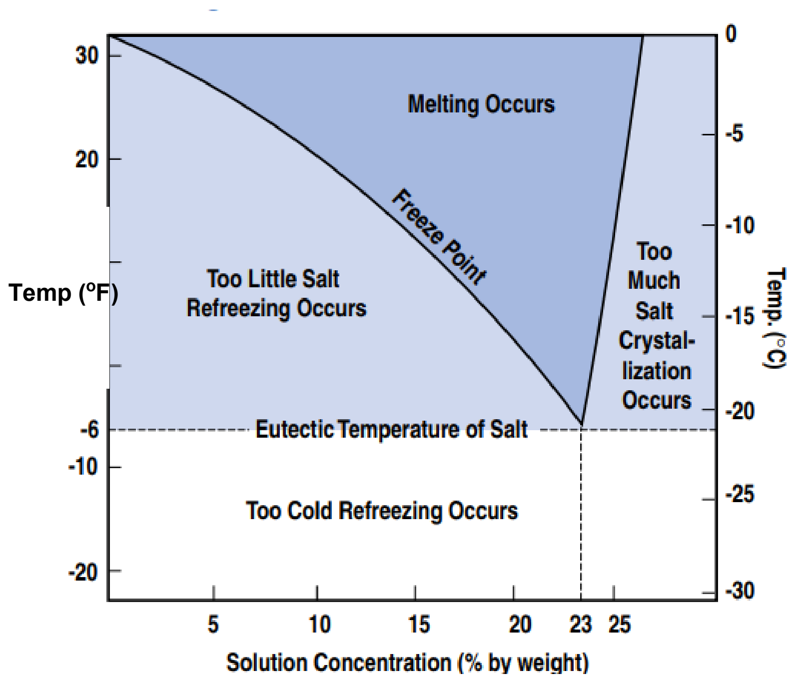


Figure 8. Phase Diagram for salt (sodium chloride) at various concentrations and temperatures. Left axis is in Fahrenheit, and right axis is in Celsius (Salt Institute, 2019b).

Table 3. Salt Institute suggestions for road treatment during winter storm events (Salt Institute, 2019b).

Conditions	Treatment
Temperature: Around 30°F Precipitation: Snow, sleet, freezing rain Road Surface: Wet	Snow/sleet- 500 lbs/ 2-lane mile Accumulation- plow and apply salt Freezing rain- 200 lbs/ 2-lane mile
Temperature: <30°F and decreasing Precipitation: Snow, sleet, freezing rain Road Surface: Wet or sticky	300-800 lbs/ 2-lane mile Accumulation- plow and apply salt Freezing rain- 200-400 lbs/ 2-lane mile
Temperature: <20°F and decreasing Precipitation: Dry snow Road Surface: Dry	Plow without salting Apply salt to treat wet snow or ice
Temperature: <20°F Precipitation: Snow, sleet, freezing rain Road Surface: Wet	600-800 lbs/ 2-lane mile Accumulation- plow and apply salt Temperature increases- 500-600 lbs/ 2-lane mile
Temperature: <10°F Precipitation: Snow or freezing rain Road Surface: Packed snow or ice	800 lbs/ 2-lane mile Alternative: 1500-2000 lbs salt/abrasives / 2-lane mile Accumulation- plow and apply salt Freezing rain- 200-400 lbs/ 2-lane mile

While there are numerous types of winter storms that can be encountered, they have been simplified into five basic scenarios that municipalities face which require different treatments (Table 3). Factors that determine the treatment include temperature, type of precipitation, and whether the surface of the road is wet or dry. The end goal is to melt the snow and ice on the roads with no excess salt leftover, though excess can be left on the roads due to variations in weather forecasts and the calibration performed on the equipment.

1.4.1.1 Consequences of Road Salting

The use of salt to treat roads can lead to several issues that include air quality degradation if the salt dries into a powder and becomes airborne. It can also lower stream and soil quality due to leaching which ultimately can harm the resident species (SW PA Water Resource Commission & PA DEP, 2013). In addition to surface water impacts, ground water can be affected by road salting activities depending on the proximity to the roads or storage facilities (SW PA Water Resource Commission & PA DEP, 2013). A study of the Northeast United States looked into salinization of streams due to road salting. Predictions based on their research show that if current practices are maintained, chloride concentration baselines will remain greater than the current 250 mg/L US EPA secondary standard for drinking water by 2105 (Kaushal et al., 2005). Figure 9 is a generalized description of the various routes that can be taken depending on the amount of impervious surface. As the percent imperviousness increases, so does the amount of runoff as the amount of infiltration decreases. Impervious surfaces have the ability to alter the hydrology of the area, provide a more direct route for pollutants to enter streams, and reduces infiltration into soil (Arnold & Gibbons, 1996; Paul & Meyer, 2001). Kaushal et. al sampled surface waters from Baltimore and found that waters in highly impervious watershed areas had higher chloride levels compared to those with more forested areas (2005). Contributions were mainly due to road salting, as large fluctuations occurred during the winter months (Kaushal et al., 2005). Changes in land use and impervious surface coverage, no matter how small, can have a substantial effect on elevated chloride levels in the streams (Kaushal et al., 2005).

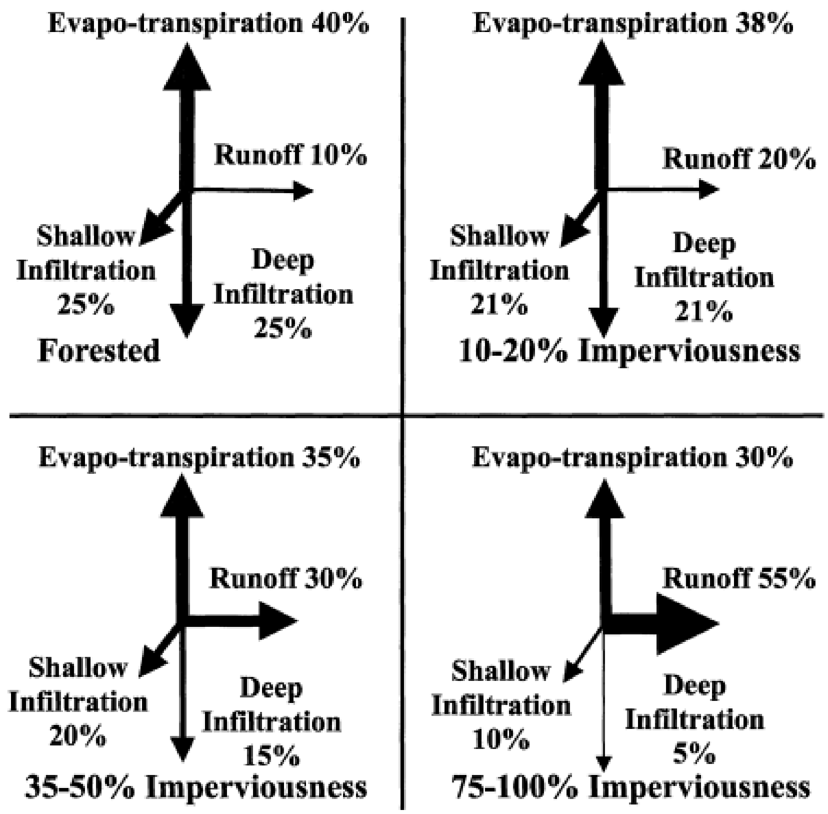


Figure 9. Consequences for different degrees of impervious surfaces relating to runoff compared to infiltration (Arnold & Gibbons, 1996; Paul & Meyer, 2001).

As road salt runs off impervious surfaces, it can end up in nearby surface waters, but it can also end up in shallow groundwater that has access to the water table, resulting in chloride contamination. A study conducted in Toronto, Canada found that 45% of the salt applied to roads that makes its way to nearby surface water is removed (flowing downstream) while the rest is presumed to enter into the groundwater (Howard & Haynes, 1993). As the streams reach baseflow and need to be recharged, chlorides are released from this groundwater source (Howard & Haynes, 1993).

From 1985-1997, PADEP monitored 475 groundwater sites throughout southern Pennsylvania within their Fixed Station Network (FSN) and Ambient Survey groundwater monitoring program. In this timespan, there was a notable and significant increase (more than 10% of the sampling sites) in chloride concentration in the groundwater, which is presumed to be due to human activities, such as road salting (Reese & Lee, 1998).

1.4.1.2 Alternative Road Treatments

Besides using sodium, calcium, or magnesium chloride, organic solutions such as potassium and sodium acetate and formate compounds can be used to treat roads during winter storms (SW PA Water Resource Commission & PA DEP, 2013). These are carboxylic acid derivatives containing carbon, oxygen, and hydrogen (NCBI, 2019). This creates an issue of increased biochemical oxygen demand, as well as increased turbidity and potential metal leaching (Fischel, 2001; SW PA Water Resource Commission & PA DEP, 2013). An unusual alternative comes from beets, specifically unsugared sugar beet molasses, which is a byproduct/waste from the process of removing sugar from the molasses. It also works in temperatures lower than chloride salts (Patent No. 6,080,330, 2000).

1.4.2 Brines

Natural brines are highly saline liquids (ranges upwards of 343 g/L salt concentration) that are found in the geological layers, commonly thousands of feet deep (Dresel & Rose, 2010). These brines are often brought to the surface through gas and oil operations (Dresel & Rose, 2010). Oil and gas wastewater can be used for road treatment in New York (not pictured), Ohio, and Pennsylvania (Figure 10). This raises several potential hazards similar to those associated with standard salting methods (Tasker et al., 2018). This type of treatment is used for treatment of unpaved, dusty roads for dust control and deicing as approved by the PA DEP (PA DEP, 2011). This, however, is not used in the Pine Creek watershed at this time, and is more commonly used in northwestern Pennsylvania (Tasker et al., 2018).

Brines come from a variety of sources. In western Pennsylvania, salt has been harvested from the Kiskiminetas River, Conemaugh River, and the Allegheny River due to the accessibility of brine from shallow wells that were created from ancient oceans (Dzombak, 2004). The shallow water brine includes remains of marine plants that contained bromine and iodine salts (Dzombak, 2004). One local salt formations is the Salina Formation, a salt bed that is very deep in western Pennsylvania, however this formation is too deep to contribute to salinization of surface waters (Dzombak, 2004).

Another source of brine in western Pennsylvania is preserved at areas where the geology has changed over time. Ocean water became trapped in the pore space from the sand of the ancient beach. This sand became compressed, forming sandstone containing brine water (Dzombak, 2004). Brines at shallow depths have resulted due to the presence of anticlines, or the upward hills of a region, and synclines, or the valleys in between (Dzombak, 2004). Salt works, were salt was actively produced, were commonly built on anticlines (Dzombak, 2004).

Surface brines vary based on the rock formations in which they resided (Dresel & Rose, 2010). Deeper brines typically contain higher salinity, but in southwestern Pennsylvania, the brines are shallow. As brines were extracted for the salt industry, brine would flow towards the extraction site to refill what was lost. Brine chemical compositions and concentrations can change through modifications such as dilution through precipitation (Piper, 1933). Just a note, there have not been any oil and gas wells directly within the Pine Creek watershed ("PA Oil and Gas Mapping," 2019).

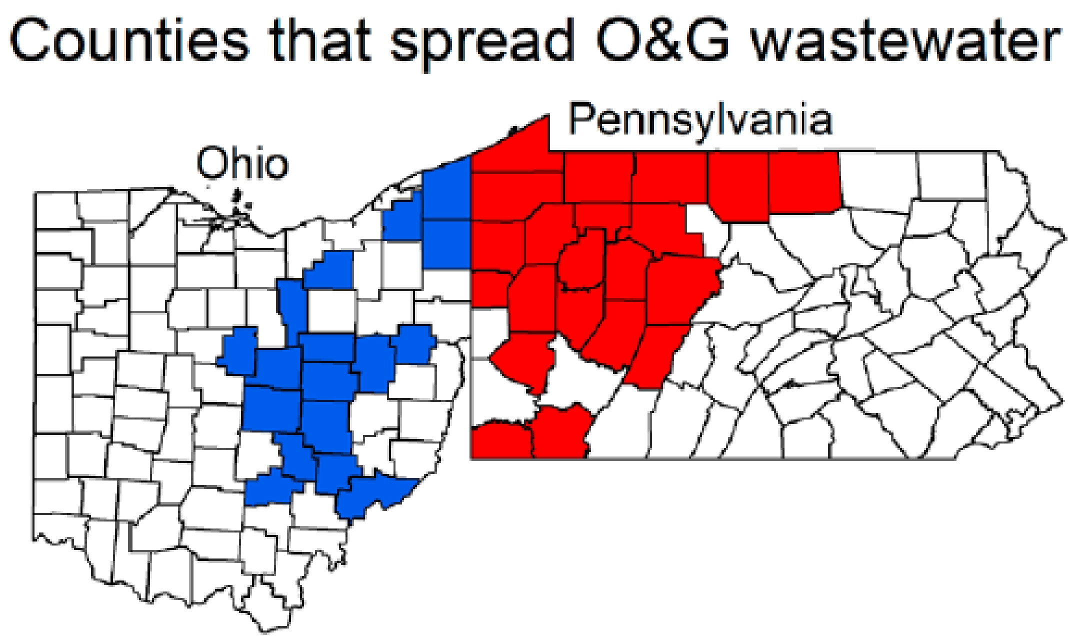


Figure 10. Counties in Ohio and Pennsylvania that spread oil and gas wastewater on roads (Tasker et al., 2018).

1.4.3 Agriculture

Agricultural discharge such as fertilizer and livestock waste can runoff into nearby streams and with it, contribute to elevated chloride concentrations. As the land is cultivated, the native plants are replaced with others suitable to farm. Plowing of fields can uproot salts in the soils that are released, and combined with irrigation to maintain these crops, this creates runoff that allows the salts to seep into the streams (Williams, 2001).

Salinization can also create issues for the agricultural industry. Salinity can reach a lethal concentration for crops, which has serious economic effects on agriculture (Williams, 2001).

1.4.4 Wastewater

Pine Creek was listed as impaired and is required to follow TMDLs set forth by the EPA due to high fecal coliform counts. A model of the ALCOSAN system revealed that the lower portion of Pine Creek is prone to sewer line leakages (Hopkins & Bain, 2018). These leaks could contribute to the high coliform counts as well as chloride contamination from unprocessed salts from the human body (Dzombak, 2004). Other contributing sources include combined sewer overflows (CSO) that release excessive rainwater mixed with untreated wastewater (“Watershed Profile,” 2012).

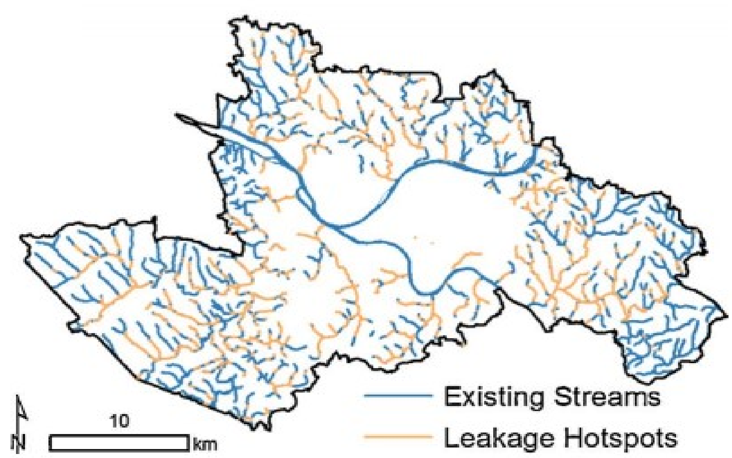


Figure 11. Alcosan service area predicting wastewater leakage hotspots based upon age, pipe material, and stream location.

1.5 Effects of Chlorides

1.5.1 Aquatic Life and Riparian Vegetation

Elevated chloride levels can offset the balance of the ecosystem and alter the biodiversity of the stream (Williams, 2001). As the waters become more saline, the less salt tolerant, or halosensitive species, will die off and the more salt tolerant, or halotolerant species, will thrive (Williams, 2001). Tolerance indicator values are used to assess survivability as to what species are considered to be tolerant, moderate, or intolerant. Tolerant fish species were determined to survive in a chloride concentration mean of 38.5 mg/L as determined by Meador and Carlisle. If they had a tolerance indicator value from 7-10, they were considered to be tolerant to chloride. Moderate species survive in a mean chloride concentration of 27.0 mg/L. Tolerance indicator values from 4-6 were considered to be moderately tolerant. Intolerant species can survive in a mean chloride concentration of 17.3 mg/L (Meador & Carlisle, 2007). Tolerance indicator values from 0-3 were considered intolerant to chloride.

Aquatic species are not the only ones affected by salts. Riparian plants located near the site of road treatments can also be harmed. As the salt runs off the road, it can end up in the soil, altering the health of the vegetation. Areas with soil chloride concentrations of 31.3 mg/L in December were noted to have moderate to severe tree damage. This concentration went down to 5.12 mg/L in April (*Priority substances list assessment report*, 2001). Sites with minimal tree damage had a soil chloride concentration of 7.2 mg/L in December and decreased to 2.9 mg/L in April (*Priority substances list assessment report*, 2001).

1.5.2 Humans

Chloride toxicity depends on the cations associated with the chloride anions based on their biological need and biochemical processes. Various salt toxicities are shown in Table 4. Sodium chloride has been shown to be lethal to a nine-week-old child at 1 gram of sodium chloride per kilogram (World Health Organization, 1979). Lethal dose that kills 50% of the sample population (LD50) is used to represent toxicity of chemicals. The LD50 for sodium chloride in rats was shown to be 3.75 $\pm$ 0.43 grams per kilogram (World Health Organization, 1979). Symptoms of increased salt intake include diarrhea, muscular abnormal functions, dehydration, convulsions, and death (World Health Organization, 1979). Besides the adverse consequences from consuming chlorides, increased salt content in water can also cause metals from water distribution systems to leach into drinking water (World Health Organization, 1979).

Table 4. Various salt exposure and dose concentrations leading to toxicity for common salts used for road deicing events. LDL_0 represents the lowest dose to kill animals exposed for 24 hours or less. LD_{50} represents the dose that kills 50% of the animal sample population *(World Health Organization, 1979)*

Compound	Animal	Exposure	Dose
$CaCl_2$	Rat Mouse Rat	Oral Intraperitoneal Intraperitoneal	LD_{50} – 1000 mg/kg LD_{50} – 280 mg/kg LDL_0 – 500 mg/kg
$MgCl_2$	Rat Mouse Rat	Oral Intraperitoneal Intraperitoneal	LD_{50} – 2800 mg/kg LD_{50} – 342 mg/kg LDL_0 – 225 mg/kg
NaCl	Rat Mouse Man	Oral Intraperitoneal Oral	LD_{50} – 3000 mg/kg LD_{50} – 2602 mg/kg LDL_0 – 8200 mg/kg 23 day

CHAPTER 2: SPECIFIC AIMS AND HYPOTHESES

2.1 Specific Aims

This thesis involved comparing contemporary and historical data on the Pine Creek watershed to analyze any chloride patterns temporally. The goals were:

1. Determine seasonal fluctuations of chloride in Pine Creek by collecting samples at regular intervals to create a dataset
2. Determine if chloride levels have changed long-term by looking at historical data for the watershed
3. Identify how chloride levels have impacted aquatic life in the system by conducting fish surveys
4. Determine potential connections between groundwater and surface water interactions through well and nearby surface water chemical analysis comparisons

2.2 Hypotheses

1. Road salting activity due to snow and ice lead to elevated chloride levels in the winter months
2. Chloride levels have increased over time due to increased use of road salting
3. Fish surveys can be useful in providing an indication of the impact on chlorides in the system

CHAPTER 3: MATERIALS AND METHODS

3.1 Surface Water Sampling

3.1.1 Sample Collection and Lab Analysis

A targeted study was conducted on five sites throughout the Pine Creek watershed to obtain water chemistry data before and during the snow season, sites shown below in Figure 12. Surface water samples were collected in 1-liter plastic containers, one per sampling site. An additional 250mL sample was collected and filtered using a 0.45 um nitrocellulose membrane (Merck) and a hand vacuum pump. Samples were stored in a plastic bottle containing nitric acid to analyze the dissolved metals. All samples were kept in a cooler filled with ice and stored at 4^{o}C until pick-up. Samples were sent to Pace Analytical under chain of custody protocol for analysis shown below in Table 5.

Table 5. Reporting limits for Pace Analytical water chemistry analyses.

Analyte	Reporting Limit	Analytical Method	Preparation Method
Dissolved Aluminum	0.050 mg/L	EPA 6010B	EPA 3005A
Dissolved Iron	0.070 mg/L	EPA 6010B	EPA 3005A
Dissolved Manganese	0.0050 mg/L	EPA 6010B	EPA 3005A
Dissolved Calcium	1.0 mg/L	EPA 6010B	EPA 3005A
Dissolved Magnesium	0.20 mg/L	EPA 6010B	EPA 3005A
Dissolved Sodium	1.0 mg/L	EPA 6010B	EPA 3005A
Dissolved Strontium	0.50 ug/L	EPA 6010B	EPA 3005A
Total Alkalinity (CaCO3)	10.0 mg/L	SM2320B-97	
Total Dissolved Solids	10.0 mg/L	SM2540C-97	
Bromide	0.020 mg/L	EPA 300.0	
Chloride	25.0 mg/L	EPA 300.0	
Sulfate	25.0 mg/L	EPA 300.0	

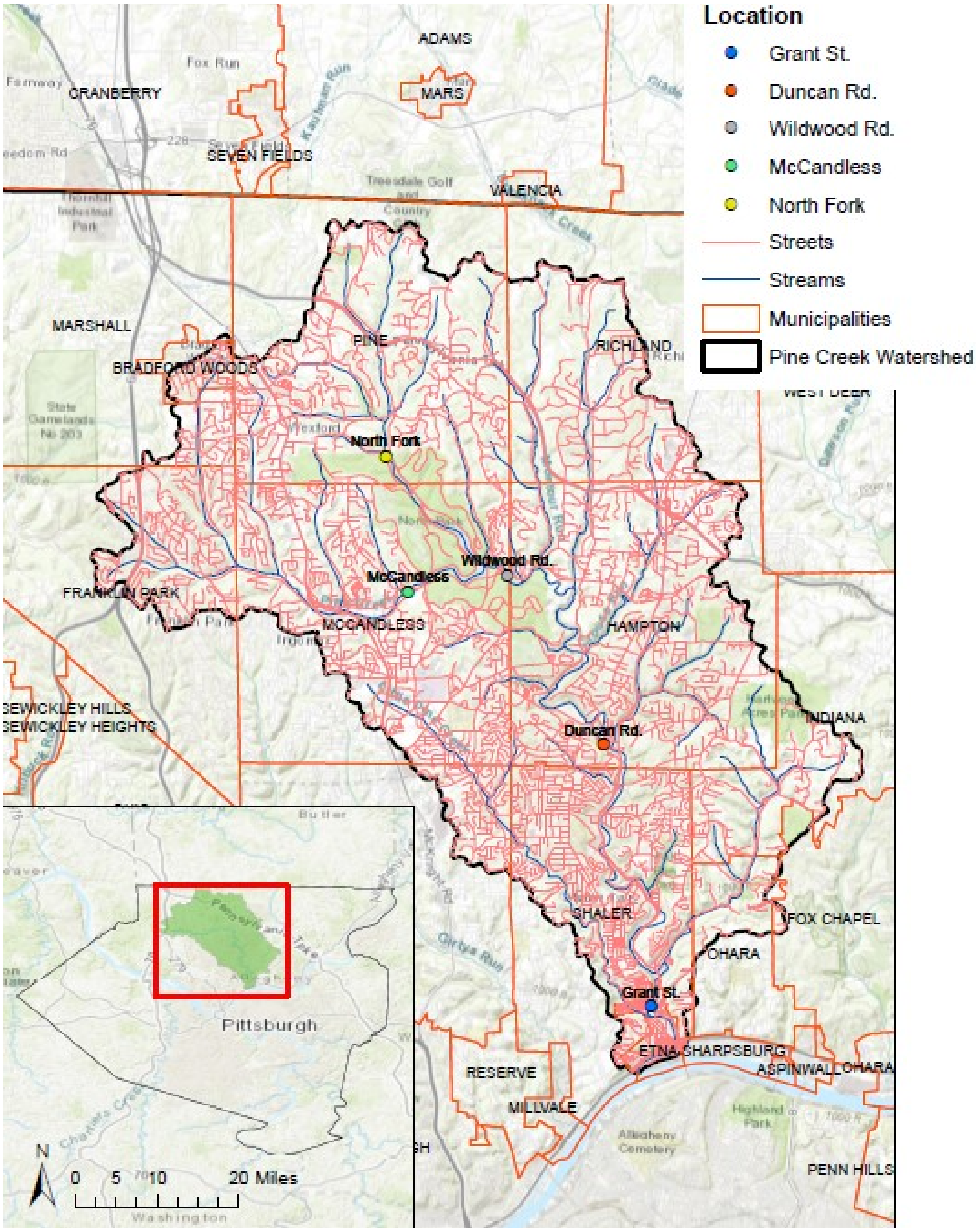


Figure 12. Locations for the Prettner five-site targeted study of Pine Creek.

From these analyses, yields were calculated for the contaminants using the equation below. Units were expressed as tons per day per watershed square mile.

$$Yield = \frac{contaminant\ concentration\ x\ stream\ discharge}{drainage\ area}$$

Chloride flux was calculated for Grant Street for the three sampling time periods using the equation below. Units were expressed as tons per day.

$$Flux = stream\ discharge\ x\ contaminant\ concentration$$

3RQ data was used to create a standard curve for determining chloride concentrations based upon SPC readings (Figure 13). A cubic function was used for the trendline equation for a better R^2 value. It also helped to address issues brought about when setting the intercept. The assumption when using SPC to determine chloride is that if SPC is zero, the chloride concentration would also be zero, as it is the main contributor to SPC in Pine Creek.

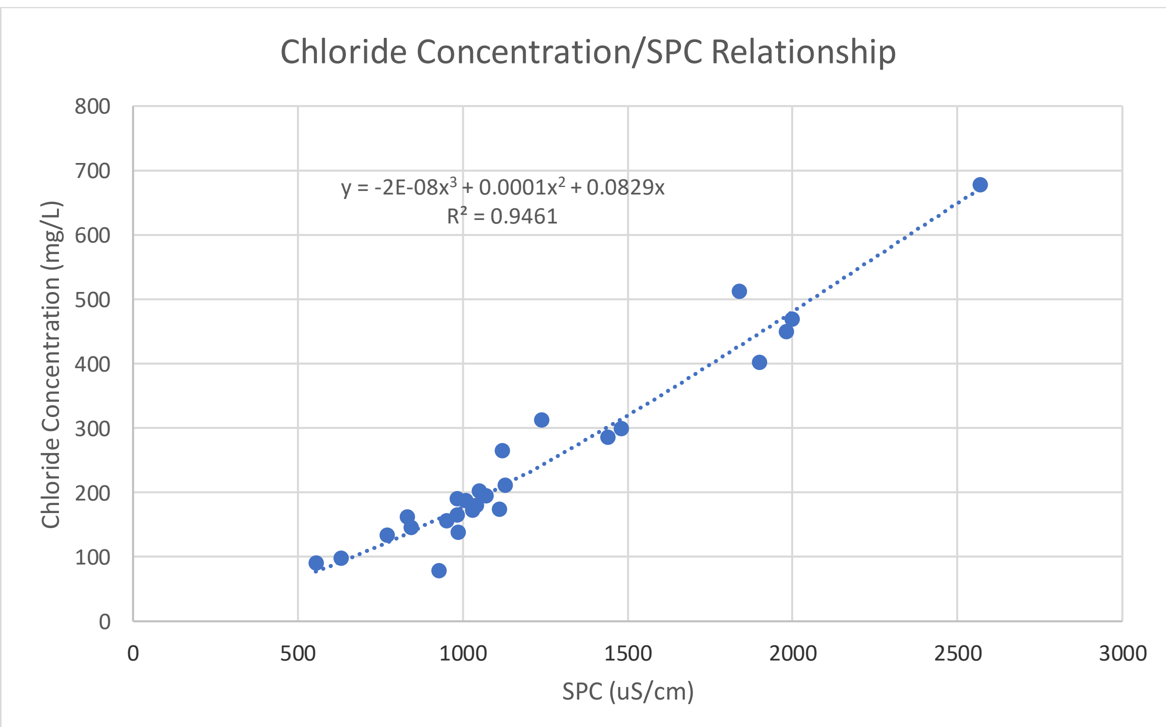


Figure 13. Standard curve for chloride determination using 2013-2014 3RQ data at Grant Street site.

3.2 Field Data

3.2.1 YSI Data Collection and Flow Measurement

A YSI-Pro Multimeter (YSI Incorporation, Yellow Springs, OH) was used to collect snapshot data of the water. Data collected included water temperature (°C), air temperature (°C), specific conductance (uS/cm), conductivity (us/cm), pH, barometric pressure (mm Hg), DO%, and DO (mg/L). Flow (ft/s) was collected using a Marsh McBrinley Flowmate, and depth (ft), and width (ft) of sampling site were measured in order to calculate discharge (ft^3/s).

3.2.2 Other Physical and Chemical Parameters

Chlorides were measured in the field using the Hach 8-P test kit. Chloride concentrations were determined following the accompanying Hach 8-P instructions. Turbidity was measured using the Hach 2100P portable turbidimeter, and the turbidimeter instructions were followed to determine NTUs.

Yield was calculated to compare sampling sites based upon a few factors. Those considered include pollutant concentration, stream flow, and drainage area to obtain units of tons per day per watershed square mile. It was calculated by multiplying the concentration by the unit conversion, then dividing by the specified site's drainage area (determined using Stream Stats).

3.2.3 Conductivity

With the assistance of Lou Reynolds, USEPA Region 3, a data logger (HOBO Conductivity Logger) was placed at Pine Creek (Grant St.) in Etna, PA on May 10, 2018 to collect conductivity readings every 30 minutes. After a span of months (May-September 2018), the data was downloaded and HOBO data assistance software (ONSET, HOBOware) was used to correct the data. It corrected for drift using the initial and final readings of the YSI-Pro

Multimeter readings of conductivity and specific conductivity as well as converted the conductivity into specific conductance. USGS gage, Pine Creek at Etna (03049807) was used to record gage height. From 3RQ data, flow was extrapolated from recorded gage heights. Specific conductance data for the winter period (September 2018-April 2019) was unable to be collected due to an issue with relaunching the probe.

3.2.4 Historical Data

Data including specific conductivity obtained for Pine Creek from 2002 to 2007 was gathered from reports created by the Environmental Alliance for Senior Involvement (EASI) and Pennsylvania Senior Environment Corps (PaSEC) program for the North Area Environmental Council (S. Prettner, personal communication, August 27, 2018). Groundwater and surface water samples from Pine Creek collected by Linnea Manley in 2016 were also included in this study (Manley, 2017)

. Further, 3RQ data gathered at the Grant Street site from January 2013 to January 2014 were used to determine a standard curve to calculate chloride concentrations from specific conductance readings (Figure 14). The use of this standard curve gave way to the ability to estimate the chloride concentrations based upon continuous logger readings.

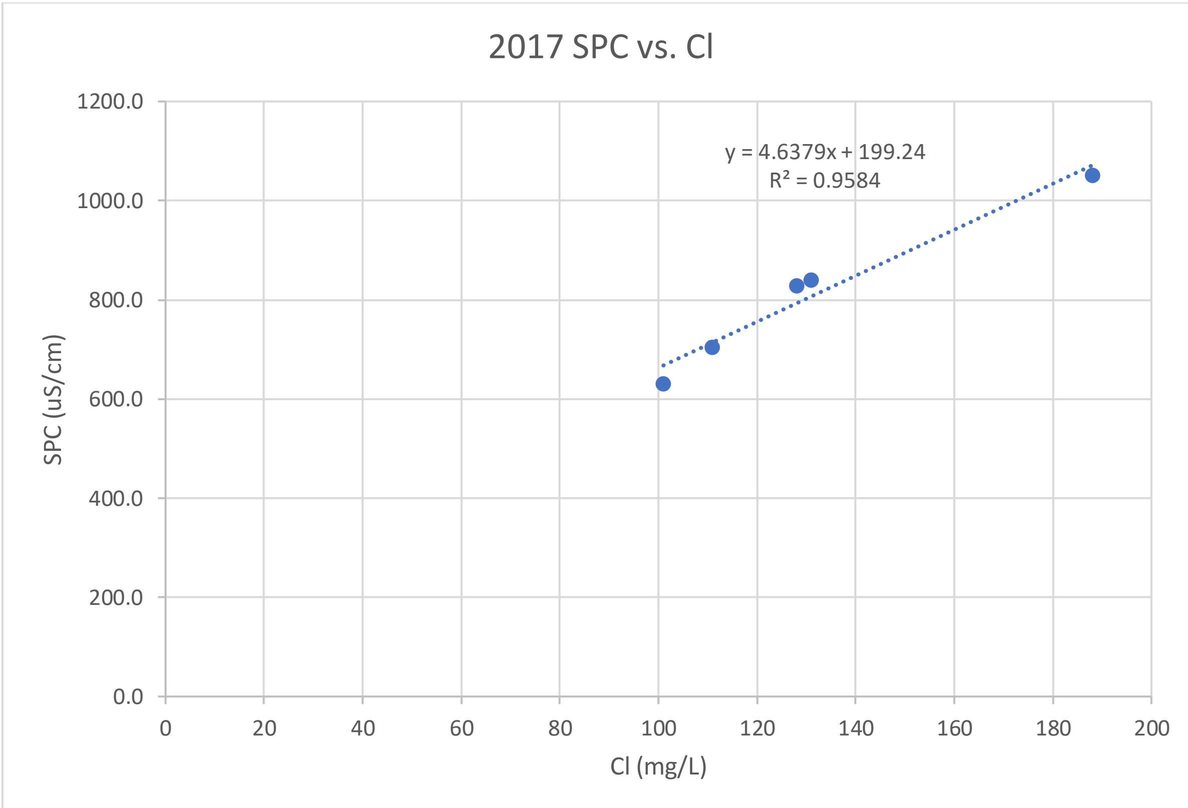


Figure 14. Five site study on Pine Creek in November 2017 showing direct chloride relationship with specific conductivity.

3.3 GIS Mapping

3.3.1 Land Coverage Determination

Data was collected for the area of Pine Creek and projected in the NAD 1983 (US Feet) coordinate system. Datasets included the Allegheny County boundary selected by location from the Pennsylvania county boundaries. The same was done for the hydrologic unit code (HUC) 12 dataset to select the Pine Creek area, and then the two sub watersheds of interest were merged using the editor tool. In the HUC 12 attribute data, area was calculated using the calculate geometry function ("Data | Multi-Resolution Land Characteristics (MRLC) Consortium," 2016; "Pennsylvania Spatial Data Access," 2019; ESRI, 2019).

Soil data was obtained from the USDA's web soil survey in which soil types were then classified into hydrologic soil groups A-D in the shapefile's attribute data (USDA, 2019). Soils that had excessive drainage were placed into group A. Soils with proper drainage were group B. Soils that had moderately poor drainage were grouped into C. Soils with poor drainage were put into group D.

Land use raster data was clipped to the Pine Creek area using the raster clip tool. It was then converted to a polygon and dissolved based upon the land use category. Symbology was added to show the different areas of land use. Calculations were performed in the attribute table. Percent of cover was added as an attribute and the field calculator was run in which it divided the area by the total area.

3.4 Electrofishing

Electrofishing was conducted on October 16, 2018 for Pine Creek towards the headwaters. Historical data was available for the Pine Creek headwaters, which has historically been known to be higher quality water. Electrofishing was conducted using an electrofishing backpack (Smith-Root LR-24), a seine, as well as hand nets. Stream sampling length was ten times the stream width or a minimum of 100M.

Fish species had a chloride tolerance level in which tolerance was determined on a scale from 0-10. They were also grouped into a stream condition tolerance level of tolerant, moderate tolerance, and intolerant by Carlisle and Meador (2007), however chloride tolerance values will be the main focus. Tolerance indicator values from 7-10 were grouped as tolerant to chloride. 4-6 were moderately tolerant and 0-3 were intolerant to chloride.

CHAPTER 4: RESULTS

4.1 Seasonal Chloride Data

4.1.1 3RQ Monthly Monitoring Data

Water quality data was collected by 3RQ from 2013-2018 and the chloride results for the 21 lower Allegheny River sites sampled by Duquesne University are shown below in Figure 15. Data displayed includes a median represented by the line within the box-and-whisker plot and mean (x). The lower and upper portions of the box represent the lower and upper quartiles. Pine Creek noticeably stands out when compared to the other sites.

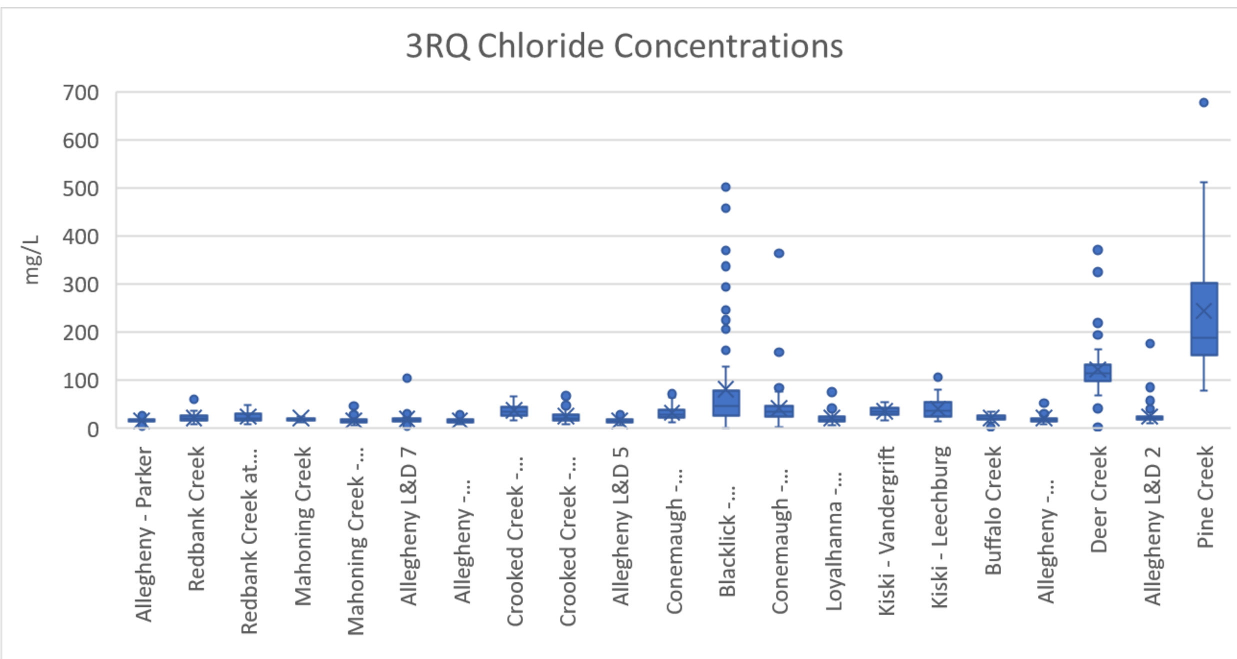


Figure 15. 3RQ chloride sampling concentrations compared with Pine Creek (2013-2018 data) (Dakin, 2019).

Biweekly chloride concentrations of Pine Creek at Grant Street are shown below in Figure 16 along with the secondary drinking water standard and freshwater aquatic life chronic life concentration limit.

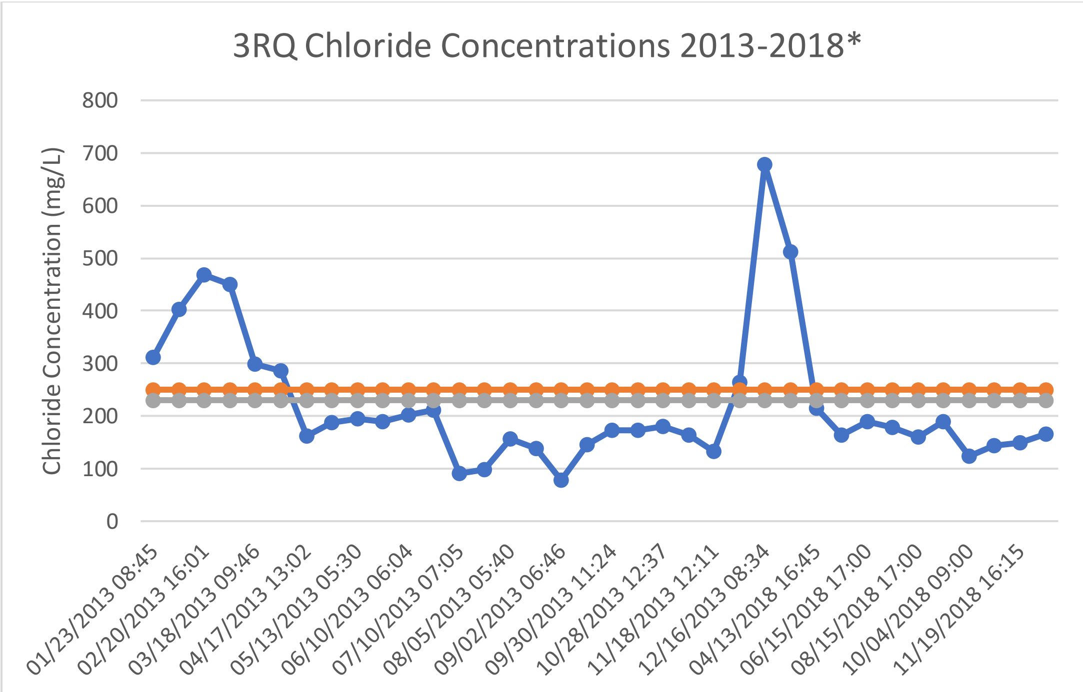


Figure 16. Grant Street site chloride concentrations from Pace Analytical. Accompanying lines represent the USEPA secondary drinking water standard as well as the aquatic life chronic concentration limits, both unenforceable. * Data was not collected continuously for the full amount of time.

Chloride flux was calculated for the Grant Street site towards the mouth of Pine Creek for November 2017, March 2018, and October 2018 to note for any changes in chlorides between pre-salting and post-salting times (Table 6).

Table 6. Calculated chloride flux at Grant Street which is the closest sample site to the mouth of Pine Creek.

Grant Street	Chloride Concentration (mg/L)	Flux (mg*ft^3/L*s)	Yield (Tons per day per watershed square mile)
November 2017	131	4240	0.19
March 2018	225	9740	0.44
October 2018	123	11568	0.52

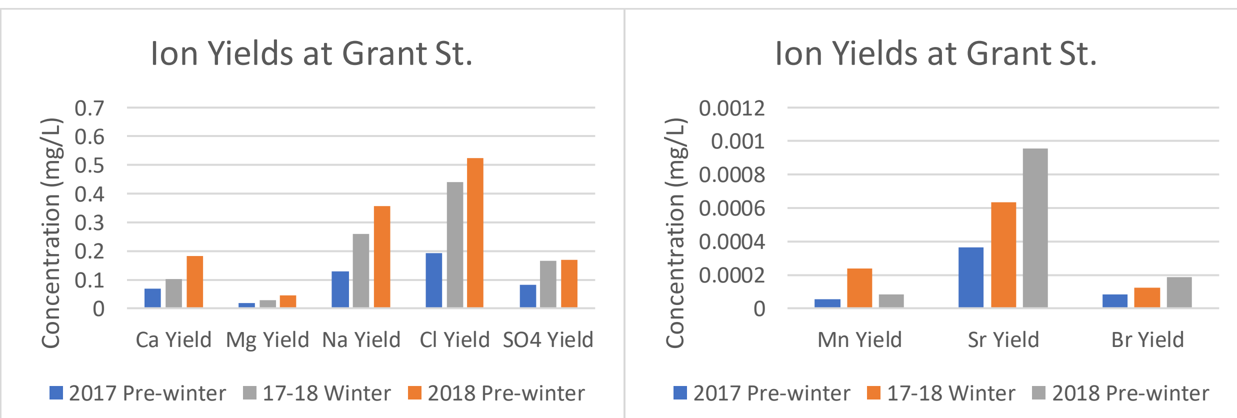
4.1.2 Pine Creek Prettner 5-Site Targeted Study

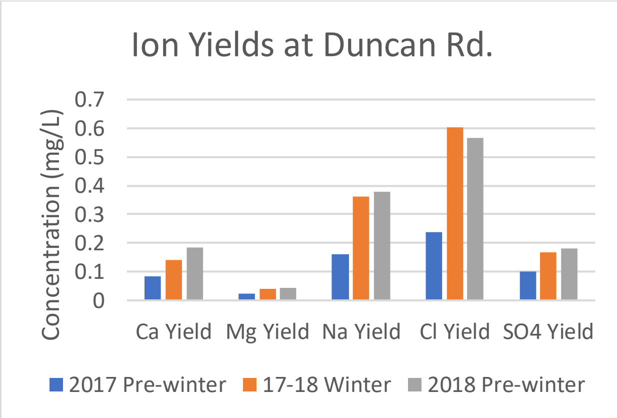
Five sites along Pine Creek were sampled in November 2017, March 2018, and October 2018. Flow was determined for each site for each of the 3 sampling time periods (Table 7).

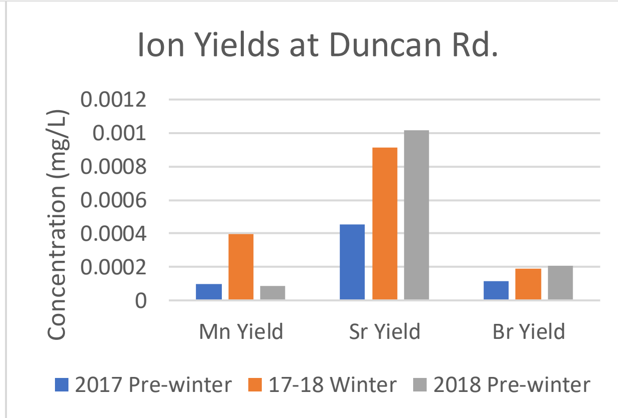
Table 7. Flow measured for each of the Prettner 5-site targeted study.

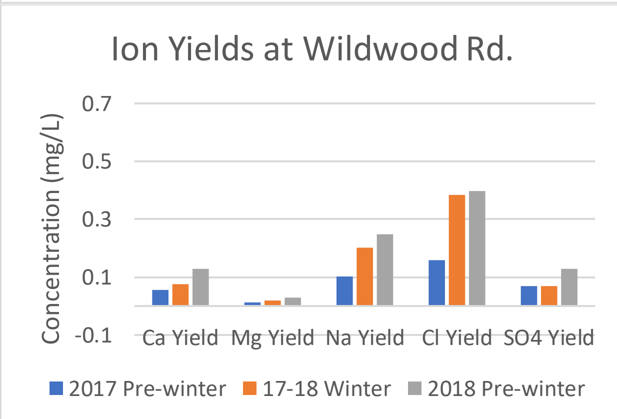
Site	November 2018	March 2019	October 2019
Grant St.	32.37	43.29	94.05
Duncan Rd.	30.06	45.35	72.65
Wildwood Rd.	14.41	14.73	33.75
McCandless	4.30	3.64	9.73
North Fork	6.28	6.23	17.65

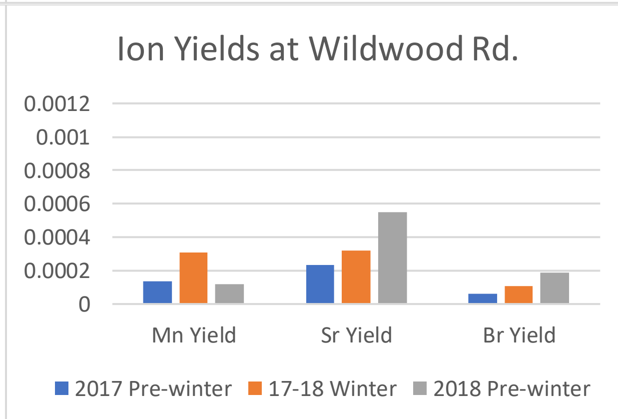
Ion yields from these samples are shown in Figures 17, 18, and 19. Data was split into two graphs per site due to varying scales. Graphs are arranged from downstream, closest to the Allegheny River, to upstream. Each sampling time was compared to one another in terms of yield and labeled as the year and either pre-winter (October or November) or winter (March).

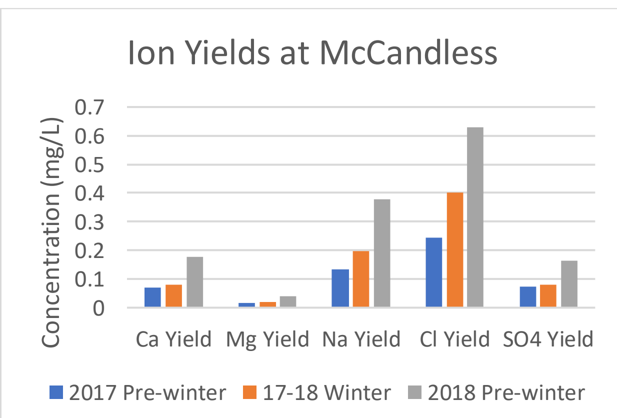


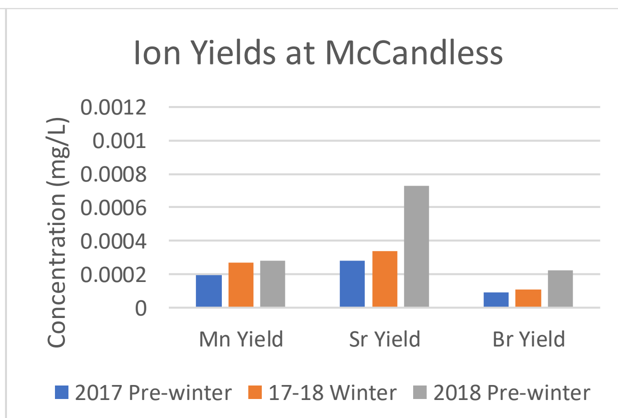

Ion Yields at Duncan Rd.
Concentration (mg/L)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Ca Yield
Mg Yield
Na Yield
Cl Yield
SO4 Yield
2017 Pre-winter
17-18 Winter
2018 Pre-winter


Ion Yields at Duncan Rd.
Concentration (mg/L)
0.0012
0.001
0.0008
0.0006
0.0004
0.0002
0
Mn Yield
Sr Yield
Br Yield
2017 Pre-winter
17-18 Winter
2018 Pre-winter


Ion Yields at Wildwood Rd.
Concentration (mg/L)
0.7
0.5
0.3
0.1
-0.1
Ca Yield
Mg Yield
Na Yield
Cl Yield
SO4 Yield
2017 Pre-winter
17-18 Winter
2018 Pre-winter


Ion Yields at Wildwood Rd.
0.0012
0.001
0.0008
0.0006
0.0004
0.0002
0
Mn Yield
Sr Yield
Br Yield
2017 Pre-winter
17-18 Winter
2018 Pre-winter


Ion Yields at McCandless
Concentration (mg/L)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Ca Yield
Mg Yield
Na Yield
Cl Yield
SO4 Yield
2017 Pre-winter
17-18 Winter
2018 Pre-winter


Ion Yields at McCandless
Concentration (mg/L)
0.0012
0.001
0.0008
0.0006
0.0004
0.0002
0
Mn Yield
Sr Yield
Br Yield
2017 Pre-winter
17-18 Winter
2018 Pre-winter

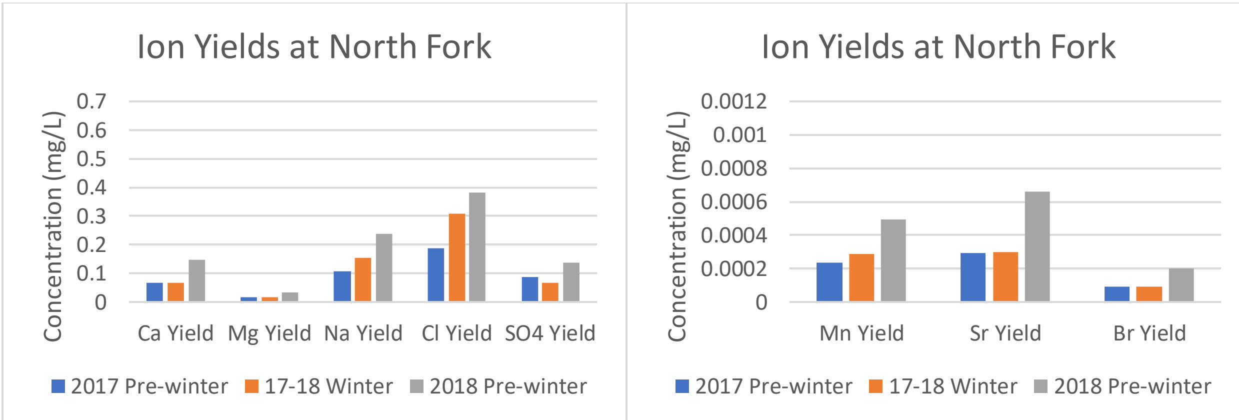


Figure 17. Water chemistry yields from the five-site study comparing data before deicing events with a deicing event.

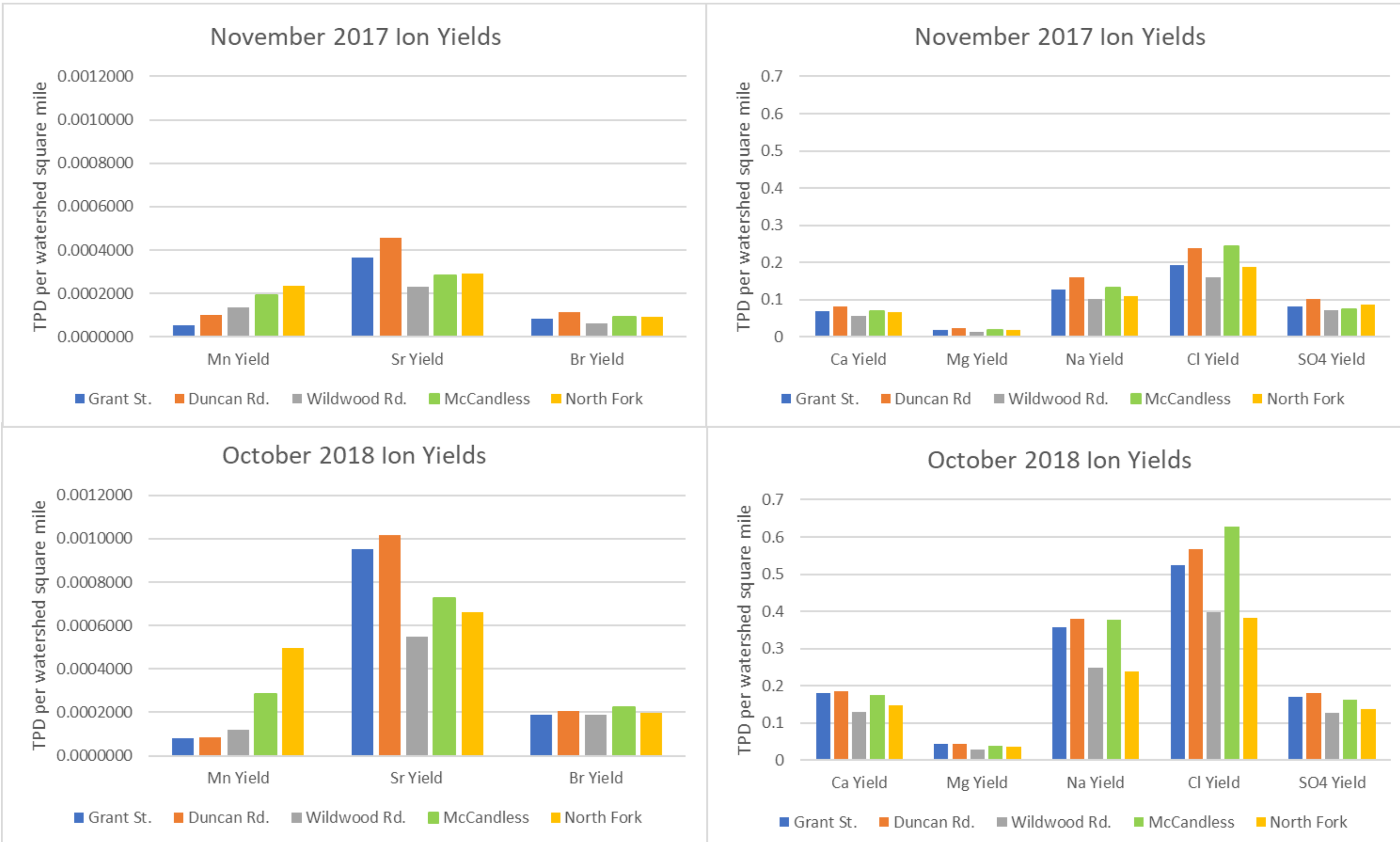


Figure 18. Analyte yields of the data representing pre-winter results of the Pine Creek watershed.

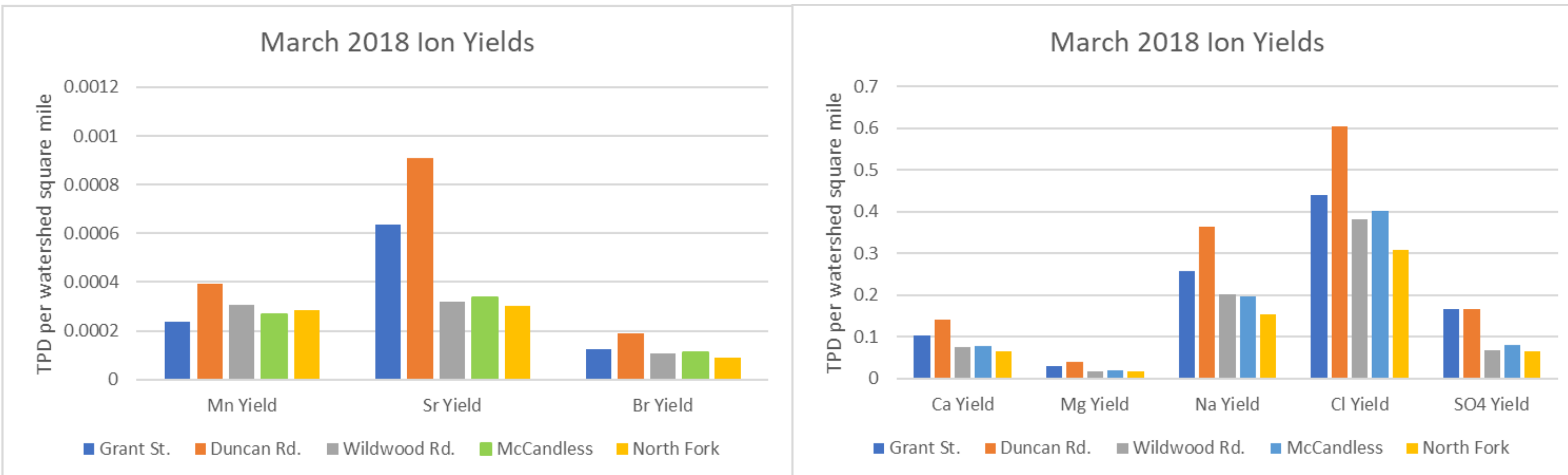


Figure 19. Analyte yields of the data representing winter result of the Pine Creek watershed.

Data obtained from the five study sites from 2017-2018 showed a direct relationship between specific conductivity and chloride concentrations ($R^2 = 0.9584$, $R^2 = 0.9623$) as seen in Figure 20. This suggests that chloride anion concentrations are directly correlated to specific conductivity in Pine Creek

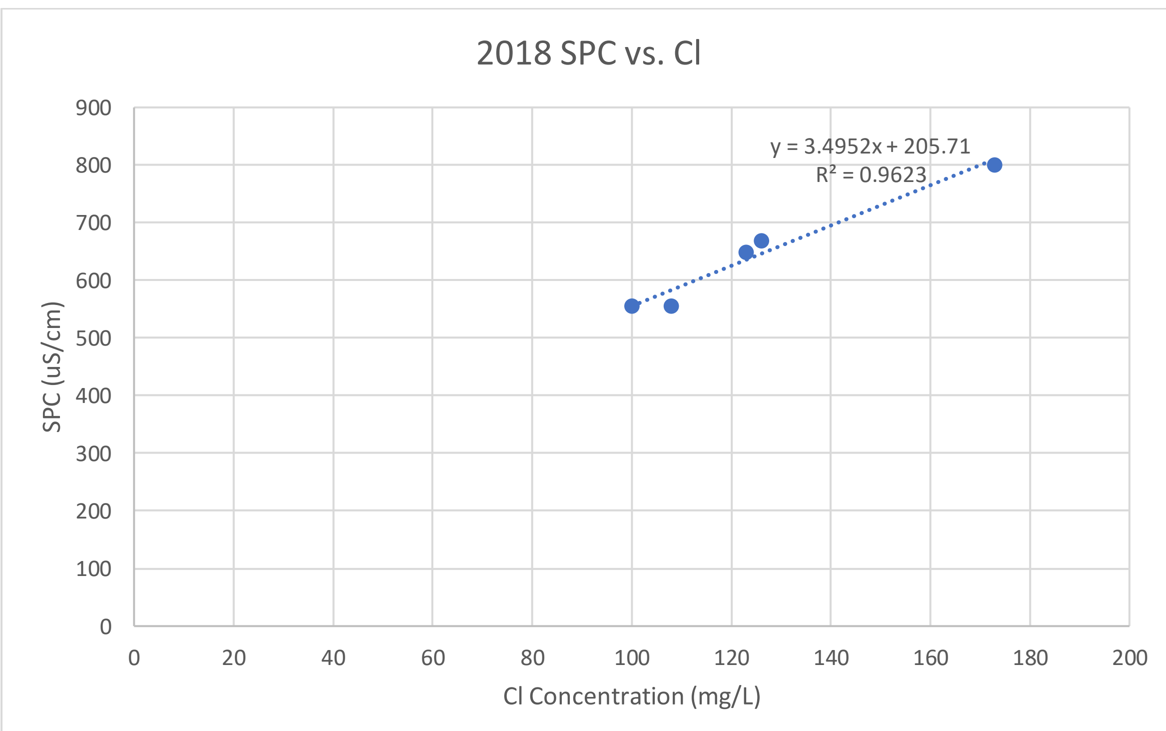


Figure 20. Five site study on Pine Creek in October 2018 showing direct chloride relationship with specific conductivity.

4.1.3 Chloride Concentrations Based Upon Data Logger

A logger was placed at the Grant Street site near USGS gage (3049807). Using the conductivity readings, specific conductivity was used to estimate chloride concentrations over time (Figure 23). The 3RQ SPC and chloride concentration relationship was used to extrapolate chloride concentrations at 15-minute intervals. The May to September 2018 data represents baseline or pre-winter data prior to road salting events in the watershed.

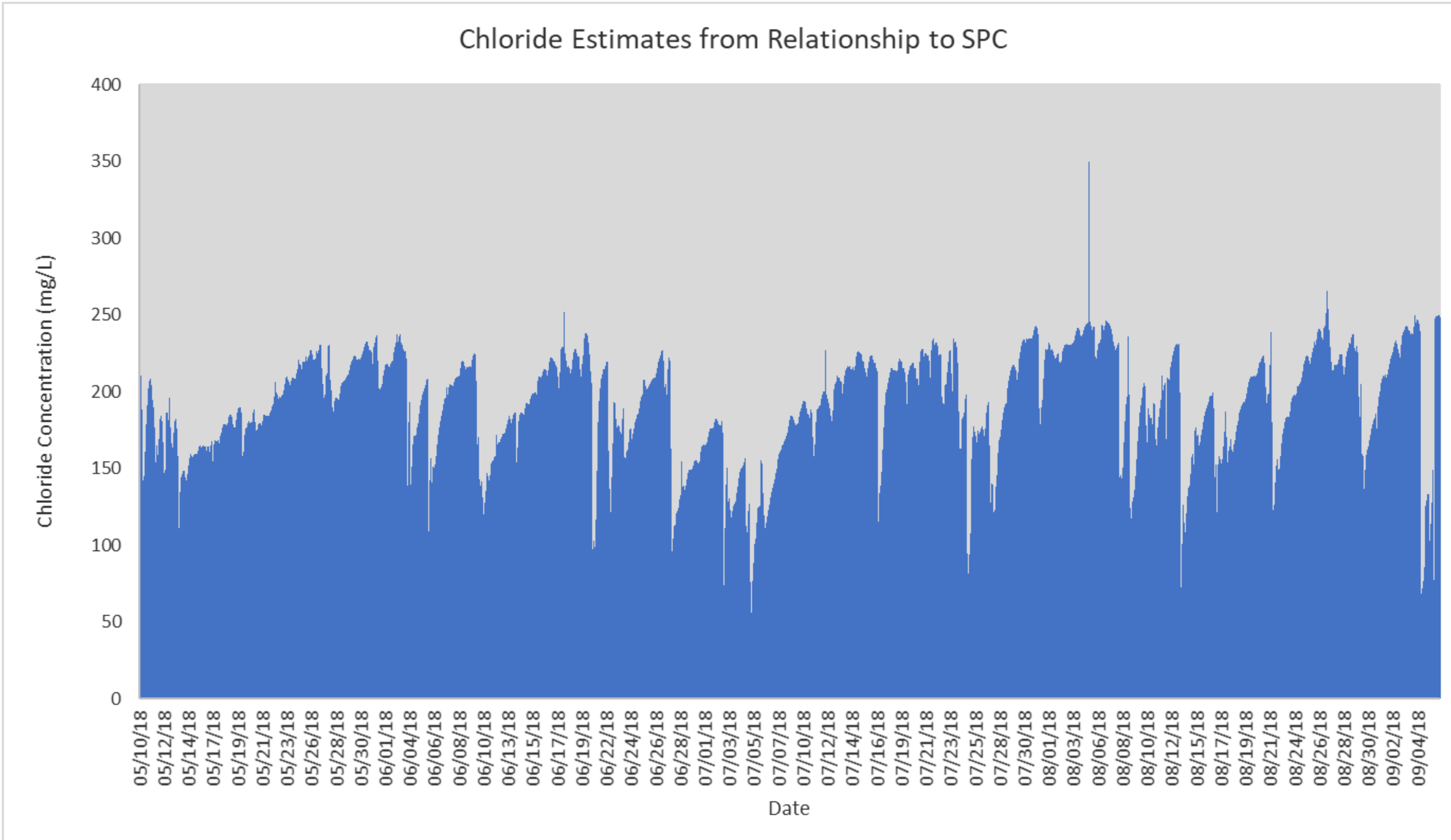


Figure 21. SPC derived chloride concentrations of the Grant St site from the data logger obtaining samples every 15 minutes.

4.2 Historical Chloride Data of Pine Creek

4.2.1 SPC-Derived Chloride Concentrations in Comparative Sites

Specific conductivity data were obtained from a study conducted on Pine Creek for the North Area Environmental Council (NAEC) (S. Prettner, personal communication, August 27, 2018). Specific conductance was used to calculate chloride concentrations at several sites using the 3RQ standard curve (Figure 22). Five of these sites were compared to their respective sampling locations from the Prettner five-site targeted study (Figure 23). These pre-winter comparisons include October and November dates from 2003-2007 (NAEC) and November 2017 and October 2018 dates (shown in Table 8). Figures 24-28 show the individual comparative NAEC sites with the Prettner 5-site targeted study locations. This provides a rough estimate of how SPC and therefore chloride concentrations have changed over time.

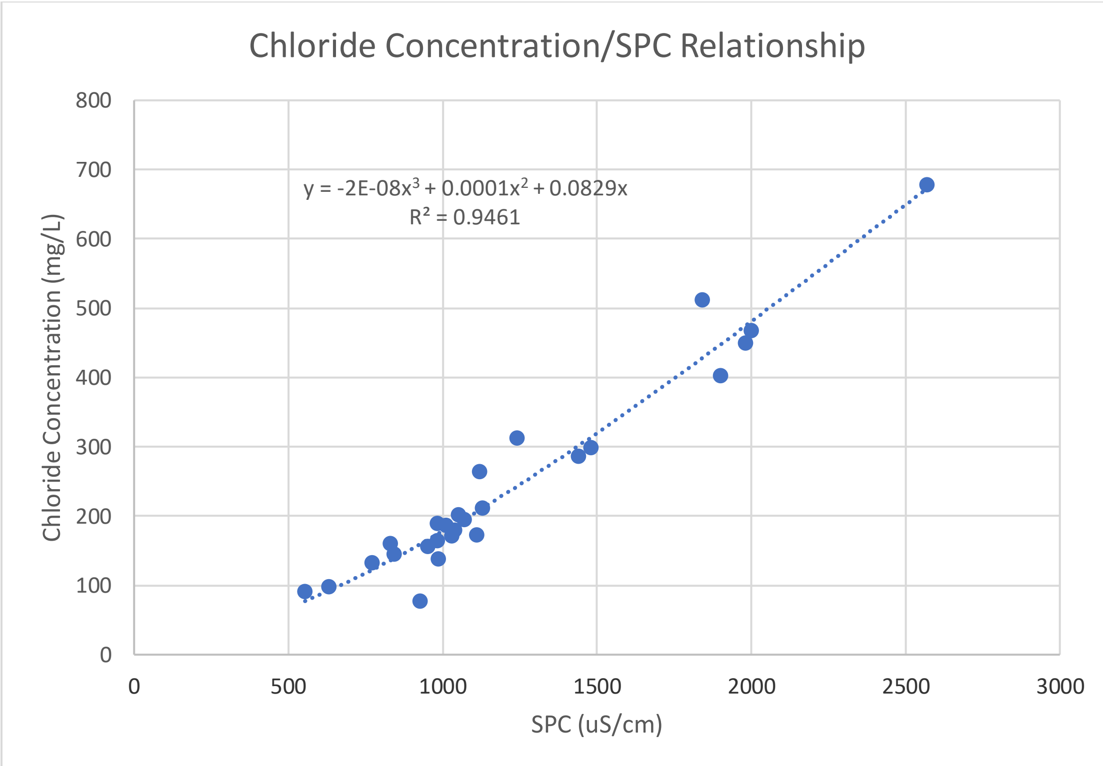


Figure 22. Relationship between chloride concentration and SPC using 3RQ collected data using a cubic function.

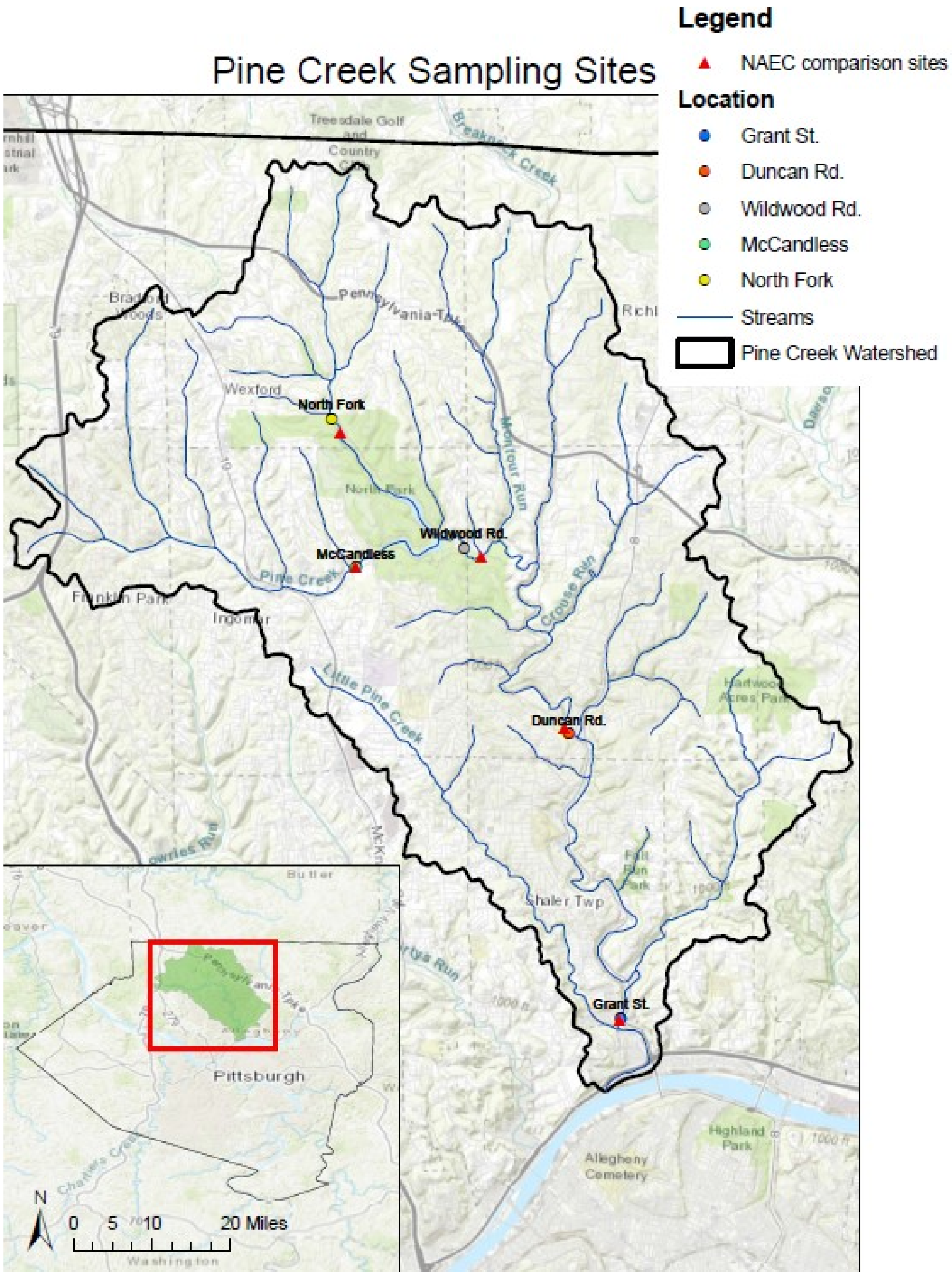


Figure 23. Chloride comparison locations of NAEC sites and pre-winter Prettner 5-site targeted study.

Table 8. Historical locations (4-digit IDs) and their respective Prettner 5-site targeted study locations. Chloride concentrations for the NAEC sites were SPC derived chloride concentrations using the 3RQ. A standard deviation was calculated from the raw data. A range of plus or minus one standard deviation was calculated to show the variations.

NAEC Comparative Sites	5-Site Targeted Study	Chloride Average (mg/L)	Standard Deviation	Average +/- 1 Std. Dev.
1153		87.94	25.83	62.11-113.77
	Grant St.	127.00	5.66	121.34-132.66
1109		76.73	18.08	58.65-94.81
	Duncan Rd.	127.00	1.41	125.59-128.41
1151		111.91	34.38	77.53-146.29
	Wildwood Rd.	104.50	4.95	99.55-109.45
1154		86.16	27.49	58.67-113.65
	North Fork	105.50	7.78	97.72-113.28
1150		90.09	43.54	46.55-133.63
	McCandless	180.50	10.61	169.89-191.11

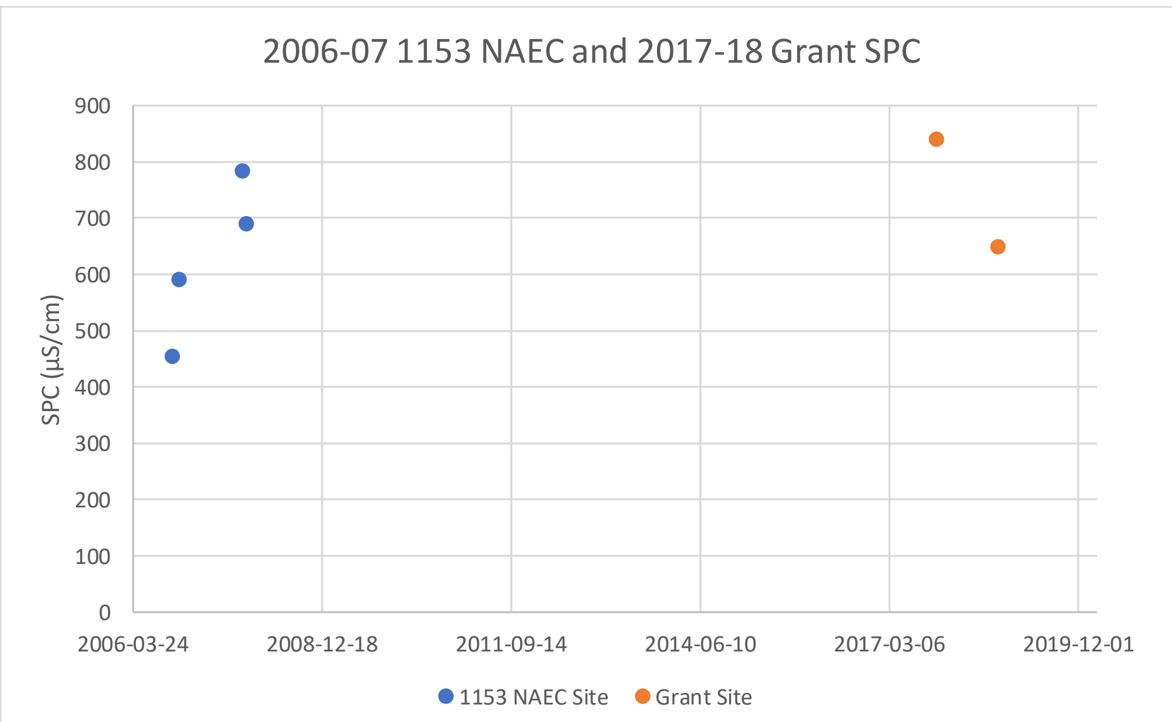


Figure 24. Historical NAEC site 1153 and its respective Grant Street SPC readings from 2006-2018.

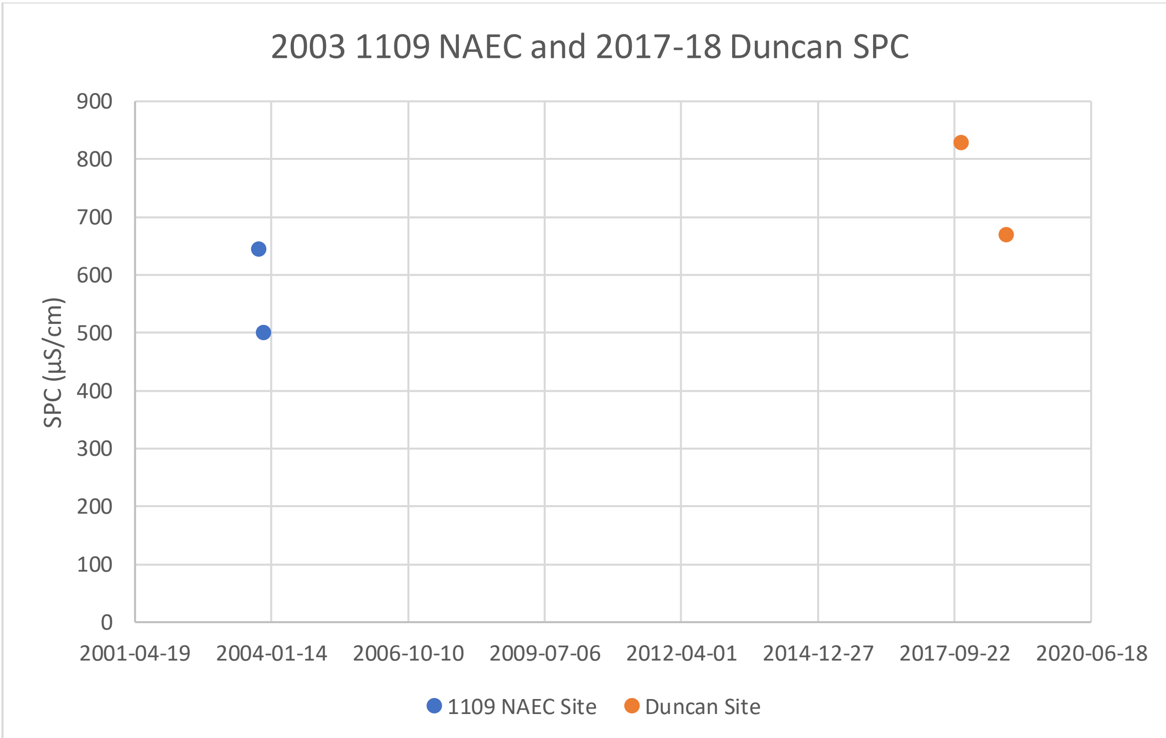


Figure 25. Historical NAEC site 1109 and its respective Duncan Rd SPC readings from 2003-2018.

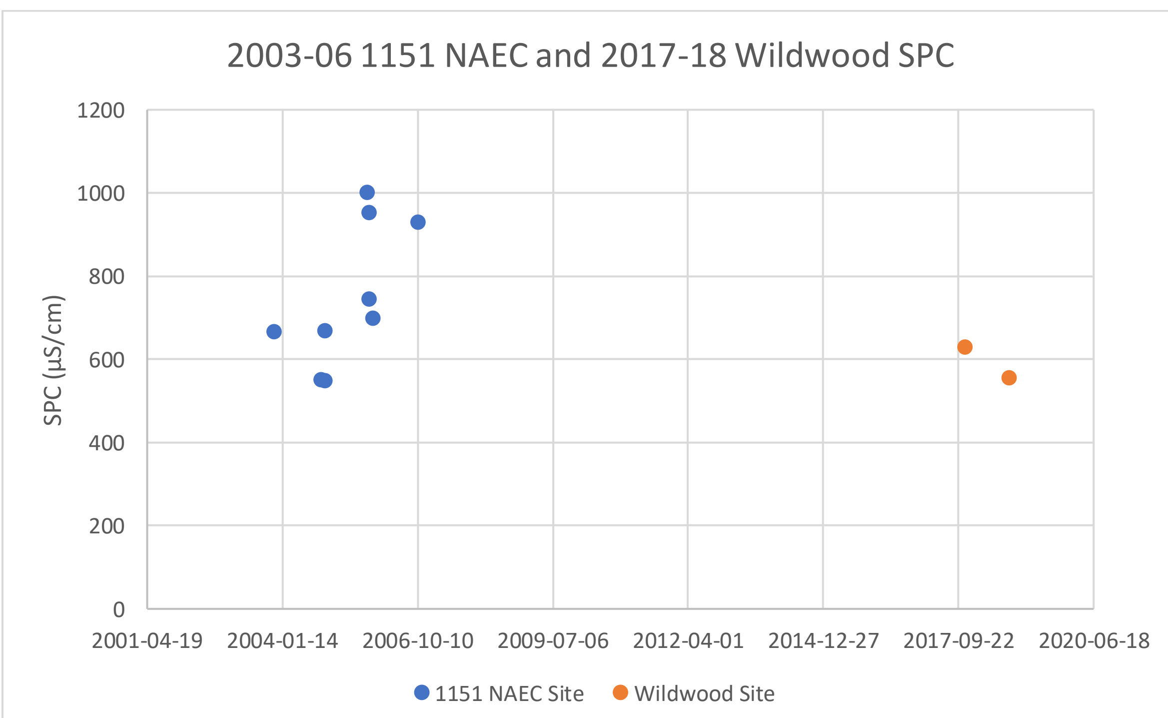


Figure 26. Historical NAEC site 1151 and its respective Wildwood Rd SPC readings from 2003-2018.

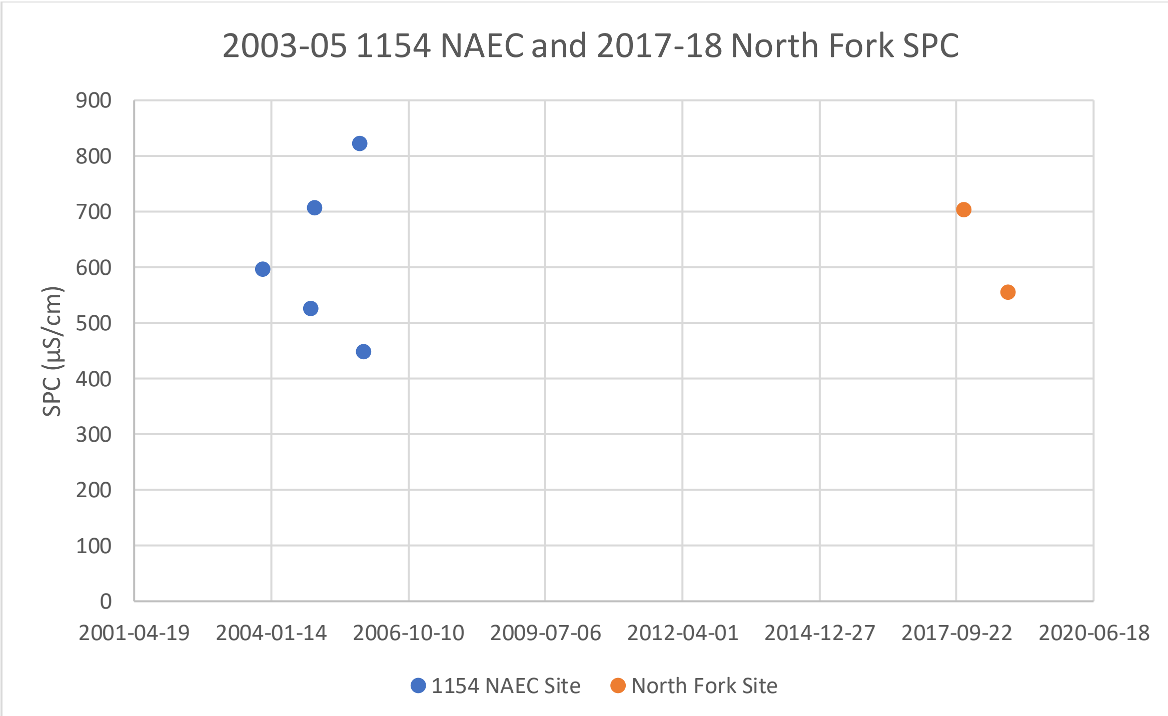


Figure 27. Historical NAEC site 1154 and its respective North Fork SPC readings from 2003-2018.

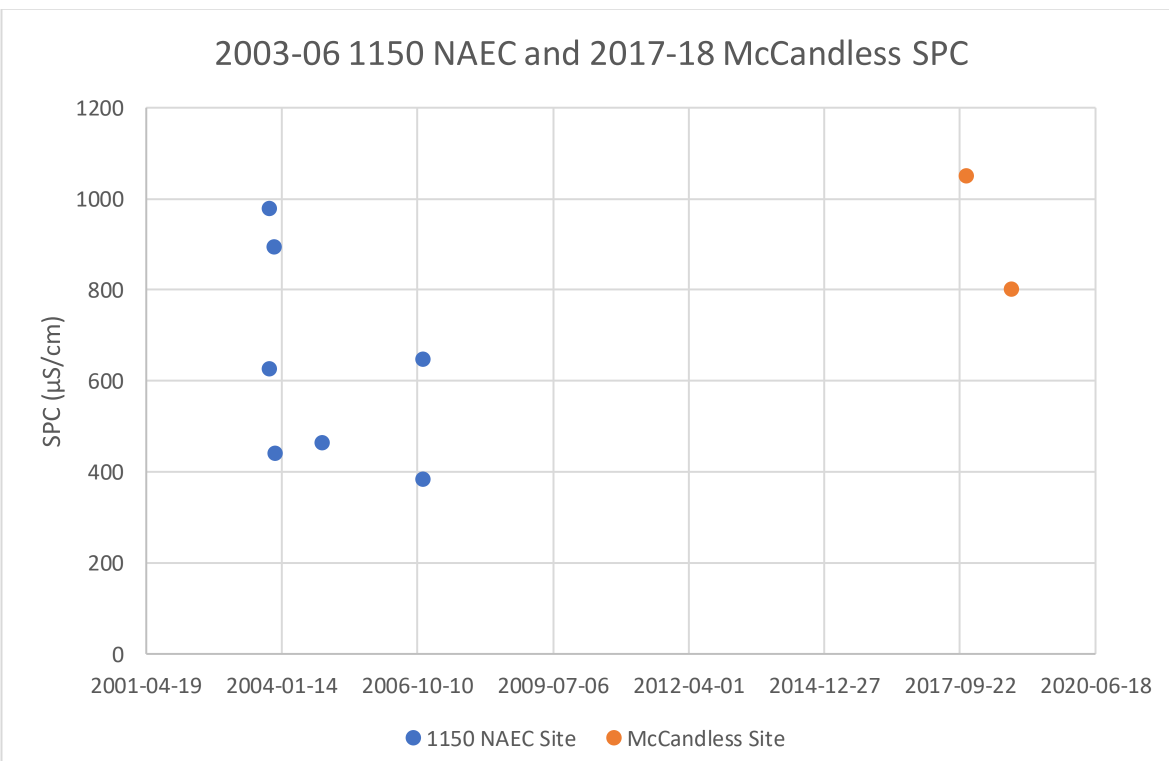


Figure 28. Historical NAEC site 1150 and its respective McCandless SPC readings from 2003-2018.

4.3 Fish Surveys of Pine Creek Headwaters

4.3.1 Fish Sampling and Chloride Tolerance Indicator Values

Table 9 shows fish species found in the Ohio River drainage that could be found in Pine Creek. There are 143 fish species total, and out of this, only 34 species from that list are considered to be chloride tolerant (Table 10). Species that were found in Pine Creek during the 2018 sampling trips are shown in Table 11 and Figure 29. Figure 29 shows the number of species caught. Table 12 and Figure 30 show the species found in Pine Creek from 1971 (Jarmus & Ulanoski, 1971). Table 13 breaks down the total number of fish caught in each sampling period.

Table 9. Fish species found in Ohio River drainage *(PA* Fish *and Boat Commission, 2019)*.

Common Name	Species
Ohio Lamprey	*Icthyomyzon bdellium*
Mountain Brook Lamprey	*Icthyomyzon greeleyi*
Least Brook Lamprey	*Lampetra aepyptera*
American Brook Lamprey	*Lampetra appendix*
Lake Sturgeon	*Aceipenser fulvescens*
Shovelnose Sturgeon	*Scaphirhynchus platorynchus*
Paddlefish	*Polyodon spathula*
Longnose Gar	*Lepisosteus osseus*
Shortnose Gar	*Lepisosteus platostomus*
Bowfin	*Amia calva*
Goldeye	*Hiodon alosoides*
Mooneye	*Hiodon tergisus*
American Eel	*Anguilla rostrata*
Skipjack Herring	*Alosa chrysochloris*
Gizzard Shad	*Dorosoma cepedianum*
Central Stoneroller	*Campostoma anomalum*
Goldfish	*Carassius auratus*
Northern Redbelly Dace	*Chrosomus eos*
Southern Redbelly Dace	*Chrosomus erythrogaster*
Redside Dace	*Clinostomus elongatus*
Grass Carp	*Ctenopharyngodon idella*
Spotfin Shiner	*Cyprinella spiloptera*

Steelcolor Shiner	*Cyprinella whipplei*
Common Carp	*Cyprinus carpio*
Gravel Chub	*Erimystax x-punctatus*
Streamline Chub	*Erimystax dissimilis*
Tonguetied Minnow	*Exoglossum laurae*
Brassy Minnow	*Hybognathus hankinsoni*
Bigeye Chub	*Hybopsis amblops*
Bigmouth Shiner	*Hybopsis dorsalis*
Striped Shiner	*Luxilus chrysocephalus*
Common Shiner	*Luxilus cornutus*
Redfin Shiner	*Lythrurus umbratilis*
Silver Chub	*Macrhybopsis storeriana*
Allegheny Pearl Dace	*Margariscus margarita*
Hornyhead Chub	*Nocomis biguttatus*
River Chub	*Nocomis micropogon*
Golden Shiner	*Notemigonus crysoleucas*
Popeye Shiner	*Notropis ariommus*
Emerald Shiner	*Notropis atherinoides*
River Shiner	*Notropis blennius*
Silverjaw Minnow	*Notropis buccatus*
Ghost Shiner	*Notropis buchanani*
Blackchin Shiner	*Notropis heterodon*
Blacknose Shiner	*Notropis heterolepis*
Spottail Shiner	*Notropis hudsonius*
Silver Shiner	*Notropis photogenus*
Rosyface Shiner	*Notropis rubellus*
Sand Shiner	*Notropis stramineus*
Mimic Shiner	*Notropis volucellus*
Channel Shiner	*Notropis wickliffi*
Pugnose Minnow	*Opsopoeodus emiliae*
Bluntnose Minnow	*Pimephales notatus*
Fathead Minnow	*Pimephales promelas*
Bullhead Minnow	*Pimephales vigilax*
Blacknose Dace	*Rhinichthys atratulus*
Longnose Dace	*Rhinichthys cataractae*
Rudd	*Scardinius erythrophthal*
Creek Chub	*Semotilus atromaculatus*
Fallfish	*Semotilus corporalis*
River Carpsucker	*Carpiodes carpio*
Quillback	*Carpiodes cyprinus*
Highfin Carpsucker	*Carpiodes velifer*
Longnose Sucker	*Catostomus catostomus*
White Sucker	*Catostomus commersonii*
Blue Sucker	*Cycleptus elongatus*
Northern Hogsucker	*Hypentelium nigricans*

Smallmouth Buffalo	*Ictiobus bubalus*
Bigmouth Buffalo	*Ictiobus cyprinellus*
Black Buffalo	*Ictiobus niger*
Spotted Sucker	*Minytrema melanops*
Silver Redhorse	*Moxostoma anisurum*
Smallmouth Redhorse	*Moxostoma breviceps*
River Redhorse	*Moxostoma carinatum*
Black Redhorse	*Moxostoma duquesnei*
Golden Redhorse	*Moxostoma erythrurum*
White Catfish	*Ameirus catus*
Black Bullhead	*Ameirus melas*
Yellow Bullhead	*Ameirus natalis*
Brown Bullhead	*Ameirus nebulosus*
Blue Catfish	*Ictalurus furcatus*
Channel Catfish	*Ictalurus punctatus*
Mountain Madtom	*Noturus eleutherus*
Stonecat	*Noturus flavus*
Tadpole Madtom	*Noturus gyrinus*
Brindled Madtom	*Noturus miurus*
Northern Madtom	*Noturus stigmosus*
Flathead Catfish	*Pylodictis olivaris*
Rainbow Trout	*Oncorhynchus mykiss*
Golden Rainbow Trout	*Oncorhynchus mykiss*
Atlantic Salmon	*Salmo salar*
Brown Trout	*Salmo trutta*
Brook Trout	*Salvelinus fontinalis*
Grass Pickerel	*Esox americanus vermiculatus*
Northern Pike	*Esox lucius*
Tiger Muskellunge	*Esox lucius x Esox masquinongy*
Muskellunge	*Esox masquinono*
Chain Pickerel	*Esox niger*
Central Mudminnow	*Umbra limi*
Trout Perch	*Percopsis omiscomaycus*
Burbot	*Lota Iota*
Brook Silverside	*Labidesthes sicculus*
Banded Killifish	*Fundulus diaphanus*
Mummichog	*Fundulus heteroclitus*
Brook Stickleback	*Culaea inconstans*
Mottled Sculpin	*Cottus bairdi*
White Perch	*Morone americana*
White Bass	*Morone chrysops*
Striped Bass Hybrid	*Morone saxatilis x Morone chrysops*
Rock Bass	*Ambloplites rupestris*
Green Sunfish	*Lepomis cyanellus*
Pumpkinseed	*Lepomis gibbosus*

Bluegill	*Lepomis macrochirus*
Longear Sunfish	*Lepomis megalotis*
Redear Sunfish	*Lepomis microlophus*
Warmouth	*Chaenobryttus gulosus*
Smallmouth Bass	*Micropterus dolomieu*
Spotted Bass	*Micropterus punctulatus*
Largemouth Bass	*Micropterus salmoides*
White Crappie	*Pomoxis annularis*
Black Crappie	*Pomoxis nigromaculatus*
Eastern Sand Darter	*Ammocrypta pellucida*
Greenside Darter	*Etheostoma blennioides*
Rainbow Darter	*Etheostoma caeruleum*
Bluebreast Darter	*Etheostoma camurum*
Iowa Darter	*Etheostoma exile*
Fantail Darter	*Etheostomaflabellare*
Spotted Darter	*Etheostoma maculatum*
Johnny Darter	*Etheostoma nigrum*
Tippecanoe Darter	*Etheostoma tippecanoe*
Variegate Darter	*Etheostoma variatum*
Banded Darter	*Etheostoma zonale*
Yellow Perch	*Perca flavescens*
Logperch	*Percina caprodes*
Channel Darter	*Percina copelandi*
Gilt Darter	*Percina evides*
Longhead Darter	*Percina macrocephala*
Blackside Darter	*Percina maculata*
Sharpnose Darter	*Percina oxyrhyncha*
River Darter	*Percina shumardi*
Sauger	*Sander canadensis*
Walleye	*Sander vitreus*
Freshwater Drum	*Aplodinotus grunniens*

Table 10. Chloride tolerant fish species found in the Ohio River drainage *(Meador & Carlisle, 2007)*.

Common Name	Species	Chloride Tolerance
Longnose Gar	*Lepisosteus osseus*	7
American Eel	*Anguilla rostrata*	9
Gizzard Shad	*Dorosoma cepedianum*	10
Common Carp	*Cyprinus carpio*	10
Golden Shiner	*Notemigonus crysoleucas*	9
Silverjaw Minnow	*Notropis buccatus*	10
Sand Shiner	*Notropis stramineus*	7
Bluntnose Minnow	*Pimephales notatus*	8
Fathead Minnow	*Pimephales promelas*	10
Bullhead Minnow	*Pimephales vigilax*	10
Blacknose Dace	*Rhinichthys atratulus*	8
Creek Chub	*Semotilus atromaculatus*	9
River Carpsucker	*Carpiodes carpio*	10
Quillback	*Carpiodes cyprinus*	7
Longnose Sucker	*Catostomus catostomus*	7
White Sucker	*Catostomus commersonii*	9
Smallmouth Buffalo	*Ictiobus bubalus*	7
Black Bullhead	*Ameirus melas*	7
Yellow Bullhead	*Ameirus natalis*	9
Brown Bullhead	*Ameirus nebulosus*	9
Channel Catfish	*Ictalurus punctatus*	8
Stonecat	*Noturus flavus*	10
Tadpole Madtom	*Noturus gyrinus*	8
Flathead Catfish	*Pylodictis olivaris*	8
White Bass	*Morone chrysops*	10
Green Sunfish	*Lepomis cyanellus*	9
Pumpkinseed	*Lepomis gibbosus*	10
Bluegill	*Lepomis macrochirus*	7
Redear Sunfish	*Lepomis microlophus*	8
Warmouth	*Chaenobryttus gulosus*	7
Largemouth Bass	*Micropterus salmoides*	9
Black Crappie	*Pomoxis nigromaculatus*	8
Johnny Darter	*Etheostoma nigrum*	10
Central Stoneroller	*Campostoma anomalum*	7

Table 11. List of species found in Pine Creek headwaters during Fall 2018 sampling.

Common Name	Species	# Individuals Found	Chloride Tolerance
Least Brook Lamprey	*Lampetra aepyptera*	16	NA
Central Stoneroller	*Campostoma anomalum*	30	7
Sand Shiner	*Notropis stramineus*	0	7
Spotfin Shiner	*Cyprinella spiloptera*	1	6
Creek Chub	*Semotilus atromaculatus*	99	9
Yellow Bullhead	*Ameirus natalis*	8	9
Silverjaw Minnow	*Ericymba buccata*	21	10
Bluntnose Minnow	*Pimephales notatus*	123	8
Redside Dace	*Clinostomuc elongatus*	66	NA
Blacknose Dace	*Rhinichthys atratulus*	72	8
Yellow Bullhead	*Ameirus natalis*	8	9
White Sucker	*Catostomus commersonii*	40	9
Northern Hogsucker	*Hypentelium nigricans*	119	6
Largemouth Bass	*Micropterus salmoides*	11	9
Smallmouth Bass	*Micropterus dolomieu*	7	4
Bluegill	*Lepomis macrochirus*	14	7
Green Sunfish	*Lepomis cyanellus*	14	9
Pumpkinseed Sunfish	*Lepomis gibbosus*	0	10
Johnny Darter	*Etheostoma nigrum*	53	10
Banded Darter	*Etheostoma zonale*	1	2
Mottled Sculpin	*Cottus bairdii*	54	NA

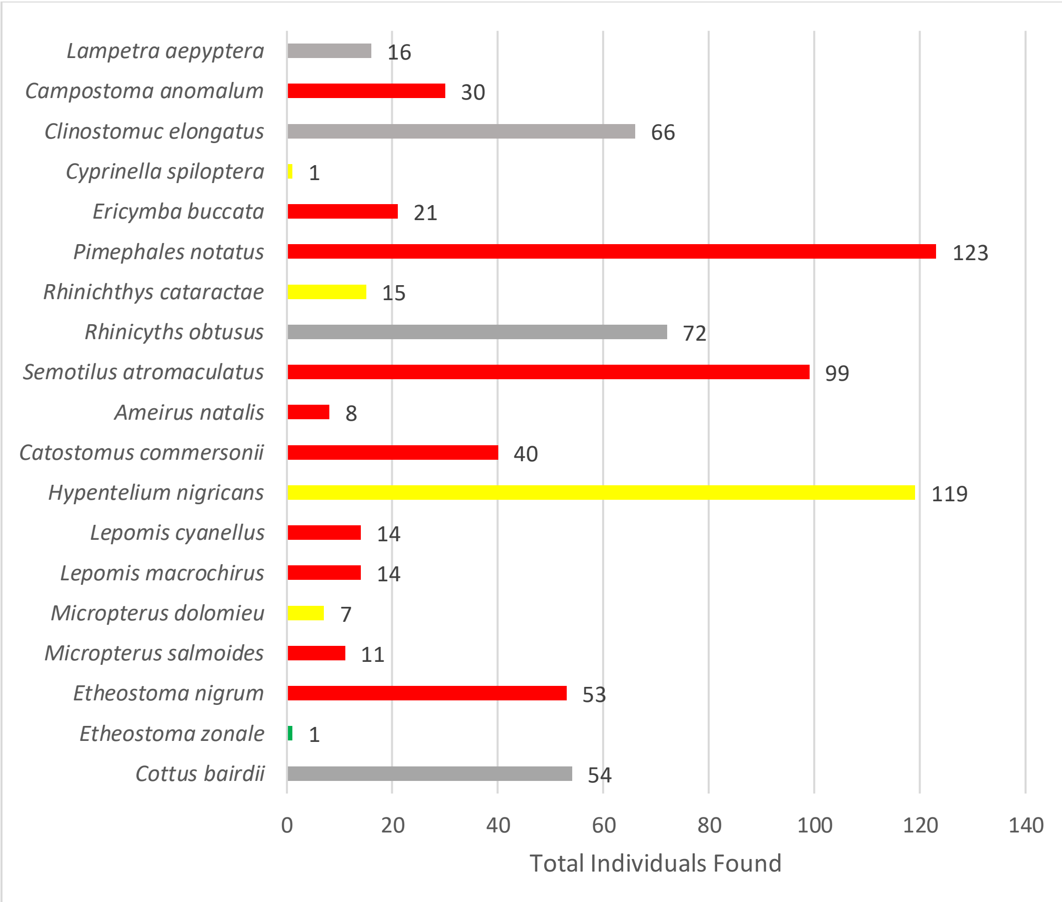


Figure 29. Breakdown of species found in Pine Creek in 2018. Green bars represent species that are considered to be chloride intolerant. Yellow bars represent species that are considered to have a moderate chloride tolerance. Red bars represent species that are considered to be tolerant to chlorides. Grey bars represent species that do not have available data on chloride tolerance.

Common Name	Species	Total Found	Chloride Tolerance
Central Stoneroller	*Campostoma anomalum*	65	7
Sand Shiner	*Notropis stramineus*	29	7
Bluntnose Minnow	*Pimephales notatus*	9	8
Blacknose Dace	*Rhinichthys atratulus*	14	8
Creek Chub	*Semotilus atromaculatus*	20	9
White Sucker	*Catostomuc commersoni*	7	9
Northern Hogsucker	*Hypenetelium nigricans*	23	6
Pumpkinseed Sunfish	*Lepomis gibbosus*	15	10
Smallmouth Bass	*Micropterus dolomieui*	2	4
Common Shiner	*Luxilus cornutus*	7	4

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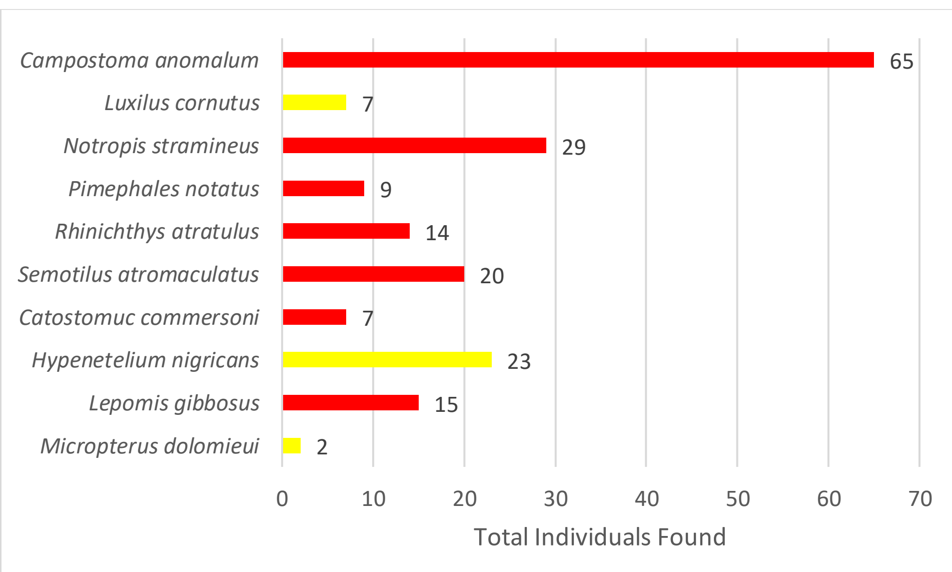

Figure 30. Breakdown of species found during 1971 fish sampling. The red text signifies chloride intolerant species. Yellow bars represent species that are considered to have a moderate chloride tolerance.

Table 12. Comparison of total fish and chloride intolerant versus tolerant fish species sampled in August 1971 and October 2018.

	1971 Headwater Sampling	2018 Sampling
Total Species Caught	19	10
# Chloride Intolerant Species	1	0
# Chloride Tolerant Species	10	7

4.4 Land Coverage and Soil Types

4.4.1 Surface and Groundwater Comparison

As a part of Linnea Manley's thesis (2017), homeowner well water and nearby surface waters (shown in Figure 31) were sampled to investigate their water chemistry (Figures 32, 33). Groundwater samples were collected from 8/15/16 to 10/11/16 and surface water samples were sampled on 11/5/16. The chloride concentrations from this sampling were compared with extrapolated data determined from the 3RQ derived standard curve from Grant St data. This served as a way to check and compare how well the 3RQ equation could predict the system's chloride concentrations from specific conductivity. This calculated chloride concentration was referred to as the SPC derived Cl, representing what the concentration was predicted to be compared to what was measured. The resulting percent error was calculated for groundwater as well as surface water (Table 14). The average percent error when comparing the actual chloride concentrations to the predicted SPC chloride values varied between the groundwater and the surface water. The groundwater average percent difference was 262.53% with a standard deviation of 781.71 while the surface water average percent difference was 34.39% with a standard deviation of 9.67. Figure 34 shows the relationship between chloride concentration and SPC, which are directly related with an R^2 value of 0.9759.

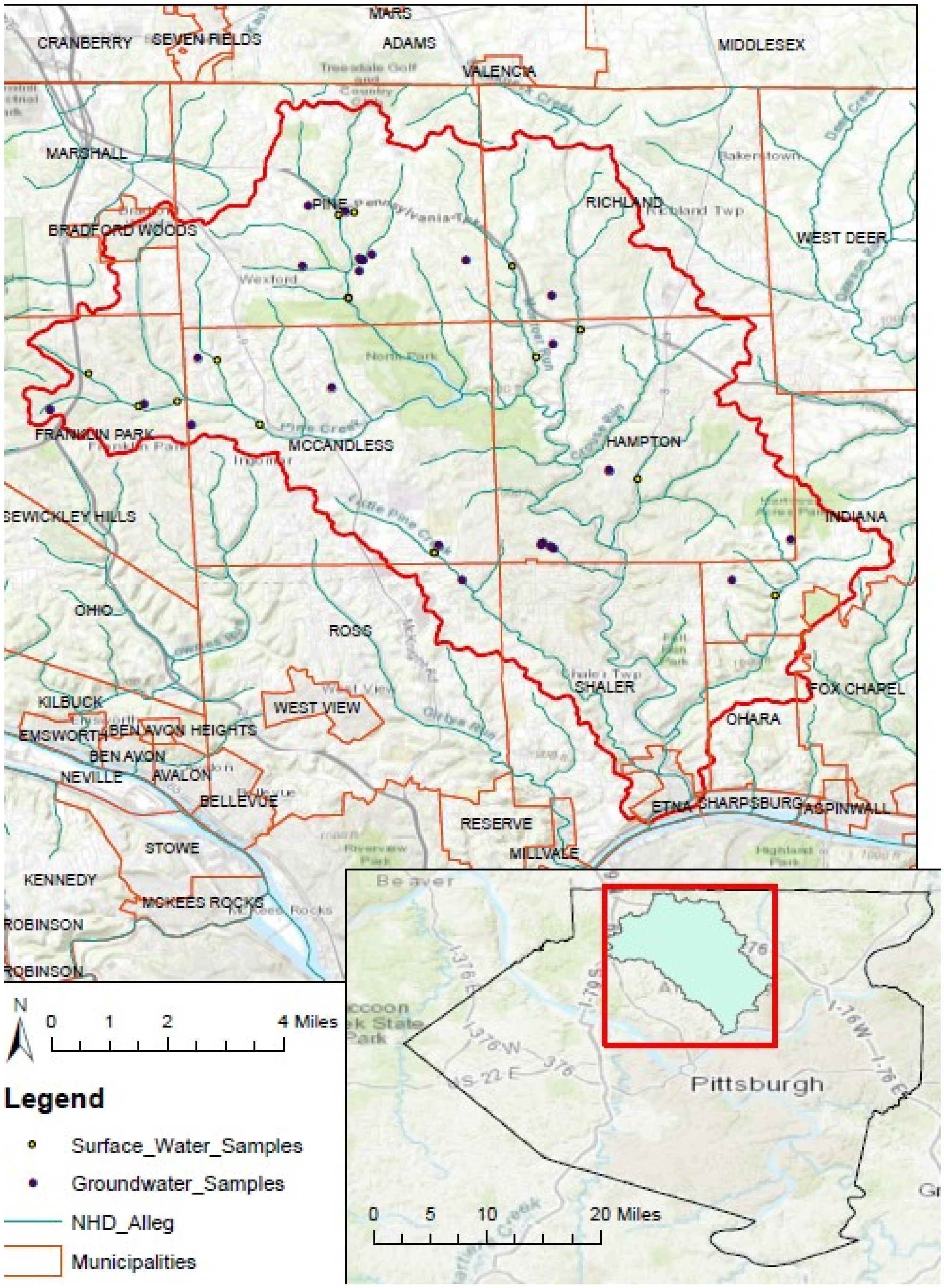

Figure 31. Locations of groundwater and nearby surface water sampling sites collected during Linnea Manley's studies.

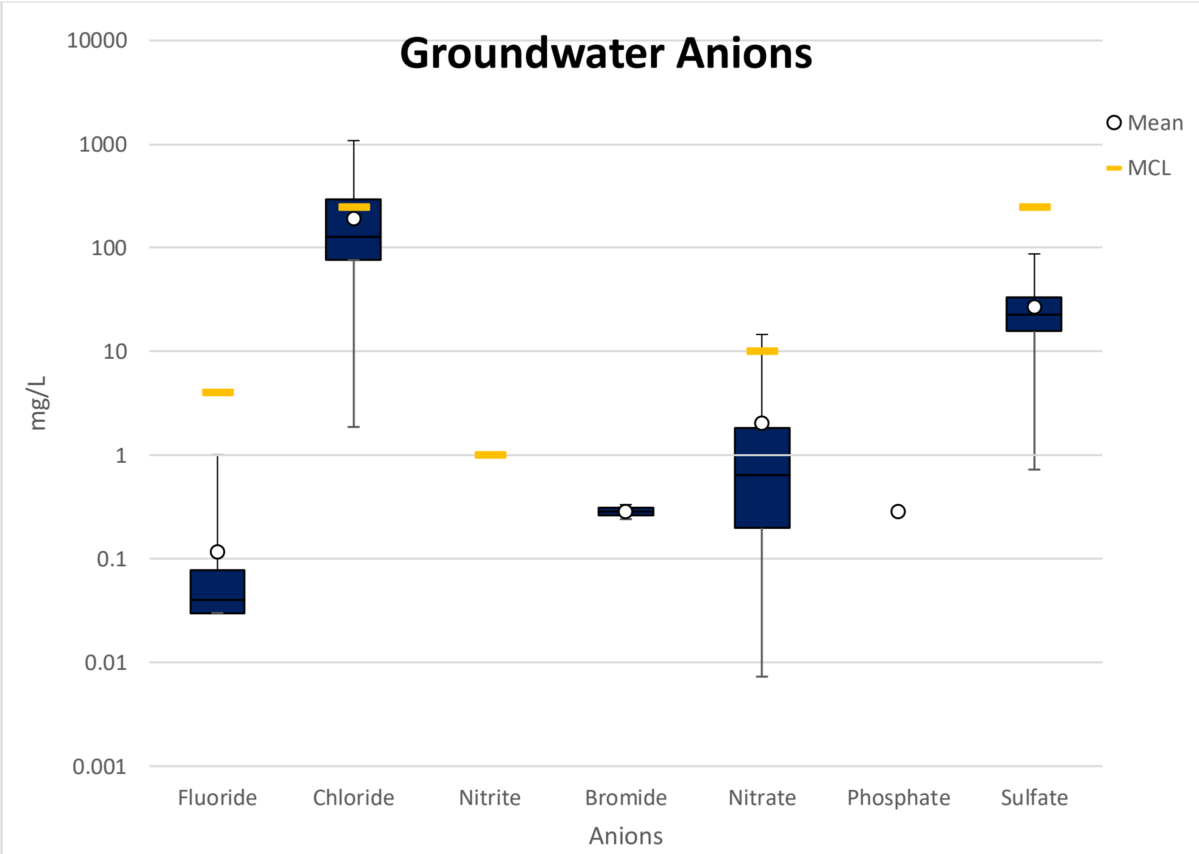

Figure 32. Anion water chemistry yields from homeowner well water sampling (Manley, 2017). 26 homeowner wells were sampled in this dataset.

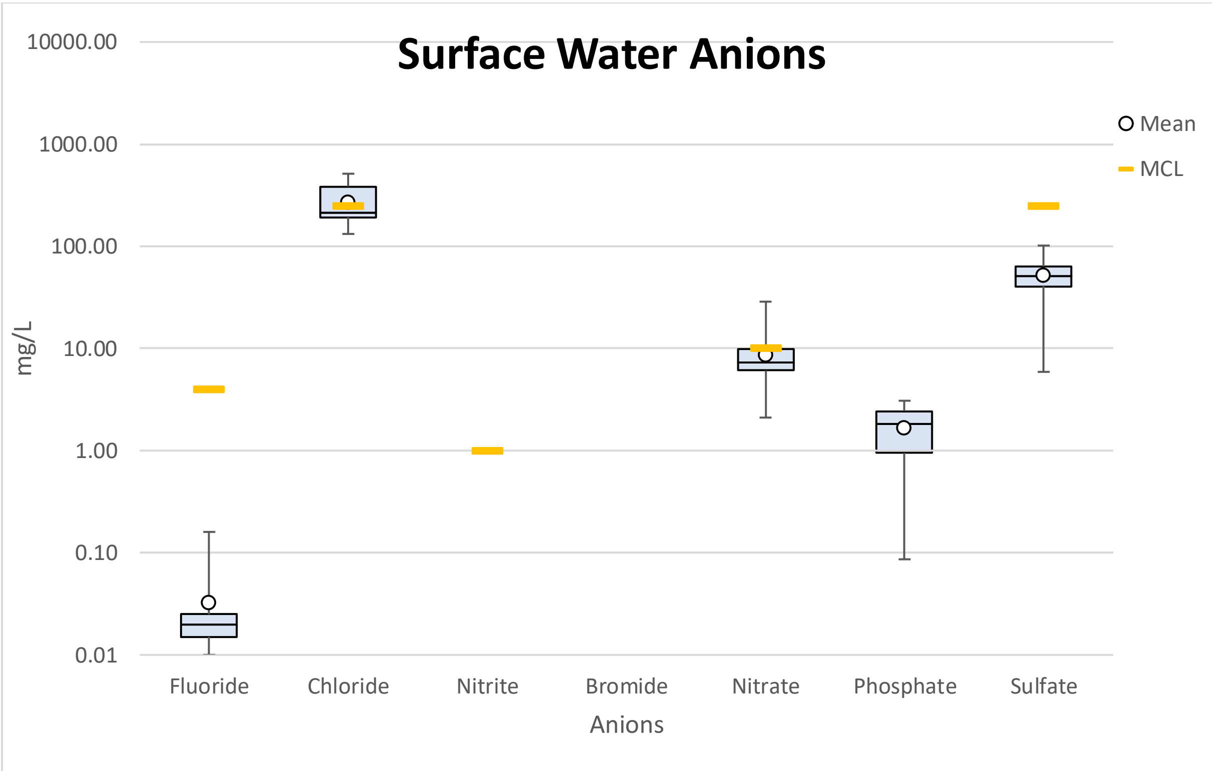

Figure 33. Anion water chemistry yields from nearby surface waters (Manley, 2017). 17 surface water samples were collected for this dataset.

Table 13. Groundwater and surface water specific conductivity, chloride concentrations, and specific conductivity derived chloride concentrations using the standard curve derived from the 3RQ Grant St data.

Sample	Sample Type	SPC (µS/cm)	Chloride	SPC Derived Cl (µS/cm)	% Error
MS819	Groundwater	453.90	5.78	56.36	875.87
MS820	Groundwater	429.90	25.81	52.53	103.57
MS821	Groundwater	804.50	138.32	121.00	12.52
MS822	Groundwater	1184.00	244.75	205.14	16.18
MS823	Groundwater	552.95	1.87	73.03	3803.66
MS824	Groundwater	1024.50	208.72	168.38	19.33
MS825	Groundwater	560.00	6.51	74.27	1040.05
MS826	Groundwater	618.50	106.08	84.80	20.07
MS827	Groundwater	867.50	154.81	134.11	13.37
MS828	Groundwater	1209.50	306.60	211.17	31.12
MS829	Groundwater	842.50	83.36	128.86	54.59
MS830	Groundwater	1266.00	311.17	224.65	27.81
MS831	Groundwater	1069.50	222.82	178.58	19.86
MS832	Groundwater	1458.00	337.67	271.46	19.61
MS833	Groundwater	688.50	97.02	97.95	0.96
MS850	Groundwater	782.00	140.35	116.42	17.06
MS851	Groundwater	708.00	89.02	101.72	14.27
MS852	Groundwater	878.00	88.46	136.34	54.13
MS853	Groundwater	650.50	36.22	90.74	150.52
MS854	Groundwater	3545.00	1082.29	659.58	39.06
MS855	Groundwater	1437.00	312.32	266.28	14.74
MS856	Groundwater	-	315.58	-	-
MS857	Groundwater	576.90	73.62	77.27	4.96
MS858	Groundwater	1892.00	490.69	379.36	22.69
MS916	Groundwater	960.00	119.64	154.05	28.76
MS917	Groundwater	460.80	22.24	57.48	158.49
MS887	Surface Water	1516.00	392.14	285.82	27.11
MS888	Surface Water	1204.00	298.98	209.87	29.81
MS889	Surface Water	1279.00	314.09	227.77	27.48
MS890	Surface Water	1485.00	385.94	278.13	27.93
MS892	Surface Water	1232.00	311.16	216.52	30.42
MS893	Surface Water	1386.00	402.23	253.75	36.91
MS894	Surface Water	1265.00	395.13	224.41	43.21
MS895	Surface Water	856.00	212.03	131.69	37.89
MS896	Surface Water	790.00	139.61	118.04	15.45
MS898	Surface Water	1735.00	513.65	340.40	33.73
MS899	Surface Water	681.30	195.55	96.57	50.62
MS900	Surface Water	669.50	132.18	94.32	28.64
MS901	Surface Water	578.80	182.84	77.61	57.56
MS902	Surface Water	850.00	209.42	130.43	37.72
MS903	Surface Water	826.00	192.32	125.43	34.78
MS904	Surface Water	865.00	206.27	133.59	35.24
MS905	Surface Water	671.00	135.46	94.61	30.16

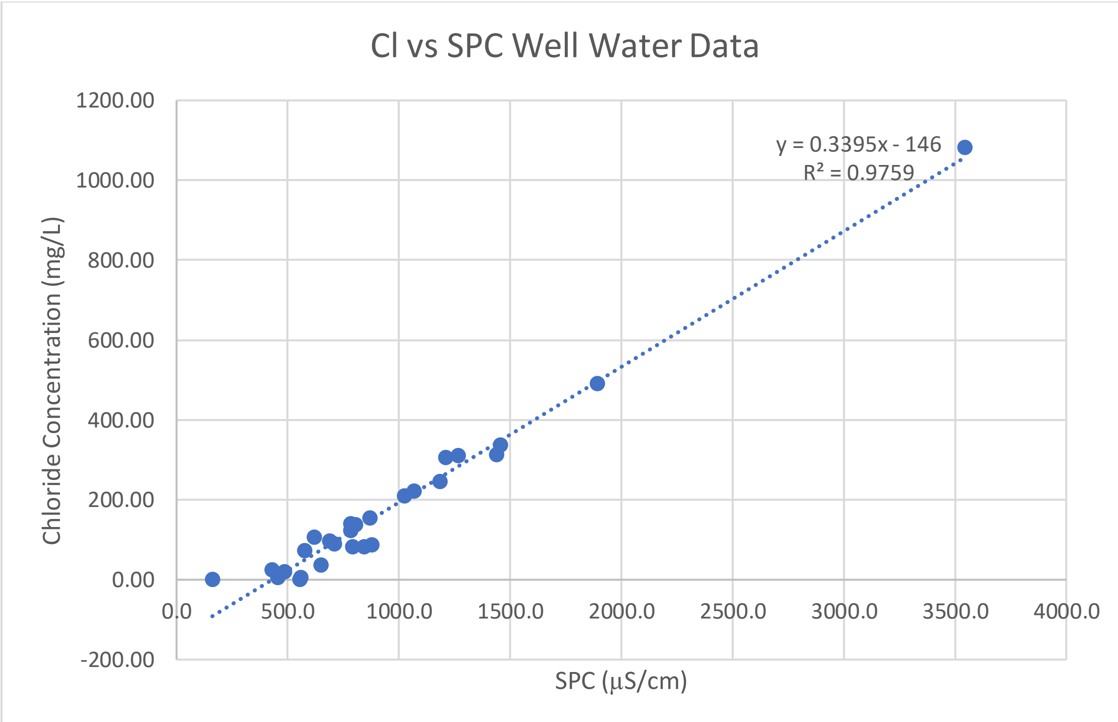

Figure 34. Well Water Chloride and SPC Data Relationship from Linnea Manley's dataset.

4.4.2 Deer Creek

Pine Creek land cover and soil types were compared to Deer Creek and Squaw Run (see next section). Deer Creek's land cover can be seen in Figure 35. The data is numerically displayed in Table 15. The soil types based upon ability to drain are shown in Figure 36. The four categories used to describe the soils are excessively drained, well to moderately drained, somewhat poorly drained, and poorly to very poorly drained. Deer Creek's chloride concentration data obtained through 3RQ from January 2014 to March 2018 is shown in Figure 37.

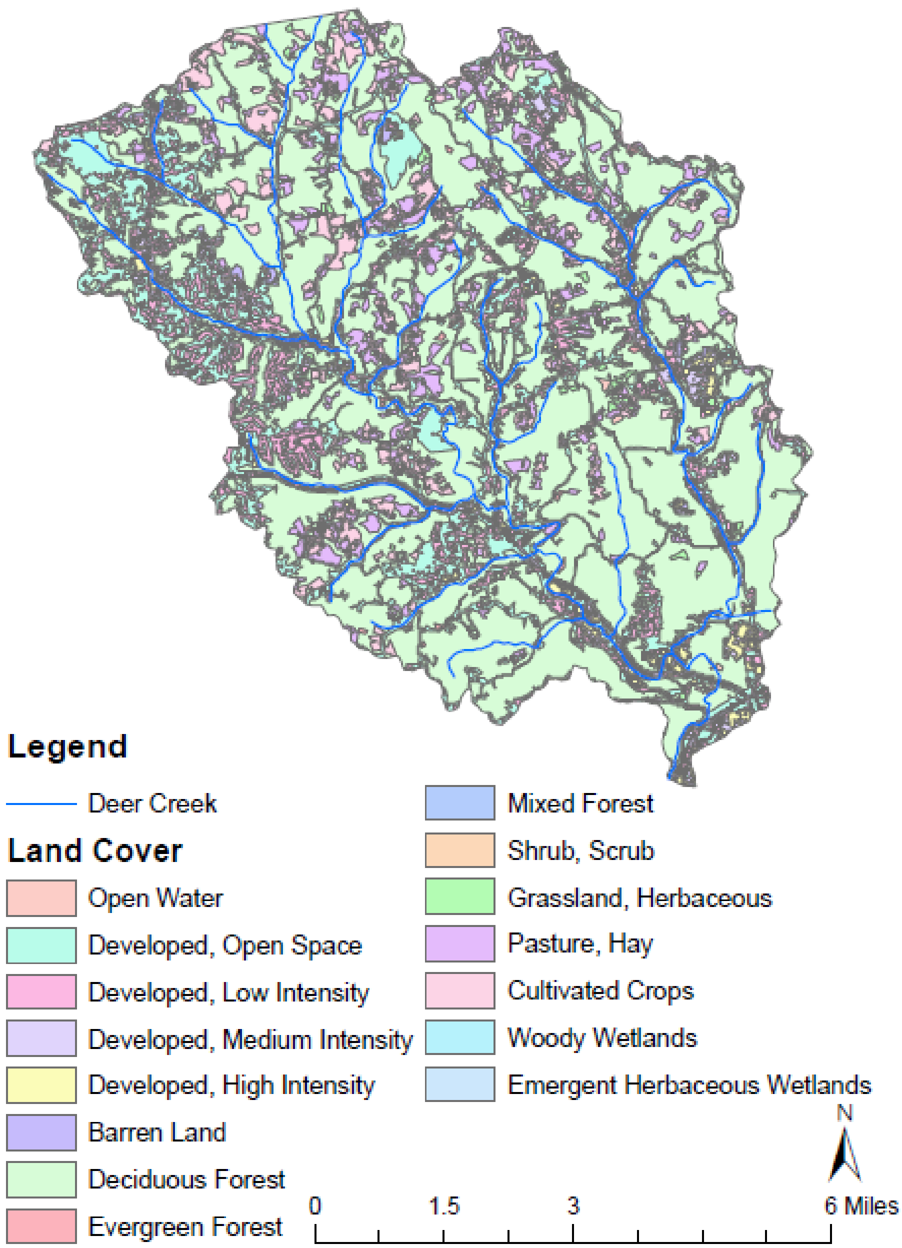

Figure 35. Deer Creek watershed land coverage from the National Land Cover Dataset (2011).

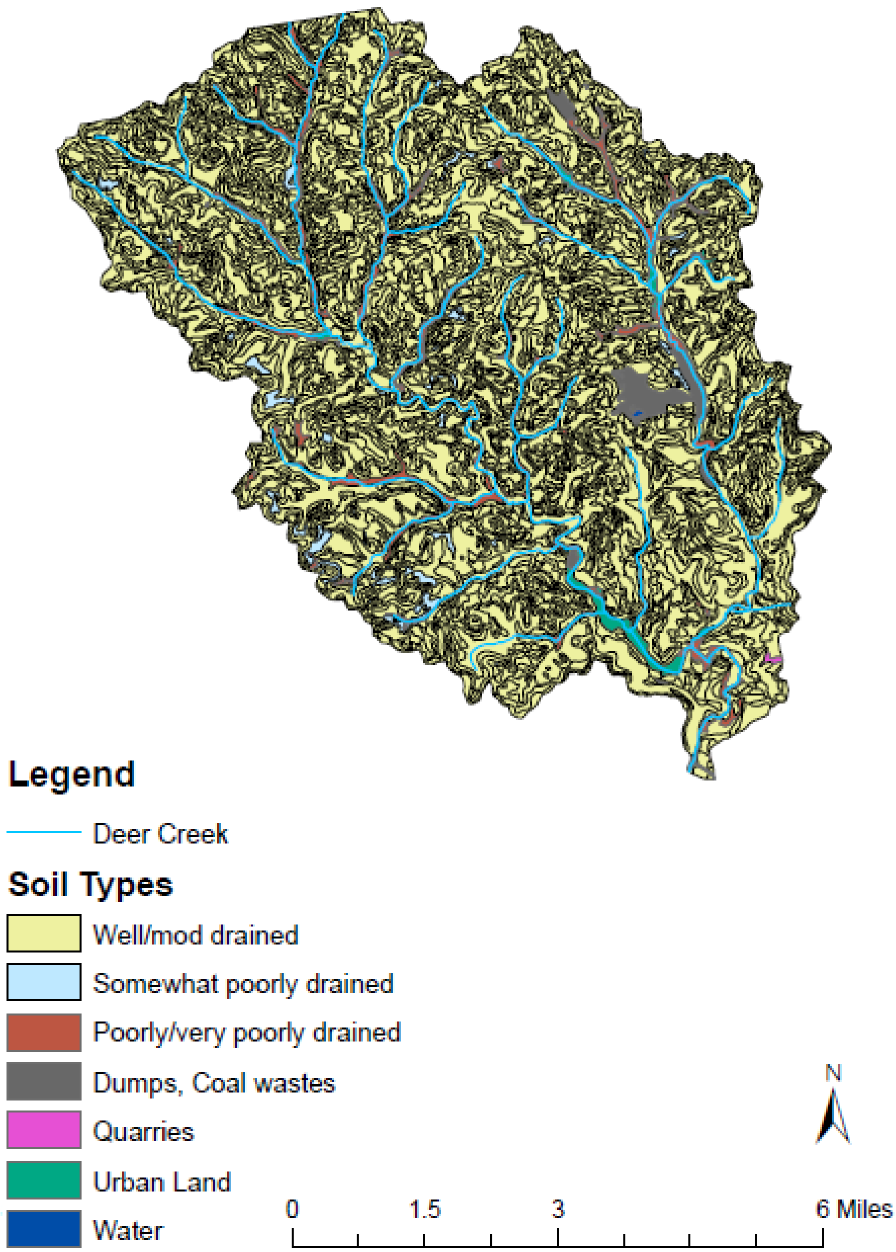

Figure 36. Deer Creek soil types throughout the watershed.

Table 14. Land coverage of Deer Creek from the National Land Cover Dataset (2011).

Land Cover	% Land Cover
Open Water	0.0897345
Developed, Open Space	17.8786336
Developed, Low Intensity	8.1481556
Developed, Medium Intensity	2.6290854
Developed, High Intensity	0.9885642
Barren Land (Rock/Sand/Clay)	0.2578037
Deciduous Forest	58.4889153
Evergreen Forest	0.2343879
Mixed Forest	0.0399216
Shrub/ Scrub	0.0143450
Grassland/ Herbaceous	0.8389097
Pasture/ Hay	5.5638682
Cultivated Crops	4.8095502
Woody Wetlands	0.0706238
Emergent Herbaceous Wetlands	0.0110627

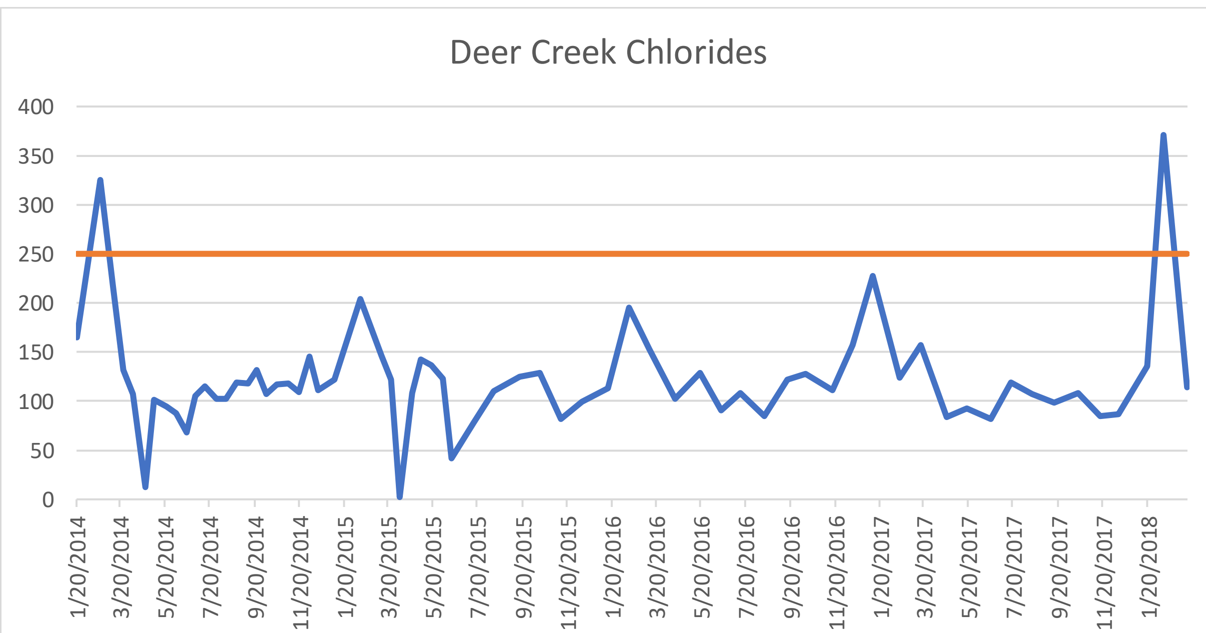

Figure 37. Deer Creek 3RQ chloride concentration data collected from January 2014 to March 2018.

4.4.3 Squaw Run

Squaw Run's land cover can be seen in Figure 38. The data is numerically displayed in Table 16. The soil types based upon ability to drain are shown in Figure 39. The four categories used to describe the soils are excessively drained, well to moderately drained, somewhat poorly drained, and poorly to very poorly drained. Table 17 shows the comparison in impervious and pervious surfaces of Pine Creek, Deer Creek, and Squaw Run. Table 18 shows the chloride concentrations sampled around the same date of the five sites of Pine Creek along with one site in Deer Creek and one site in Squaw Run to get a snapshot in a single time of the watersheds.

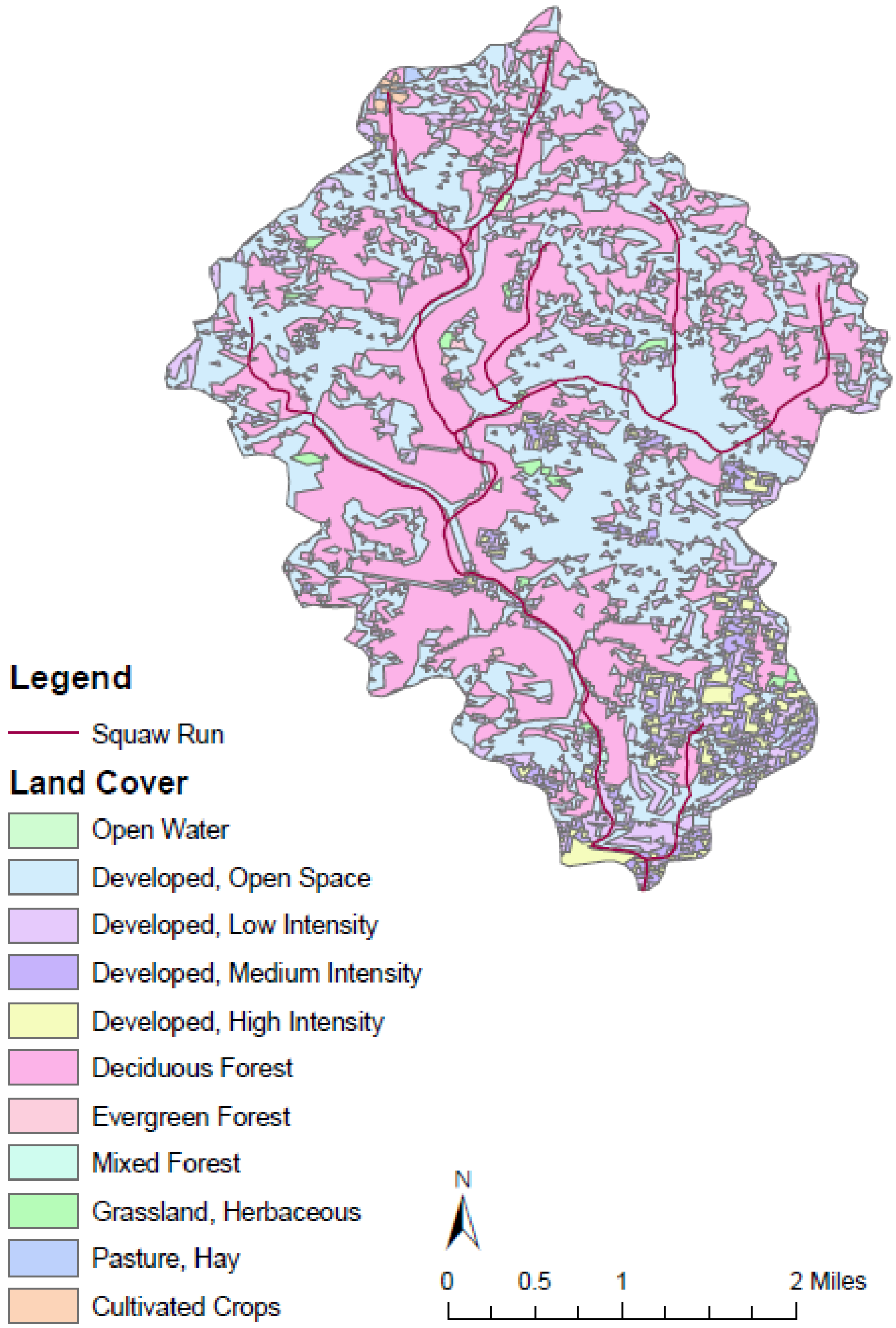

Figure 38. Squaw Run watershed land coverage from the National Land Cover Dataset (2011).

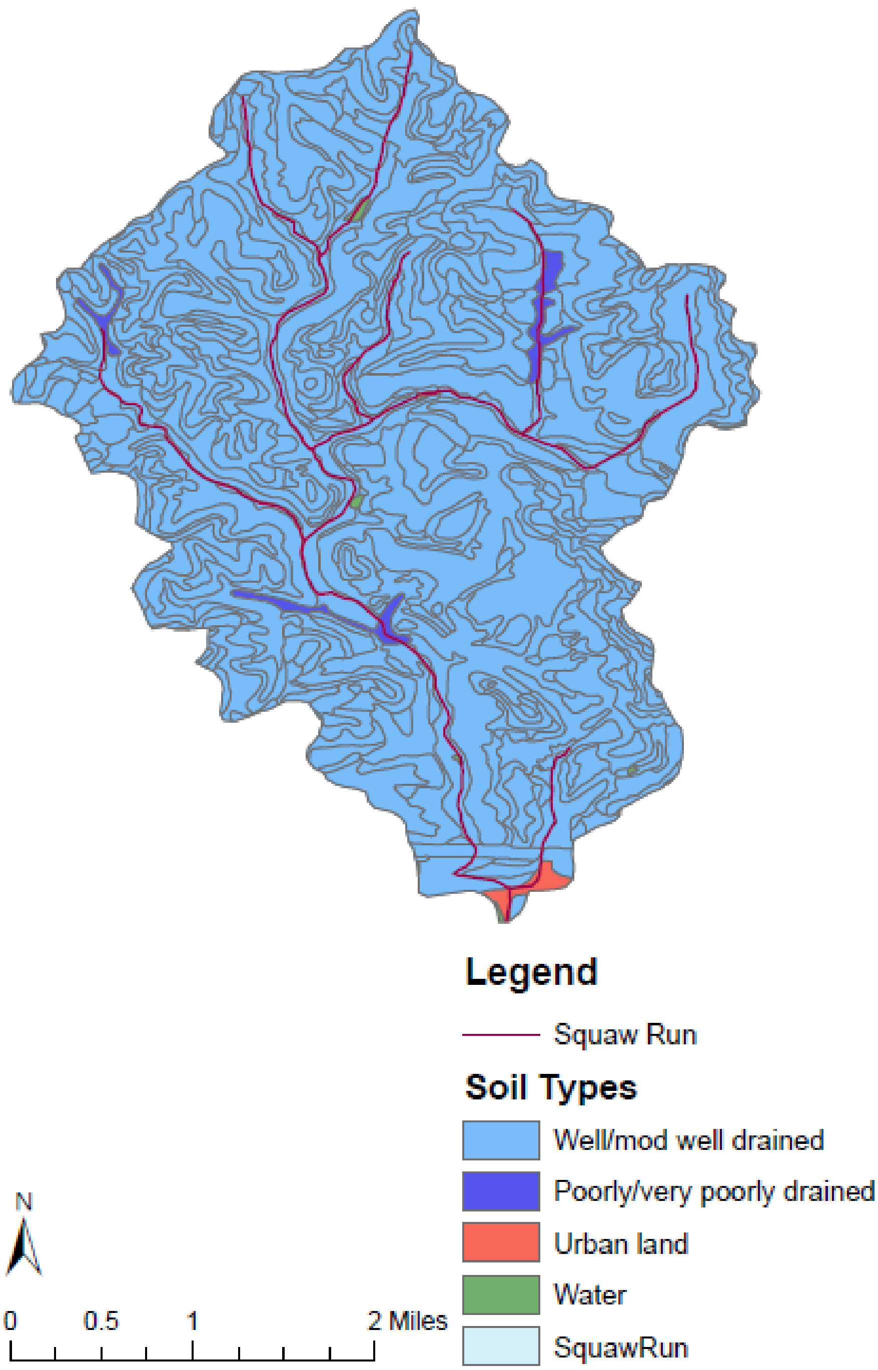

Figure 39. Squaw Run soil types throughout the watershed.

Table 15. Land coverage of Squaw Run from the National Land Cover Dataset 2011.

Squaw Run Land Cover	% Land Cover
Open Water	0.0802952
Developed, Open Space	43.9974756
Developed, Low Intensity	10.1739727
Developed, Medium Intensity	3.5378312
Developed, High Intensity	1.8479176
Deciduous Forest	39.4288940
Evergreen Forest	0.1173965
Mixed Forest	0.0236853
Grassland/ Herbaceous	0.5376387
Pasture/ Hay	0.1285885
Cultivated Crops	0.1263047

Table 16. Impervious and pervious coverage for the comparative watersheds to Pine Creek.

Watershed	% Imperviousness	% Pervious
Pine Creek	58.51	41.49
Deer Creek	29.90	70.10
Squaw Run	59.56	40.44

Table 17. Winter chloride concentration sample data for Pine Creek's 5 target sites, Deer Creek, and Squaw Run.

Watershed	Date	Chloride Concentration (mg/L)
Pine Creek- Grant St	3/16/2018	225
Duncan Rd	3/16/2018	215
Wildwood Rd	3/16/2018	238
North Fork	3/16/2018	216
McCandless	3/16/2018	314
Deer Creek	3/15/2018	114
Squaw Run	3/17/2018	180

CHAPTER 5: DISCUSSION

5.1 3RQ Pine Creek Water Chemistry Data

When comparing Pine Creek to other watersheds using the 3RQ data, it stands out as one of the highest for chloride concentration. Looking further into the watershed alone, it exceeds the USEPA's secondary drinking water standard of 250 mg/L from December to early April. This corresponds with the winter months in which snow events can occur, leading to road salting. The secondary drinking water standard limit most relates to drinking water intakes, as the concentrations can vary farther out, however there are no recorded drinking water intakes on Pine Creek. This is the point at which drinking water starts to be treated for distribution, though it does not remove chlorides in the process. The chronic chloride concentration for aquatic life is 230 mg/L and that was also exceeded from December to early April. This aquatic life limit relates more to the Pine Creek watershed, as aquatic life is spread throughout the watershed and it has portions of trout stocked waters and warm water fisheries designations.

5.2 Prettner 5-Site Targeted Study

Five sites throughout the watershed were sampled in pre-winter conditions as well as one during the winter months. The pre-winter samples of November 2017 and October 2018 revealed an increase in analyte yield from 2017 to 2018 throughout all five sites. Specifically, pre-winter 2018 chloride values resemble the winter 2018 chloride values which could suggest a need for earlier sampling if road deicing occurred. This could also represent salt barn runoff as shipments are sent to stock up before the winter storms. If not properly stored, this salt can runoff into Pine Creek. The McCandless site is immediately downstream from a salt barn located on an impervious surface, making it easier for the salt runoff to enter Pine Creek. This site also had the highest chloride yield of all the sites for the pre-winter 2018 sample. When looking at the Grant Street site for chloride yield and flux, there is no obvious seasonal chloride change occurring within the watershed.

5.3 3RQ Pine Creek Water Chemistry Data

Chloride concentrations varied throughout the months of 3RQ monitoring from 2013-2018. Values ranged from 12.17 mg/L to 678.0 mg/L, rarely exceeding the secondary or aquatic life standards from May to September. During these months, it is not expected to experience snow, so deicing does not explain the higher values. These could be attributed to low flow, resulting in higher chloride concentrations. This could also be due to other pollutants, such as potential sewage leaks from the sewer lines that run through the watershed. An example is shown below in which certain times, the water runs over the manhole covers that lead to these underground sewage pipes (Figures 40, 41).

Figure 40. Sewer line manhole covers in Pine Creek at low flow situations.

Figure 41. Sewer manhole covers with Pine Creek flowing over them at high flow situations.

5.4 Historical Data

The NAEC data obtained was compared to the 5-site targeted study. The pre-winter results did not yield a definitive pattern. It showed that there was an increase from the historical data and the more current data at the Grant Street, Duncan Road, and McCandless sites, all in the lower part of the watershed. This increase could be related to increased impervious surfaces. However, there was an overlap in ranges for the Wildwood and North Fork and their comparative sites which could not determine any temporal patterns in the upper watersheds. When looking at the graphs for each individual comparison for each of the five sites, Grant, Duncan, and McCandless show minor SPC increases over time; however, Wildwood and North Fork show no noticeable changes in SPC.

5.5 Tolerance Indicator Values and Pine Creek Fish Species

Using an ANOVA calculation for data collected on 97 fish and the conditions they live in, chloride concentrations in the tolerant range of 35.4–41.6 mg/L and a mean of 38.5 mg/L (Barbour, Gerritsen, Snyder, & Stribling, 1999; Meador & Carlisle, 2007). This range is well below the average chloride concentrations observed in Pine Creek. The list of chloride tolerant species does not include trout, which are stocked in Pine Creek each year. Stocked trout species (Brown and Rainbow Trout) in general are expected to be tolerant of salinity, as they are anadromous species that move between ocean and streams habitats in their native ranges. Table 13 shows that the number of species that are feasibly residing in Pine Creek were 12 out of 34 total potential expected chloride tolerant species. A few less tolerant species were also found; the banded darter being the most sensitive of the sampled species with a mean chloride tolerance value of 27.0 mg/L with 95% confidence limits from 23.2-30.8 mg/L (Meador & Carlisle, 2007).

When comparing the data of fish collections from August 1971 and October 2018, there was a large difference in the total number of fishes caught. This could be due to length of time for sampling, but this could also be due to differences in how populated the stream was in 1971 versus 2018. In 1971, only 9 of the 191 total fish caught were chloride intolerant species as opposed to 122 of 351 total fish caught in 2018. This could be due to fish becoming desensitized to chloride, in which the 2007 determination of tolerance indicator values would have to be updated. This could also be due to fish diets changing as the chemical parameters change. If the invertebrates a fish typically feeds on die from less-than-ideal chemical conditions. As urban salinization increases in the northwest as previously noted, this can create issues for both intolerant and tolerant species. It should be noted that fish species were categorized based solely on chloride tolerance. Other chemical and physical parameters including ammonia concentrations, chloride concentrations, specific conductance, dissolved oxygen, nitrate and nitrite, pH, total phosphorus, sulfate, suspended solids, and water temperature could play a role in the fish's ability to survive in varying chloride concentrations.

5.6 Groundwater and Surface Water Study

Linnea Manley's groundwater and surface water study of Pine Creek showed that the groundwater concentration of chloride from homeowners' wells varied greatly, while the surface water samples did not. Respectively, these ranges went from 1.87-1082.29 mg/L and 132.18-513.65 mg/L. When using the standard curve developed from the 3RQ data to predict chloride concentrations based upon specific conductivity, the surface water chloride concentrations from the lab corresponded with the predicted chloride concentrations more than the groundwater values as seen in Table 7. The average percent error in predicted chloride versus actual chloride concentrations of groundwater was 262.53% with a standard deviation of 781.71% showing that this standard curve is not a proper method to apply for groundwater in the area. Figure 20 shows the chloride and SPC relationship for the groundwater samples, still suggesting a direct relationship. Groundwater movement and composition might be affecting the water chemistry before it reaches the surface. Unlike the groundwater, the surface water average percent error was 34.39% with a standard deviation of 9.67%.

5.7 Land Coverage and Soil Types of Pine Creek, Deer Creek, and Squaw Run

Pine Creek and Squaw Run have similar land coverage percentages based upon pervious and impervious surfaces. Pine Creek is comprised of 58.51% impervious surfaces and 41.49% pervious surfaces. Squaw Run has 59.56% impervious surfaces and 40.44% pervious surfaces. Squaw Run, however, is smaller in overall drainage area than Pine Creek (only 8.56 square miles vs. 67.3 square miles) ("StreamStats," 2019). Deer Creek more resembles the Pine Creek watershed size in terms of drainage area (49.3 square miles vs. 67.3 square miles), however the coverage varies greatly ("StreamStats," 2019). It is made of 29.90% impervious surfaces and 70.10% pervious surfaces. This means that it would be expected that Deer Creek would have less runoff contributing to the watershed than Pine Creek. When comparing a snapshot of one day of Pine Creek, Deer Creek, and Squaw Run, Pine Creek had the highest chloride concentrations. All three of these watersheds are considered to have well to moderately draining soil, which helps runoff to percolate into the ground instead of becoming runoff. Since Squaw Run has similar land coverage to Pine Creek as well as soil type, it would be expected that its chloride concentration would be similar. This was not the observed, however this is just a snapshot at the watershed level. Further regular monitoring would help to better understand how these factors play in to chloride variations in these three watersheds.

CHAPTER 6: FUTURE DIRECTIONS

Future work includes monitoring the watershed at major confluences to try to detect if any pollutants are coming from a smaller tributary within the Pine Creek watershed, or if high levels of chlorides are ubiquitous throughout the entire watershed. This would require about 20 sites to obtain snapshots of the watershed as a whole. Monitoring these sites should include sampling during each season for water chemistry and discharge in order to calculate yield and provide further evidence on which tributaries might be acting as a point source for chloride contamination in the Pine Creek watershed. Monitoring should also include Squaw Run and Deer Creek to obtain better information on comparative chloride concentrations as they relate to Pine Creek apart from drainage size.

Further, monitoring should be done at salt barns to note any changes upstream and downstream of their locations to see if they contribute to stream chloride contamination. This would have to be done before or during a rain event to detect if runoff occurs, and if so, how significant is that compared to the baseline data.

Gathering precipitation data has proven to be tricky for the Pine Creek watershed. A new method needs to be formulated to more accurately determine precipitation in the watershed that could affect in-stream concentrations and runoffs into the creek.

Further investigation of the role of natural brines and geology in Pine Creek chloride levels, as well as additional well data should be collected along with collecting core data from when the wells were drilled, if available. Detecting any geographical patterns could suggest a geological influence on the great variance of the chloride well data.

CHAPTER 7: REFERENCES

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