

THE FATE AND TRANSPORT OF CHLORIDE IN A
CONSTRUCTED STORMWATER WETLAND

By

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Thesis

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DEDICATION

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NOMENCLATURE

BTI – Bio-infiltration Traffic Island

CSW – Constructed Stormwater Wetland

IN – Average of Villanova Constructed Stormwater Wetland Inlet Duplicate Samples

OUT – Average of Villanova Constructed Stormwater Wetland Outlet Duplicate Samples

SCM – Stormwater Control Measure

TDS – Total Dissolved Solids

TSS – Total Suspended Solids

ABSTRACT

Road de-icing salt is one contaminant of concern in stormwater runoff, as it has been shown to have negative effects on plant and animal species, decrease biodiversity, and degrade environmental quality. It has been assumed that road de-icing salt would wash through watersheds with spring rains, as road salt (usually NaCl) is soluble, and chloride (Cl^-) has long been considered a conservative tracer. However, many recent studies suggest that significant proportions of chloride mass may be retained within a watershed and that chloride levels resulting from winter salting activities may remain elevated late into summer months. Stormwater control measures (SCMs) have been praised for both volume reduction and improved water quality, but recent studies are showing that certain SCMs may increase the negative effects of road salting on the surrounding environment, such as contamination of groundwater, trace metal leaching, stratification in ponds, toxic effects, and reduced biodiversity. Because chloride poses a possible threat to downstream waters, a study was performed to study the fate and transport of chloride through one SCM, a constructed stormwater wetland (CSW), on Villanova's campus.

The study had three main goals: i.) to determine if effluent concentrations of chloride from the CSW meet recommended EPA standards for both chronic and acute criteria; ii.) to compare total dissolved solids (TDS), conductivity, and chloride concentration data in order to further validate the data sets and also quantify correlations between each parameter; and iii.) to perform a mass balance of chloride to study the fate and transport of chloride upstream, within, and downstream of the CSW. Chloride concentrations and TDS/conductivity/chloride correlations were analyzed over a period of four years, from December 2011 - November 2015 and a mass balance was done with flow data for 2013 and 2014. High chloride spikes were

observed during the Salt Application period, between December and May, and heightened baseflow chloride concentrations lasted through summer months, even when storm event concentrations were low approaching > 10 mg/L. In using EPA freshwater quality criteria of chronic (230 mg/L) and acute (860 mg/L) toxicity as benchmarks, it was found that the CSW effluent concentration was below chronic only 33% of sampled baseflow events (10% exceeded acute) and 77% of sampled storm events (12% exceeded acute). On a yearly basis, it was estimated that the CSW effluent is below chronic criteria only 39% of the year, exceeds the chronic criterion 61% of the year, and exceeds the acute criterion 12% of the year. Because this study was unable to assess the precise EPA criteria definitions (based on 1 and 4-day averages), this serves only as an estimate of the CSW's performance.

Chloride/TDS/conductivity correlations were created between each parameter and the Villanova CSW had a TDS/conductivity k constant of 0.64 (mg/L)/(μ S/cm) for TDS $< 1,000$ mg/L and a k constant of 0.54 (mg/L)/(μ S/cm) for values above 1,000 mg/L TDS. A comparison to a bio-infiltration basin also on campus showed that correlations were similar, even for subsurface samples at that location.

A mass balance of the Villanova CSW showed that about 40-50% of volume is reduced between the inlet and the outlet, and an equal, if not slightly greater percentage of chloride mass is retained within the CSW as well. In comparison to road de-icing salt application estimates, there is evidence that there is a greater amount of chloride mass entering the CSW than from impervious surfaces alone. This leads to questioning the possibility that groundwater flow interacts with the CSW and carries additional chloride mass from upstream locations. Analysis of discharge and chloride concentration data of Mill Creek, the natural water body immediately downstream of the CSW, showed that a large amount of chloride mass is added to Mill Creek

after the CSW. This indicates that the CSW is not the only source of chloride loading to Mill Creek and that it is only a small percentage of the total chloride loading throughout the creek. Of the available dataset, Mill Creek chloride concentrations were below 230 mg/L for all sampling events but one that occurred in mid-winter of 2014.

CHAPTER I: INTRODUCTION

1.1 Literature Review

Stormwater runoff is a concern in metropolitan areas due to both increased quantity and degraded quality of the runoff generated by impervious areas. High volumes of runoff erode natural waterways and/or overwhelm wastewater treatment facilities during large events, and high pollutant loadings that collect on impervious surfaces are flushed out into natural waterways. The quality of stormwater runoff is affected when contaminants such as nutrients and heavy metals are washed off during rain events. One highly soluble contaminant of concern for stormwater runoff is chloride.

Chlorides, in the form of de-icing salts, are heavily applied to roadways and other impervious areas during the winter season in populated areas experiencing freezing temperatures across the world, but the fate and the resulting environmental effects have not been thoroughly understood. In the United States alone, approximately 18 million tons of NaCl are applied to roadways every year, with most of it applied to the Northeastern and Midwestern states; six states (New York, Ohio, Michigan, Illinois, Pennsylvania, and Wisconsin) use 75% of the total salt applied (Jackson and Jobbágy 2005).

Before the 1940s, plowing and abrasives were the primary strategies in clearing roadways, but after World War II salt became much more common as a method for clearing highways, which were now much more vital to the U.S. economy. Road de-icing salt exploded during the 50s and 60s and usage increased at an unprecedented rate, growing from 1 million tons in 1955 to almost 10 million in 1970 (Figure 1.1).

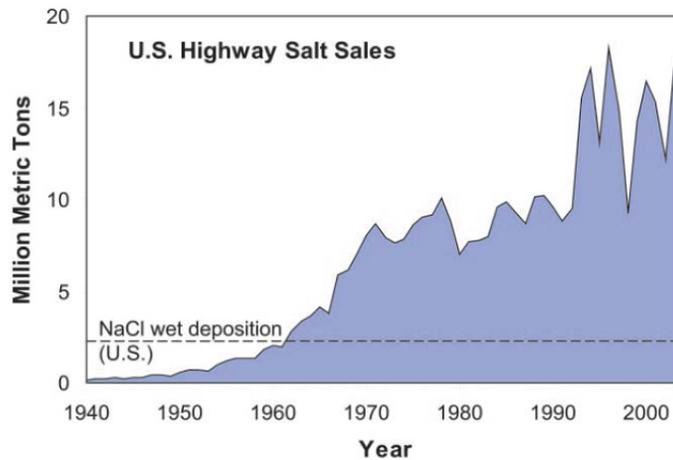


Figure 1.1: Sales of Rock Salt for Highway Use in the U.S. from 1940 to 2004 (Jackson and Jobbágy 2005)

Around this time, the possible environmental repercussions of road de-icing salt were first being discovered, and some efforts were made to curb the effects. Currently, salt usage averages near 18 million tons per year, depending on the severity of winter conditions for a particular year (Jackson and Jobbágy 2005).

Most of road de-icing salts applied to U.S. roadways is composed mainly of sodium chloride (NaCl), with both the sodium (Na^+) and the chloride (Cl^-) ions being contaminants of concern. Other salt formulas may use calcium (Ca), magnesium (Mg), or potassium (K) rather than Na^+ , as well as other additives and trace compounds, however, only chloride will be addressed in this study. Chloride occurs naturally in the environment at low levels and there are EPA limits to which sampled concentrations can be compared to for freshwater compliance criteria. Chloride has been long regarded as a conservative tracer, although some recent studies have indicated that this may not always be the case.

While chloride occurs naturally in the environment, increased use of road de-icing salts in urban areas has been shown to increase chloride levels in the watershed (Sherwood 1989,

Ramakrishna and Viraraghavan 2005). Chloride concentration has been shown to increase with increasing road density or increased impervious land use (Wulkowicz and Saleem 1974, Siver et al. 1996, Rhodes et al. 2001, Kaushal et al. 2005, Gardner and Royer 2010, Corsi et al. 2014, Swinton et al. 2014, Smith 2015). In a study of the Scituate Reservoir Drainage Area, from 1983-2002 there were upward chloride concentration trends, with concentrations leveling off from 2003-2012 due to more sustainable practices (Smith 2015). On that same Scituate Reservoir system, it was found that de-icing salts accounted for 90% of the chloride, indicating that road de-icing salts can be a large contributor to elevated chloride concentrations in a watershed (USGS 2002). In a study of long-term data from the Schuylkill River, the downstream receiving waters of the Villanova Constructed Stormwater Wetland (CSW), it was found that sodium and chloride increased over time and were more elevated during winter due to road salt application, and that the increased solute transport in the most recent decades was due to suburban development in the watershed (Interlandi and Crockett 2003).

The presupposition made when first applying salts was that they would flush out during the spring rains, leaving little effect on the application areas (Sadowski 2002), however, current research that has delved into the fate and transport of chloride through watersheds shows that up to 77% of chloride may be retained within the watershed (Novotny et al. 2009), with many studies showing evidence of some retention through mass balance studies (Wulkowicz and Saleem 1974, Howard and Haynes 1993) or through export monitoring (Demers and Sage 1990, Brown and Scorca 1995, Godwin et al. 2003, Kelly et al. 2008, Gardner and Royer 2010, Findlay and Kelly 2011, Corsi et al. 2014).

Retention of chloride and the mechanisms by which it is retained are not yet well understood. The complex interactions between groundwater, soils, surface waters, and flow

patterns make chloride difficult to trace. It is also being questioned in terms of both soil interactions and density stratification, whether chloride is as conservative as was previously thought. Studies have shown that chloride can collect in groundwater (Wulkowicz and Saleem 1974, Howard and Haynes 1993, Brown and Scorca 1995, Rosenberry et al. 1999, Ruth 2003, Aghazadeh et al. 2012) and lakes (Demers and Sage 1990, Siver et al. 1996, Rosenberry et al. 1999, Swinton et al. 2014); in many cases these concentrations increase over time, and may grow to toxic and non-potable levels. De-icing salts affect much larger areas over longer time frames than what was originally expected. One study (Findlay and Kelly 2011) showed increasing retention of chloride without increasing chloride loads within a watershed, which implies chloride retention with slow release over time. The study also showed that accumulation of salt in long-residence hydrologic pools and flow paths could delay appearance of high concentrations, meaning that even with complete suppression of salt application, concentrations would continue to rise long after the change.

If road salt is applied at the same rates that are currently used, groundwater levels in high urban density areas may reach chloride concentrations much higher than the water quality objective for potable water of 250 mg/L (Howard and Haynes 1993) and freshwater stream and drinking water reservoir salt concentrations will continue to rise (Kaushal et al. 2005). In one study groundwater wells in the Twin Cities Metropolitan Area of Minnesota (an area receiving 142,000 tons of Cl^- per year) contained concentrations even as high as 2,000 mg/L, when pre-urbanization concentrations were only 3 mg/L (Novotny et al. 2009). Not only is there a large amount of chloride retention in watersheds, but it has also been found that levels of chloride can remain elevated long after salt was applied, after the snow melt and spring rains, even late into the summer months (Demers and Sage 1990, Brown and Scorca 1995, Kaushal et al. 2005,

Gardner and Royer 2010, Sadowski 2002, Corsi et al. 2014). A study of the northeastern U.S. from 1967 to 2006 found that maximum chloride concentrations were 2000 mg/L, that concentrations in the summer remained up to 100 times greater than un-impacted forest streams, and predicted that within the next century, current management practices will eventually result in toxic chloride levels throughout the northeastern U.S. (Kaushal et al. 2005).

Chloride has been assumed to be conservative in soils and to be a reliable groundwater tracer, however a growing number of studies indicate that chloride may be retained in soils (Bastviken et al. 2006, Svensson et al. 2007, Notovny et al. 2009, and Aghazadeh et al. 2012). A study on the natural cycle of chloride in uncontaminated soils in a forested catchment in Sweden (soils unaffected by any road de-icing salt runoff) showed that the soil pool was dominated by chlorinated organic carbon, while transport was dominated by chloride (Cl^-) (Svensson et al. 2007). Soils may serve as either a sink or a source of chloride through this complex biogeochemical cycle, where chloride can be transformed from one form to another in conjunction with available organic matter. Another study in Sweden showed evidence that longer residence times in soil and higher chloride loading resulted in higher initial retention and release rates, and that retention may be due to organic matter or ion exchange (Bastviken et al. 2006).

In a waterbody, chloride retention may also be affected by stratification in some cases. It has been well-documented that lakes receiving high influent concentrations of salts may stratify more easily, as the saltier water is denser than salt-free waters, and will sink to the lower layer of the lake. This stratification may delay the natural cycle of lake mixing in the fall and spring seasons, preventing oxygen from mixing into the anoxic bottom layer, and catalyzing eutrophication (Siver et al. 1996, Koretsky et al. 2011). In one case, the entire Irondequoit bay in

New York was so affected by high salt loading during the 1969-70 year that complete vertical mixing in the spring did not occur (Bubeck et al. 1971).

Chloride concentrations above 250 mg/L does not meet EPA secondary drinking water standards, as that level will cause the water to have a salty taste (USEPA 2009). Heightened chloride concentrations do not only affect potable water for humans, but may be toxic to delicate freshwater species as well. At heightened levels, chloride may have an effect on the survival and health of many amphibians, especially egg and larval stages, disrupting their osmoregulation, causing lower survival rates and increased physical abnormalities (Sanzo and Hecnar 2005, Karraker and Gibbs 2011, Karraker et al. 2008, Sadowski 2002). Species closest to salt-applied roadways were the most negatively affected (Karraker et al. 2008) and species diversity decreased with increasing chloride concentrations (Sadowski 2002). Salamander clutches exposed to high chloride concentrations continued to lose mass after transfer to control water, indicating that high concentrations have an effect long after dilution occurs, though clutches exposed to low concentrations bounced back (Karraker and Gibbs 2011). Chloride also has an effect on algae and zooplankton, as it was found that both have differential susceptibility to chloride in a stormwater pond study (Van Meter and Swan 2014). As mentioned, salt concentrations may remain high late into the summer, which is when organisms are the most physiologically active; therefore it cannot be assumed that organisms will remain unaffected by chloride concentrations due to the seasonal nature of salt application. At 22°C, both high and low concentrations negatively affected the survival rates of certain larvae (Silver et al. 2009), and in conjunction with evidence of elevated chloride concentrations through the summer months, it can be postulated that organisms may be negatively affected during their most active period. Even relatively salt-tolerant species may experience lower survival rates and increased

malformations at heightened concentrations, as in the case of the green frog (Karraker 2007). A 2001 Canadian study estimated that approximately 10% of tested species experience acute effects as a result of long-term exposure to chloride concentrations as low as 240 mg/L, fifty percent by concentrations of 541 mg/L, and 90% by concentrations of 1,018 mg/L (Evans and Frick 2001).

Road de-icing salts have a negative effect on plant species survival and biodiversity as well as animal species. Heightened salt concentrations can kill off non-salt-tolerant plants on their own, or more salt-tolerant plants will grow, such as *Phragmites* (a salt-tolerant invasive giant reed), when salt concentrations increase and then choke out native species (Richburg et al. 2001). Chloride tends to accumulate in plant tissue sometimes to toxic levels, especially in leaves, and chloride accumulation is closely related to the chloride concentration in the source solution, so as more chloride is available to the plant, the more it accumulates (Hajrasuliha 1980). Chloride uptake in mung bean root tips showed a similar result, where net uptake of chloride increased steadily with increasing source concentrations (Gerson et al. 1972). High concentrations of salt may harm less salt-tolerant plants by causing osmotic stress (as it might do in amphibians), specific toxicity of the ions, or by altering soil/water pH, nutrient availability, nutrient balance in the plant, and (in rare cases) due to soil permeability (Davison 1971). A study of Norway maple (*Acer platanoides*), silver birch (*Betula pendula*), Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*) seedlings grown in a series of NaCl concentrations found that leaf necrosis (death of leaves due to deficiencies of nitrogen, phosphorus, potassium, and magnesium that first results in chlorosis (yellowing)) correlated significantly with leaf concentrations of both sodium and chloride (Fostad and Pedersen 2000). The study also indicated that in addition to the NaCl effects, seedlings grown in sandy soils had more severe necrosis than those grown in loam, silt

loam, and peat, and that drought also significantly increased necrosis. Given that some stormwater control measures (SCMs), such as bio-infiltration systems, sometimes rely on sandy soils as a relatively quick infiltration mechanism that results in dry periods, elevated NaCl concentrations may have an even greater impact on SCM biota in conjunction with these conditions.

Chloride also has an effect on suspended metals concentrations in stormwater, as free chloride moving through the soil-water interface may serve as an available source for complexation of positively charged ions, and as Na^+ is highly exchangeable in organic matter in soils. Increased chloride concentrations have been shown to result in increased cation concentrations, including heavy metals (Calmano et al. 1992, Mason et al. 1997, Endreny et al. 2012, Tromp et al. 2012). Concentrations of chromium (Cr), lead (Pb), nickel (Ni), iron (Fe), cadmium (Cd), and copper (Cu) increased with increasing salt concentration, mostly due to dispersion of organic matter under conditions of high exchangeable Na^+ and low electrolyte concentration (Amrhein et al. 1992). In column experiments testing chloride concentrations of 80, 315, and 935 ppm, increased chloride concentrations resulted in increased effluent Zn concentrations, and this was also demonstrated in terms of microbial activity (Endreny et al. 2012). Increased NaCl concentrations correlated with dissolved zinc in another study (Ruth 2003).

Chloride has been largely ignored in the pollutant removal aspects of green stormwater infrastructure, with research mainly putting emphasis on plant-available phosphorus and nitrogen species as well as heavy metals (Carlisle and Mulamootil 1991, Carleton et al. 2000, Dietz et al. 2005, Flint and Davis 2007). In stormwater from non-industrial urban areas, these influent concentrations of nutrient and metal contaminants of concern are dwarfed in comparison to the

loading of road de-icing salts in many urban areas, and the location of SCMs will largely determine the severity of road de-icing salt influence on the surrounding environment. Many SCMs aim for volume reduction through infiltration, and therefore they funnel stormwater, and likely with it road de-icing salts, more directly into the natural water cycle than do traditional storm sewers. Some recent studies have shown that certain SCMs may increase the negative effects of road salting on the surrounding environment, such as contamination of groundwater, trace metal leaching, stratification in ponds, toxic effects, and reduced biodiversity (Pitt et al. 1999, Marsalek 2003). As systems that emphasize infiltration and volume reduction, as well as direct connections to natural water systems, including both surface and groundwater, SCMs should be carefully designed to take into account the fate and transport of road de-icing salts through the SCM and into the natural downstream waters.

A constructed stormwater wetland (CSW) is one type of SCM used in cases where a large area of land is available and a large volume of runoff is expected, and can be designed with different parameters in order to achieve certain stormwater mitigation goals, such as peak flow reduction, volume reduction, and water quality improvement. CSWs are advantageous in instances where large volumes of stormwater from impervious surfaces need to be mitigated in terms of both water quantity and quality, and may also serve as a permanent thriving ecological habitat. Wetlands are natural buffer areas that are important for the health of an ecosystem, and bio-retention systems have proven to be effective in improving quality of stormwater through biological, chemical, and physical interactions (Coleman et al. 2001, Davis 2007, Li and Davis 2009). Plants growing in a CSW use nutrients, sediments adsorb nutrients and metals, and long detention times allow suspended solids to settle out (Wadzuk et al. 2010). While these systems have been shown to improve water quality, it has been suggested that wetland systems are

generally unable to succeed in both water quality improvement and aquatic habitat enhancement, as the impact of certain contaminants may not be mitigated due to bioaccumulation (Helfield and Diamond 1997). Not much is known on how CSWs perform in terms of removal and transport of chloride, and in research done thus far there is no definitive pattern. One study showed an annual mass reduction of 45% of chloride in a constructed wetland, with 93% of that estimated to be due to volume reduction (Natarajan and Davis 2015). Another study found that while shallow groundwater samples taken before and after installation of a CSW showed significant decrease in arsenic (As), chromium (Cr), nickel (Ni), and zinc (Zn) after installation, that chloride concentrations significantly increased from pre-installation concentrations, also evidence of removal through infiltration (Ouyang 2013). A previous study conducted on the Villanova CSW in 2010 estimated that there was no significant removal of chloride through the system, and observed higher baseflow loading than storm loading, postulating a possible additional source of chloride loading through groundwater flow (Wadzuk et al. 2010).

Overall, it has been shown that road de-icing salts do cause negative environmental impacts, and that chloride is a contaminant of concern. As it becomes more and more apparent that these salts are not flushed out of delicate natural water systems as easily as was presupposed, the amounts of salt being applied to urban areas should be reassessed and measures should be taken to mitigate their negative effects on both the surrounding environment and on the availability of potable water for future generations to come. Because SCMs, and particularly CSWs, are designed to be a part of the natural system and benefit the surrounding watershed, one of the top priorities of an SCM design should be to minimize the influence of road de-icing salts on the surrounding environment.

1.2 Research Plan

In this study, the concentrations, seasonal fluctuation, and fate and transport of chloride are analyzed at a Constructed Stormwater Wetland (CSW) at Villanova University over the time period from December 2011-November 2015. The study had three main goals: i.) to determine if effluent concentrations of chloride meet recommended EPA standards for both chronic and acute criteria; ii.) to compare total dissolved solids (TDS), conductivity, and chloride concentration data in order to further validate the data sets and also quantify correlations between each parameter; and iii.) to perform a mass balance of chloride to study the fate and transport of chloride upstream, within, and downstream of the CSW. Chloride, conductivity, and TDS data were collected simultaneously from samples taken at the CSW during both baseflow and storm events over the time period Dec 2011-Nov 2015. Chloride concentrations at the CSW were graphed over time during both baseflow and storm conditions and separated into Salt Application (December-May) and Non-Salt Application (June-November) seasons. The Salt Application period is defined as December through May due to high chloride concentrations observed through this month with washout from spring rains, a trend that is necessary to separate from the Non-Salt Application months for seasonal comparison. TDS, conductivity, and chloride data sets were analyzed for the CSW as well as a Bio-infiltration Traffic Island (BTI) and were used to both validate the data sets individually and compared together to determine respective correlations. Of most interest was a TDS/Conductivity equation for each site, a commonly used equation whereby the two parameters are directly related:

$$TDS = k * Conductivity$$

in which the constant k was shown to be between 0.55 – 0.7 (American Public Health Assoc. 1999). Volume data for the respective years, seasons, and baseflow or storm conditions was separated out and used with the influent and effluent chloride concentration data to calculate the

mass of chloride traveling through the CSW. These masses were then compared to both the estimated road de-icing salt mass applied to the CSW drainage area as well as the chloride mass (using concentrations and flow data) found at several points along Mill Creek (the direct downstream water body) to estimate the mass of chloride transported through the effluent of the CSW as well as the mass retained within the CSW.

SCMs, including CSWs, have been shown to minimize many of the negative effects of stormwater runoff, both quantitatively and qualitatively. With mounting evidence that chloride has negative effects on the environment, and that chloride may be retained and slowly released in surface waters, groundwater, and soils over long periods of time, SCMs may not have the same benefits for this contaminant of concern that it does for others. This study aims to quantify what, if any, influence a CSW may have on chloride concentration and chloride mass transport through the surrounding watershed.

CHAPTER II: METHODS

2.1 Villanova Stormwater Wetland

Villanova's Constructed Stormwater Wetland (CSW) is located on the northeastern edge of campus next to the Villanova School of Law and is at the headwaters of Mill Creek, a high-priority stream on the perimeter of Philadelphia, Pennsylvania, situated in the Schuylkill watershed. It is a retrofit of an approximately one-acre stormwater detention basin that was used previous to 1999 to mitigate stormwater runoff during large storm events. The site is fed by two inlet structures which transfer stormwater runoff from Main and West campuses, two distinct geographical areas of the Villanova University property, and effluent is released through an outlet structure which regulates flow to the natural downstream waters of Mill Creek. The drainage area is an 18.2-ha suburban watershed, 9.7 ha of which are impervious surfaces and

turfed pervious areas. This gray infrastructure drainage basin was designed with an underdrain so that the site remained dry except during rain events, but in 1999 the site was analyzed for performance and a CSW was chosen as the appropriate replacement for a green infrastructure modification. The first version of the CSW was built as a unidirectional linear channel that flowed to a 40' by 40' sediment forebay, which was designed for longer detention times during baseflow and smaller storms to increase sedimentation. After the sediment forebay, flow was diverted through a series of two meanders before reaching the outlet structure. The underdrain was removed with the intention that water would remain onsite at all times.

In July 2010 the site was redesigned to lengthen the flow path of the wetland, in order to increase detention time to improve water quality and reduce flowrates (Jones et al. 2009), and this design persists today. The new design consists of a large inlet forebay directly receiving stormwater from two inlet pipes, three meanders, each separated by a sluice gate in order to regulate flow and allow water to pond in each meander, an outlet forebay, and a small flow path that leads from the outlet forebay to the same outlet structure used in the original design (Figure 2.1).

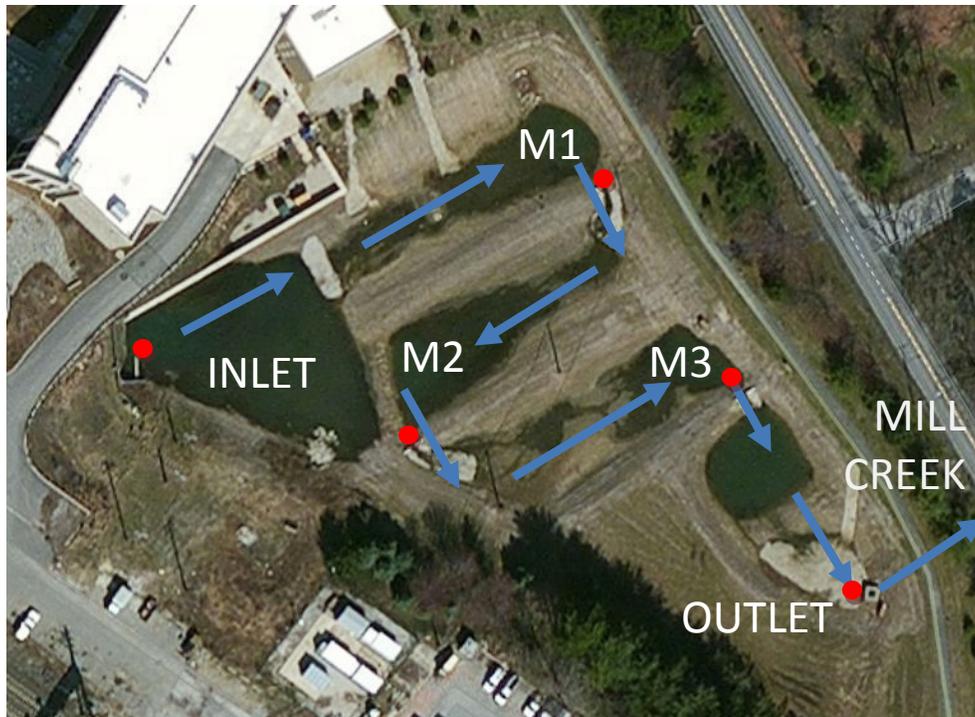


Figure 2.1: Villanova's Constructed Stormwater Wetland (CSW); flow path shown by blue arrows, sampling locations marked with a red circle; M1, M2 and M3 refer to the sampling locations at the end of meander 1, meander 2 and meander 3, respectively; credit Google Maps

The new CSW design maximizes the amount of available area, so that the flow path is as long as possible with the intent that longer detention times would improve water quality and allow for more volume to be retained within the wetland during a rain event. The entire site is vegetated and was planted with a range of native species, however, *Phragmites australis* (Type M), a salt-tolerant invasive species, often overgrows these natives. Volume is lost through evapotranspiration and possibly through infiltration. The timeline for this study was between December 2011 and November 2015, and water quality samples for this study were taken at the CSW only from the current design of the CSW. Both baseflow and storm events were sampled for water quality at the CSW over the study period and the goals for the year were to sample one baseflow event per month as well as one storm event per month, aiming for twelve of each per year. Previous to April 30th, 2014, 1 Liter container grab samples were taken at the CSW for both

storm and baseflow events, immediately after a storm event or the morning after a storm event when necessary. Sample names and locations are shown visually in Figure 2.1 and listed in Table 2A.

Table 2A: Constructed Stormwater Wetland (CSW) Samples: Grab Sample Designation for Sampling Locations - Baseflow and Storm Events

Sample Names	Description
IN 1 and IN 2	Duplicate samples taken at the inlet pond of the CSW
M1-1 and M1-2	Duplicate samples taken at meander 1 of the CSW
M2-1 and M2-2	Duplicate samples taken at meander 2 of the CSW
M3-1 and M3-2	Duplicate samples taken at meander 3 of the CSW
OUT 1 and OUT 2	Duplicate samples taken at the outlet structure of the CSW

In order to gain more information about how water quality may change over the course of a storm and to better understand flow through the wetland, beginning on April 30th, 2014, Hach Sigma 900MAX autosamplers were installed and implemented to collect several water samples at specific rainfall amounts during a rain event. Autosamplers were only installed in the Inlet, Meander 1, and the Outlet and each autosampler fills four separate 1 Liter containers with composite samples over the course of the storm, each affiliated with specific rainfall amounts, and each given a specific name (Table 2B).

Being connected to the CSW rain gauge, a Loggernet CR1000 data logger triggers the autosamplers with a pulse correlating to specific rainfall depths, and fills each of the four sample containers with composite samples taken at three individual rainfall depths. (Figure 2.2). Accounting for traveling time which was calculated by a dye tracer study at the CSW (Neptune 2015), delays in autosampler sampling times are used for both Meander 1 and the Outlet.

Meander 1 samples at a 45 minute delay and Outlet samples at a 90 minute delay. Because the Inlet is immediately receiving influent stormwater from drainage pipes, no delay is necessary.

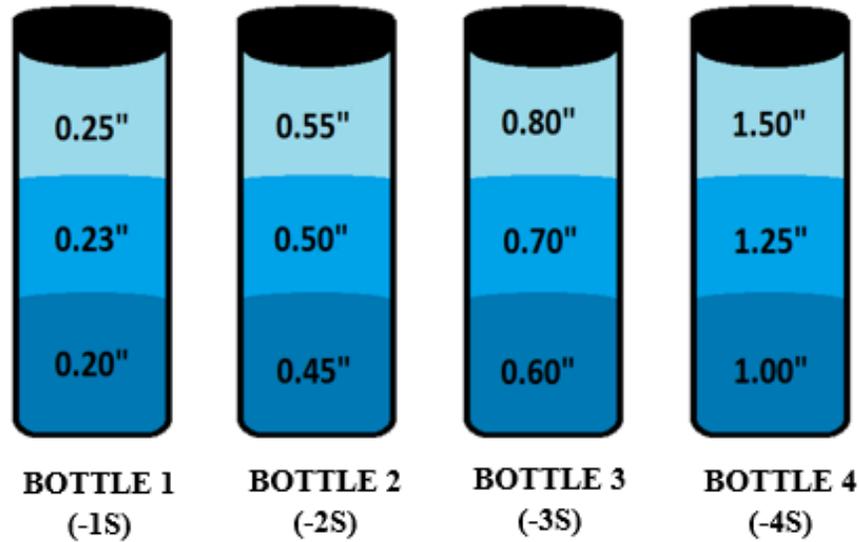


Figure 2.2: Four Autosampler Composite Samples during a Storm Event at the CSW from April 2014 - November 2015; each location (IN, M1, and OUT) fills 4 bottles as shown, and each bottle is a composite sample taken when each of the rainfall inches listed on the particular bottle occurs (Example, bottle 1 is taken when the rain gauge reads 0.20", at 0.23", and at 0.25")

Table 2B: Constructed Stormwater Wetland (CSW) Samples: Autosampler Storm Events

Sample Names	Description
AS IN 1	Composite sample at inlet at 0.20", 0.23", and 0.25"
AS IN 2	Composite sample at inlet at 0.45", 0.50", and 0.55"
AS IN 3	Composite sample at inlet at 0.60", 0.70", and 0.80"
AS IN 4	Composite sample at inlet at 1.00", 1.25", and 1.50"
AS M1-1	Composite sample at meander 1 at 0.20", 0.23", and 0.25"
AS M1-2	Composite sample at meander 1 at 0.45", 0.50", and 0.55"
AS M1-3	Composite sample at meander 1 at 0.60", 0.70", and 0.80"
AS M1-4	Composite sample at meander 1 at 1.00", 1.25", and 1.50"
AS OUT 1	Composite sample at outlet at 0.20", 0.23", and 0.25"
AS OUT 2	Composite sample at outlet at 0.45", 0.50", and 0.55"
AS OUT 3	Composite sample at outlet at 0.60", 0.70", and 0.80"
AS OUT 4	Composite sample at outlet at 1.00", 1.25", and 1.50"

2.2 Villanova Bio-infiltration Traffic Island

A bio-infiltration basin is one stormwater control measure (SCM) that is used to mitigate stormwater concerns by capturing stormwater, holding it for a prolonged time to encourage pollutant reduction and a lower peak flow, and then releasing it slowly back into the natural water cycle. Villanova's Bio-infiltration Traffic Island (BTI) (Figure 2.3) is a bio-infiltration rain garden that was built in 2001 adjoining a parking lot on the west campus as a retrofit to an existing grassy traffic island. It captures runoff from an area of approximately 1.21 acres, 52% of which is impervious. The traffic island was excavated to form a bowl shape, and porous media (a 50:50 mixture of sand and existing excavated soils) was filled in to a depth of 4 feet. Vegetation species chosen to survive both wet and dry conditions for long time periods were planted within the bowl, including grasses, herbs, and woody plants.



Figure 2.3: Villanova's Bio-infiltration Traffic Island (BTI) During a Rain Event

The BTI captures stormwater runoff from the adjoining parking lot during a storm event and it collects in the bowl, seeping into the porous media and then slowly percolating down into deeper layers of soil, eventually down to the groundwater table. While much of the volume

reduction is achieved by capture and slow release into groundwater, some is also released into the atmosphere through evapotranspiration, a combination of evaporation (vaporization directly into the air) and transpiration (release through plant leaf processes), a process that is mainly functional during the warm months (Hickman et al. 2011). Pollutant removal can be achieved through adsorption to soils and uptake by plants (Hatt et al. 2009). The BTI captures diverted stormwater runoff that would otherwise make its way to a dry detention basin without filtration of some pollutants and without infiltration of waters directly back into the water cycle.

The BTI is sampled at least once a month, with an emphasis on sampling two storm events per month, when possible. Sampling locations are shown within a schematic of the BTI from a vertical angle with water traveling through the soil, below (Figure 2.4).

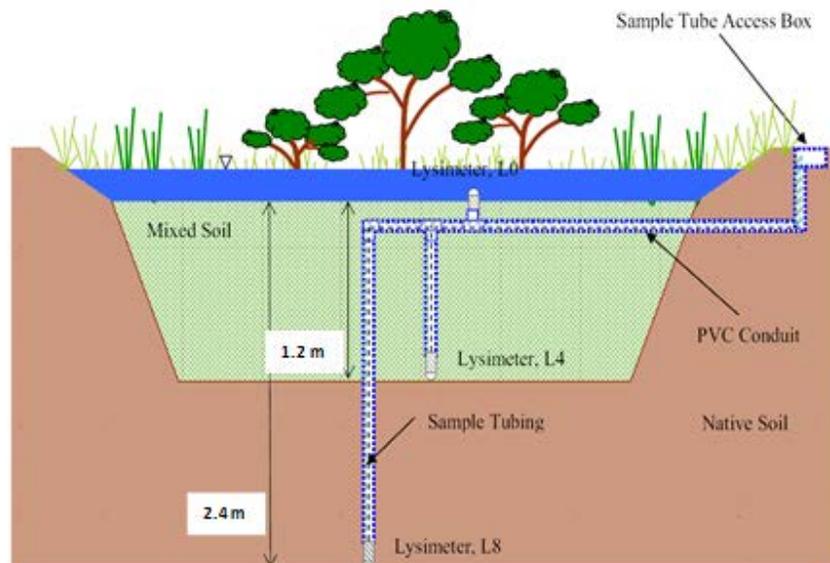


Figure 2.4: Sampling Locations of the Bio-infiltration Traffic Island (BTI); image modified from Ermilio, 2005

Samples include a first flush grab sample, an overflow sample, grab samples from the bowl during the storm event, a composite autosampler sample, and several lysimeter samples

that sample down through the soil profile at different depths both within the BTI and in a control location nearby (Table 2C). During this study, summer samples were more easily and more often taken than winter samples due to freezing of equipment, inaccessibility to the sample site (the BTI serves as good location for snow ploughs to pile snow in the winter), and the December holidays.

Table 2C: Bio-infiltration Traffic Island Samples for Storm Events

Sample Name	Description
FF02	First Flush - Sample taken immediately after storm
SA01	Grab (SA)mple - taken from the bowl at the start of the storm
SA02	Grab (SA)mple - taken from the bowl at the end of the storm
ASC1	Auto Sampler Composite – Surface composite sample taken over the length of the storm
OVER	Overflow – Overflow sample taken from the weir box outflow to the stormwater sewer
LYS0	Lysimeter 0 – Lysimeter sample taken at the surface of the bowl
LYS4	Lysimeter 4 – Lysimeter sample taken 4 feet below the surface of the bowl
LYS8	Lysimeter 8 – Lysimeter sample taken 8 feet below the surface of the bowl
BKL1	Background Lysimeter 1 – Lysimeter sample taken 1 feet below the surface
BKL3	Background Lysimeter 3 – Lysimeter sample taken 3 feet below the surface
BKL6	Background Lysimeter 6 – Lysimeter sample taken 6 feet below the surface

2.3 Sampling and Testing Methods

All data was obtained through research conducted in the Water Resources Laboratory at Villanova University as part of qualitative research done by the Villanova Urban Stormwater Partnership. Data was used from December 2011 until November 2015. Storm events were defined as an event over 0.25 inches that had been preceded by at least a 48 hour dry period. Baseflow events were defined as a dry period sampling event that had been preceded by a 72 hour dry period, and/or a time at which a baseflow inflow of 0.1 ft³/s or less was occurring. At the CSW, most samples were grab samples taken immediately after the storm event (with some exception, see below) or at the time at which baseflow conditions occurred. Samples included

duplicates at each location: Inlet Pond, Meander 1, Meander 2, Meander 3, and Outlet (Figure 2.1). Therefore, ten samples were taken at each storm or baseflow event (Table 2A). Within this time period, however, autosamplers were installed at the CSW and therefore between April 2014 and November 2015 these samples were used in the data analysis. Autosamplers were installed at the Inlet Pond, the Outlet, and Meander 1. When this data was available in place of grab samples, the samples were used individually for TDS, conductivity, and chloride correlations. For chloride concentration comparison and mass calculations, the average of the four autosampler samples taken at each location were used. At the Bio-infiltration Traffic Island (BTI), a maximum of twelve samples were taken for any given storm event, shown and described in Table 2C; baseflow events did not occur at the BTI as it is designed for water to infiltrate within 72 hours after a rain event. For certain events, some locations were not able to be sampled, due to malfunctioning of equipment or the lack of sample (for example if there was no overflow for a specific event). Storm event sampling was conducted with a CSW-only sampling, a BTI-only sampling, or a CSW and BTI combination sampling. For each of these cases, in every storm sampling and every baseflow sampling, an additional two control samples were used as a quality control for the data set. The samples consisted of purified water from the laboratory poured in sample containers, named Blank 1 and Blank 2, and were treated the same as samples for the entirety of sample testing in order to check the accuracy of the data sets in all categories. In addition to Blank 1 and 2, at the CSW, all grab samples had duplicate samples in order to compare results (Table 2A). At the BTI, one sample with ample volume was selected each sampling event to be duplicated and also used to check the accuracy of laboratory testing. This sample was denoted with a -D (for duplicate) and tested with all other samples from the event without change to procedure.

The total dissolved solids concentration (TDS) was measured using EPA Method 160.1, a simple weighing method that uses a change in weight to determine TDS (USEPA 1999). Pre-labeled 400 mL beakers labeled for each stormwater sample were acid-washed in a 10% HNO₃ solution, rinsed with deionized water, and dried in a 425° F oven for at least 24 hours, then placed in a desiccator for storage and pre-weighed on a specified labeled (A, B, or C) balance, then returned to the desiccator for storage. On a testing day, 300 mL of sample (or less if smaller volume of sample was available) was filtered through a filtering apparatus into a Buchner flask through either a nitrocellulose filter, pore size 0.45 µm, (BTI) or a Whatman 934-AH filter, pore size 1.5 µm (CSW). The filtrate was then poured into the pre-labeled and pre-weighed beaker and placed in a 425° F oven to dry for at least 24 hours. The dried beaker was placed in a desiccator to cool and then post-weighed on the same specified scale (A, B, or C). Subtracting the pre-weight from the post-weight gave the milligrams of TDS collected in the beaker. Dividing by the volume of filtered sample and accounting for units gave the resulting TDS in mg/L. Control samples Blank 1 and 2 were analyzed for each storm by the Quality Assurance Manager as part of determining the detection limits for each year's TDS data set.

Conductivity was analyzed immediately after sampling using a Hach HQ40d Conductivity meter in conjunction with a CDC401 Conductivity probe and recorded in units of µS/cm. Calibrations occurred before each use, using a 1,000 mg/L standard of NaCl. Temperature and pH were also recorded with the same instrument at the same time. All values were entered manually into a hand-written notebook and then transferred to an electronic copy at a later time. Deionized water used in the laboratory for washing was tested for conductivity readings at each storm event sampling to check the quality of the purified water as well as the control samples, Blank 1 and 2.

Chloride concentrations were determined by EPA method 325.2 through spectrophotometry with a Chinchilla Scientific EasyChem discrete nutrient analyzer, which utilizes a photospectrometer to determine chloride concentration through colorimetric analysis. Standards used ranged from 2 mg/L to 200 mg/L and any samples over that concentration were either automatically diluted and rerun by the machine or hand-diluted and rerun manually. Samples were run within 28 days of sampling as a raw sample, as specified in the method (USEPA 1984). Samples were quality checked via the control samples, Blank 1 and 2, and the duplicate samples, as well as a required Calibrant and Blank check after every 10 samples. Additionally, following 2013, a matrix spike and a matrix spike duplicate were also used as quality checks for each sample run as well as a bought independently-made source-check standard which was used to check the accuracy of in-house laboratory-made standards. Each storm event was analyzed and routinely checked for accuracy by the Quality Assurance Manager. Any data with unreliable results or insufficient quality controls was rejected and not used in any capacity.

For the chloride mass balance in the CSW, a MATLAB code was used in conjunction with a Microsoft Access database to obtain the compiled flow and volume data. At the CSW inlet pond there are two main sources of influent stormwater runoff and two smaller inputs. The two main inputs are inlet pipes, one from the main campus (IM) and one from the west campus (IW) (See full campus map with drainage areas in the Appendix, Figures A1 and A2). IM is a 42" diameter pipe which transports runoff from an approximately 21.57 acre portion of the main campus storm drains. IW is a 48" diameter pipe which transports stormwater runoff from an approximately 7.49 acre portion of the west campus. Two smaller influent pipes are from a 1.6 acre, 92% impervious area where the facilities buildings are located (designated "Facilities

Pipe”), and a 4.6 area, 85% impervious area where the Villanova law school and adjoining parking lot are located (designated “M1 Pipe”). Figure 2.5 shows the location of each of these inlets with relation to the CSW inlet pond.

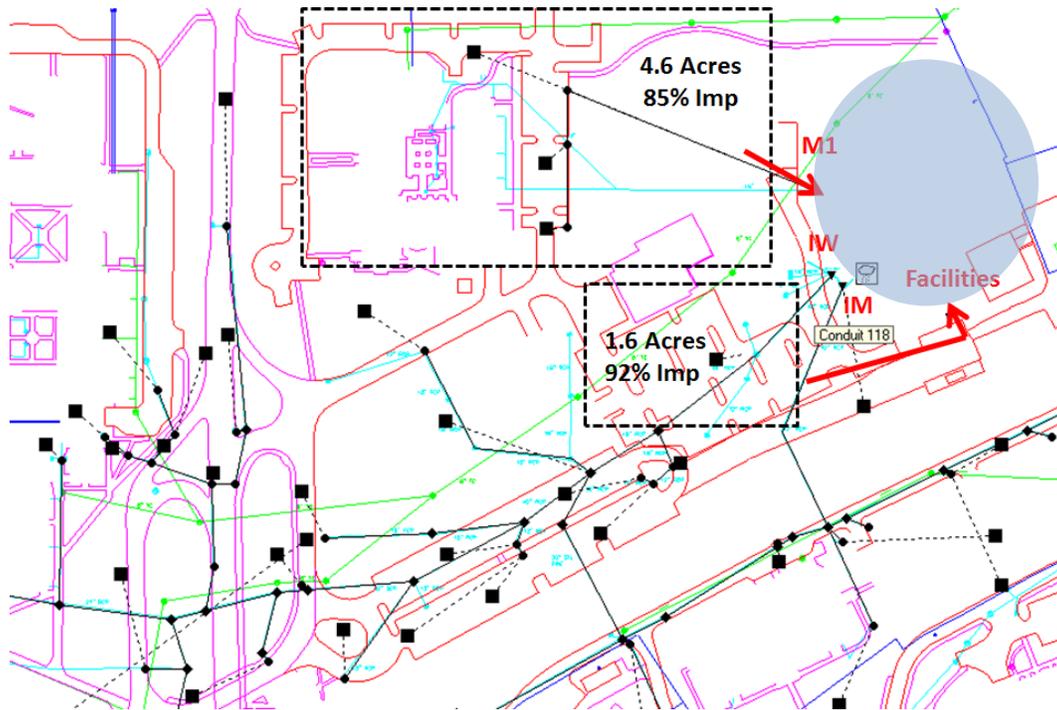


Figure 2.5: Small section of the SWMM Model mapping of the CSW inlet pond; inlet pond shown in light blue circle, inlet pipes M1, IW, IM, and Facilities are marked in red; Credit Rinker, 2013

In 2013 a SWMM model was created in order to estimate the flow contributions from each of the inlet pipes to the CSW inlet pond. From this analysis, it was determined that the combined flow from the M1 and Facilities pipes could be accounted for by multiplying the sum of IM and IW by the constant 1.17 (Rinker 2013). Therefore, the IM and IW pipes are monitored with flowmeters, and the M1 and Facilities inflows are estimated using this factor.

Inlet Main (IM) and the outlet structure are both monitored for flow with Grayline Instruments Area Velocity Flow Meters, which use a transducer to measure depth and ultrasonic

technology to measure velocity of inflowing particles. Inlet West (IW) is monitored using a Starflow flow meter. A Loggernet CR1000 data logger is connected to all three of these flow meters as well as the Villanova CSW rain gauge and weather station, located next to the inlet pond. The CR1000 collects data from all of these locations at 5 minute intervals and it is remotely downloaded once a month and backed up in the Access database.

In order to filter, compile, and transform this raw data into separate storm or baseflow events, two separate codes were used. There is a Storm Event code that uses defined parameters to separate out storm events and a Baseflow Event code that separates out baseflow events. Storms are defined as an event that is at least 0.1 inches of rainfall and a duration of at least 6 hours with no rain separates one storm event from the other. The code adds rainfall through each 5 minute interval, and if it reaches 0.1 inches, it then marks the EVENT START as the timestamp at which any rainfall began accumulating. EVENT END occurs when the outflow reaches $0.1 \text{ ft}^3/\text{s}$, the flow rate that defines the maximum flow of a baseflow testing event. EVENT LENGTH is the difference between EVENT START and EVENT END, and is therefore defined at the point in time from which rainfall begins to the point in time when outflow reaches baseflow levels again.

Baseflow is defined as an event with no rainfall at least 72 hours after the WET END of a storm so that inflow from the storm does not affect the baseflow. The WET END is defined as the point in time at which it has rained 0 inches for 6 hours. A baseflow ends once total rainfall reaches 0.09 inches. The difference between BASEFLOW START and BASEFLOW END results in the duration of the baseflow event. Because baseflow is calculated by this 72 hour rule, many days of the year are not defined as either a storm or a baseflow event, and would be considered “interflow”. For example, if it rains 30 times in a year, and baseflow does not begin

for 72 hours after each event, then 90 days of each year are “interflow” and are unaccounted for in either storm or baseflow. This inconsistency will be addressed throughout this paper as mass balance is discussed.

Volumes for each storm and baseflow event are calculated by multiplying the flow rate at each 5 minute interval by 5 minutes and then accounting for units. Then the total volumes at IM, IW, and OUT are summed for each storm event over the duration. While outflow volume is monitored directly, in calculating the cumulative inflow volume, IM and IW need to be summed and the M1 and Facilities inflow volumes estimated. The code adds IM and IW volumes together and then multiplies by 1.17 to account for M1 and Facilities, giving the ADJUSTED INLET volume.

CHAPTER III: CHLORIDE AND EPA WATER QUALITY CRITERIA

3.1 CSW Chloride Concentration

Chloride concentration data was graphed over time for the period between December 2011 and November 2015, a period representative of four Salt Application (December to May) seasons and four Non-Salt Application (June to November) seasons (Figure 3.1). This seasonal division and nomenclature were created in order to separate different trends in chloride concentrations as they pass through the CSW over a calendar year. In Villanova, PA, a temperate region of the United States that experiences winter with freezing temperatures, road de-icing salt is traditionally applied in December through early March, when temperatures are lowest and snow and ice are most prevalent. The “Salt Application” season includes spring months through May because high salt loading was still observed through spring snowmelt events and storms which flush road de-icing salt from the watershed into the CSW. The other half of the year, June

through November, high spikes in concentration were not observed, and the concentration over time followed a much different trend (Figure 3.1). Therefore the period of these months was given the name “Non-Salt Application”. This study will not only observe the different trends in chloride concentration between Salt Application and Non-Salt Application periods, but also between baseflow and storm events, which separately show different trends over time as well.

In Figure 3.1, the average of inlet (IN) chloride concentrations were graphed over the study period timeline of four years for both storm and baseflow conditions. High spikes in both baseflow and storm events occur during the Salt Application period, with maximums reaching approximately 1,700 mg/L in 2012, 1,350 mg/L in 2013, 1,820 mg/L in 2014, and 1,240 mg/L in 2015.

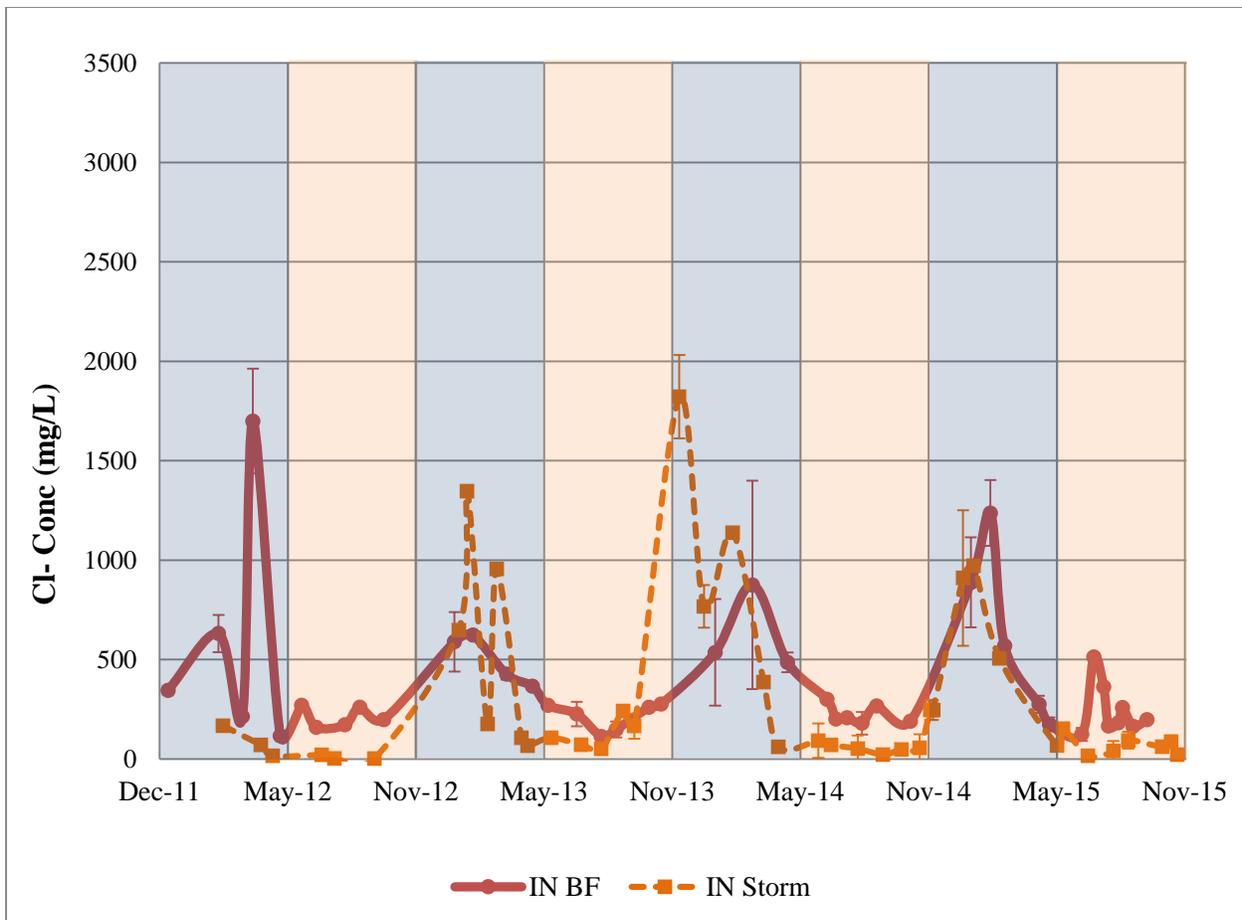


Figure 3.1: Average Inlet Chloride Concentration over Time: Both Storm and Baseflow; IN Storm in orange dashed line, IN Baseflow in red continuous line; blue background covers Salt Application period and pink background covers Non-Salt Application period; standard deviation shown in bars; Storm n = 41, Baseflow n = 42

The overall trend for storm events is high chloride spikes observed in the Salt-Application months, amidst other data points in that same period with low concentrations. (2012 does not appear to have any high spikes for storm events, however this year had no available storm data for December-February, and so is an incomplete data set.) On average, Salt Application period inlet chloride concentrations (IN storm median = 709 mg/L, stdev = 529 mg/L, n = 14) are an order of magnitude higher than the Non-Salt Application period concentrations (IN storm median = 59 mg/L, stdev = 57 mg/L, n = 19). Given that snow and ice

events occur sporadically through the winter, and that salt application would therefore also be inconsistently applied over the Salt Application season, an erratic pattern makes sense, given that road de-icing salt would be flushed out periodically with rain events, and subsequent rain events would therefore have much lower concentrations if no additional salt was applied between. Another complicated dimension of the storm concentration pattern over the Salt Application months is that there may be wildly fluctuating flow rates per specific storm (Tables A14-A17 in the Appendix), and so concentrations would vary depending on how much volume entered the wetland, independent of the amount of salt applied. Additionally, some winter events were snowmelts, in which case concentrations would be affected depending on how much snow had collected over the watershed, how quickly it melted, and how much salt had collected on watershed surfaces over time previous to the snowmelt event. Therefore, Salt Application storm chloride concentrations require more thorough statistical analysis to understand the storm by storm variations observed for each event.

During Non-Salt Application periods, storm chloride concentrations at the inlet are lower, with some event concentrations approaching non-detect (< 2 mg/L) concentrations (IN storm median = 59 mg/L, stdev = 57 mg/L, $n = 22$). During these months, there is no salt application, and therefore it is expected that influent stormwater runoff volumes would not carry large amounts of chloride from the watershed's impervious surfaces. The change in concentration during storm events from high spikes in the Salt Application period to low, sometimes non-detect values in the Non-Salt Application period is quick, and there does not appear to be a gradual decrease over time (Figure 3.1).

The highest baseflow event chloride concentrations similarly were observed during the Salt Application period (IN baseflow median = 536 mg/L, stdev = 404 mg/L, $n = 17$), although

(with the exception of 2012) these concentrations remained elevated rather than fluctuating greatly over that period. After these high concentrations were observed, concentrations decreased slowly over time, rather than quickly dropping off as observed with storm events (Figure 3.1). This slow decline lasts through July or August each year and unlike storm events, baseflow concentrations rarely reach near non-detect levels (< 2 mg/L), rather they level out around 200 mg/L (IN baseflow median = 202 mg/L, stdev = 84 mg/L, n = 25) in Non-Salt Application months.

Figure 3.2 shows the average outlet (labeled OUT) chloride concentrations graphed over the study period of four years. As with IN samples, high spikes for both baseflow and storm events occur during the Salt Application period, with maximums reaching approximately 1,840 mg/L in 2012, 1,530 mg/L in 2013, 860 mg/L in 2014, and the highest value of the study period of 3,340 mg/L in 2015.

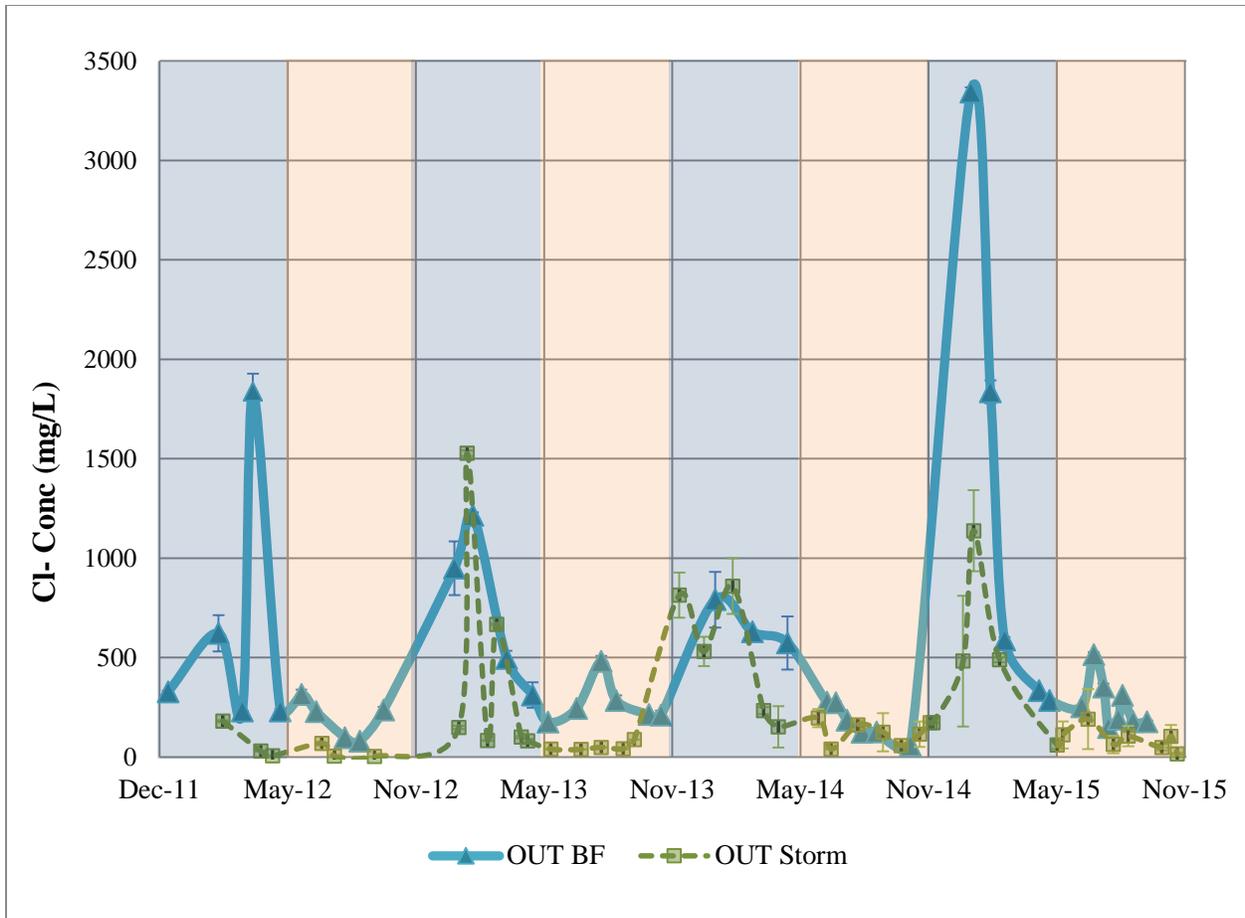


Figure 3.2: Average Outlet Chloride Concentration over Time: Both Storm and Baseflow; Storm in green dashed line and Baseflow in blue continuous line; standard deviation shown in bars; Storm n=41, Baseflow n =42

The trends seen in the OUT samples for both Storm and Baseflow events were similar to those observed for the IN samples. For storm events, high chloride spikes are seen during the Salt-Application months (2012 not included) (OUT storm median = 486 mg/L, stdev = 442 mg/L, n = 14), followed by lower concentrations in the Non-Salt Application months (OUT storm median = 62 mg/L, stdev = 55, n = 22). The same influences that affect the storm IN concentrations would also have an effect on storm OUT concentrations in the CSW, including the fact that during the Non-Salt Application period stormwater captured in the CSW would not be expected to carry a large amount of chloride from stormwater runoff. There is a rapid change

from high spikes in Salt Application periods to low, sometimes non-detect values (< 2 mg/L) in Non-Salt Application periods for storms, and there does not appear to be a gradual decrease over time, just the same as for the IN trend. Therefore the outlet has a similar contrast between Salt Application and Non-Salt Application chloride concentrations during storm events to what is observed with the inlet.

Trends are also similar for baseflow events. The highest baseflow event chloride concentrations were observed during the Salt Application period (OUT baseflow median = 588 mg/L, stdev = 814 mg/L, $n = 17$), and these concentrations remained elevated over that period (with the exception of the 2012 year). Concentrations decreased slowly over time, lasting through July or August each year. Unlike storm events, baseflow concentrations rarely reach near non-detect levels (< 2 mg/L), rather they seem to generally level out around 200 mg/L in Non-Salt Application months (OUT baseflow median = 213 mg/L, stdev = 110 mg/L, $n = 25$).

There is no clear correlation that can be made from observing these graphs about the ways in which storm inlet concentrations may specifically affect base flow inlet concentrations or storm outlet concentrations affect outlet baseflow concentrations. Because the data set is only comprised of 3-4 events per month (baseflow and storm), not a continuous or inclusive data set, and that there is such variability between winter storm and snow melt events, it is hard to pinpoint exactly what is the interaction between the observed baseflow and storms event chloride patterns. Several theories about the movement of chloride through the CSW will be addressed in the conclusions section.

In order to observe trends in chloride concentration between the inlet and the outlet, IN and OUT data were plotted for only storm events and only for baseflow events. Figure 3.3

presents the storm data only for both IN and OUT over the study period.

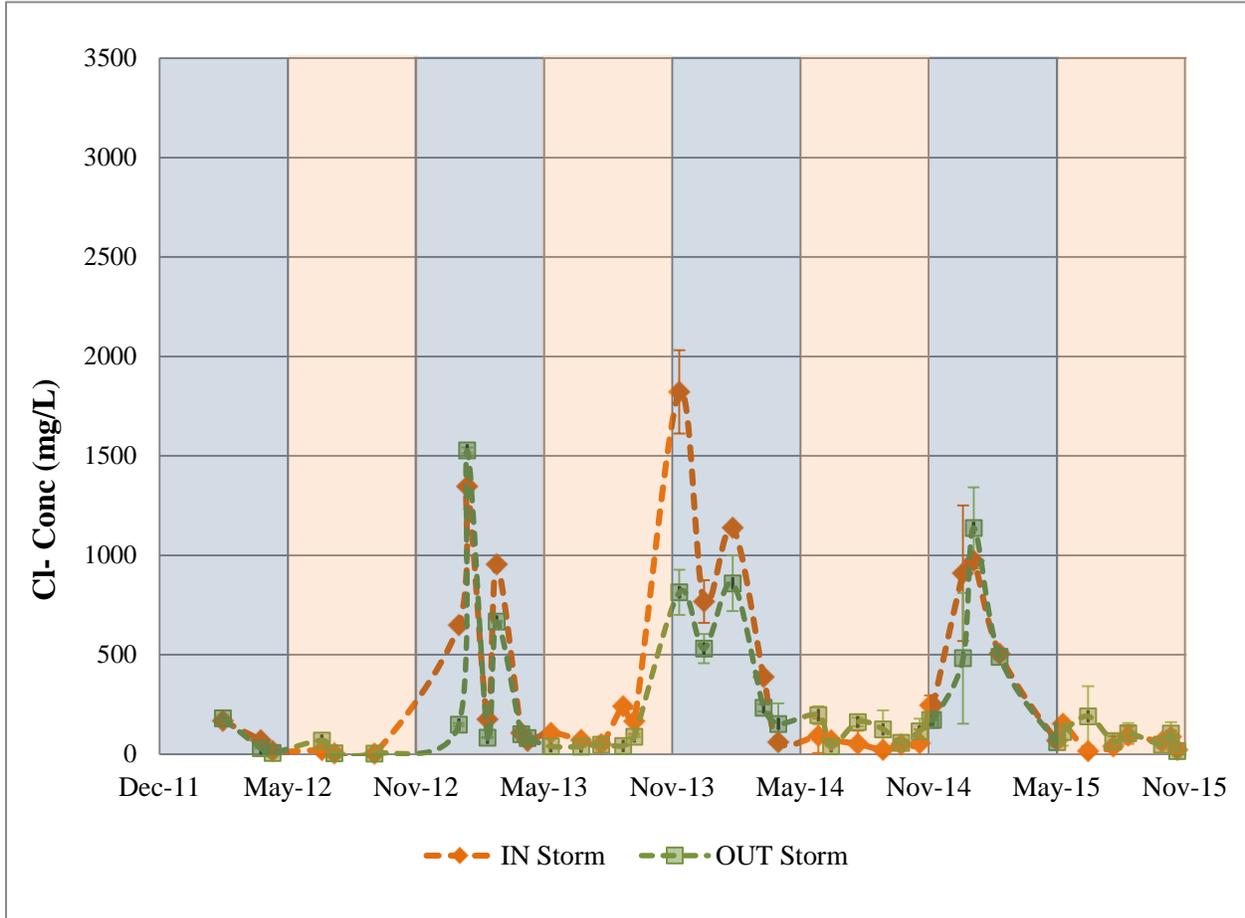


Figure 3.3: Average Storm Chloride Concentration over Time: IN and OUT; IN is shown in a dashed orange line and OUT in a dashed green line; Standard deviation shown in bars; IN n = 41, OUT n = 41

With the exception of 2012, as mentioned above, storm concentrations for both IN and OUT are highest during the Salt Application period, drop off quickly, and then level off at low concentrations approaching non-detect (< 2 mg/L) in the Non-Salt Application period. There is not a large difference between IN and OUT for the majority of storm events especially in Non-Salt Application periods, but in Salt Application months, there are a few larger gaps between IN and OUT. For example in 2013, there is an approximately 1,000 mg/L difference between IN and OUT concentrations for the first Salt Application event (IN at 1,822 mg/L and OUT at 814

mg/L). While it is difficult to discern any consistent patterns because the dataset is so small, in Salt Application periods, when inlet and outlet concentrations are not close to each other, inlet concentrations are greater than outlet concentrations. This can be seen on 1/30/13 (IN = 1,528 mg/L, OUT = 148 mg/L), 12/10/13 (IN = 1,822 mg/L OUT, = 814 mg/L), and 1/18/2015 (IN = 910 mg/L, OUT = 483 mg/L). One notable exception is on 2/2/15 (IN = 502 mg/L, OUT = 1,138 mg/L), which was a snowmelt event rather than a storm event.

Tables 3A shows the average, median, and maximum IN and OUT Storm chloride concentrations for the Salt and Non-Salt Application periods from 2012 to 2014. On average, storm Salt Application chloride concentrations (IN average = 705 mg/L, OUT average = 522 mg/L) are much higher than Non-Salt Application concentrations (IN average = 70 mg/L, OUT average = 78 mg/L). Non-Salt Application storm chloride concentrations are the lowest of the dataset, approaching non-detect (< 2 mg/L) levels, most likely due to dilution.

Table 3A: Average, median, and maximum chloride concentrations for the inlet (IN) and outlet (OUT) for the all Salt Application (n=14) and Non-Salt Application (n=22) periods from 2012 to 2015. Salt Application data from 2012 was not included because of the incomplete timeframe of sampling; all units are in mg/L

	Inlet			Outlet		
	avg ± stdev	med	max	avg ± stdev	med	max
Salt Application	705 ± 529	709	1822	522 ± 442	486	1528
Non-Salt Application	70 ± 57	59	241	78 ± 55	78	196

There was great variation of chloride concentrations observed between individual storm events during the Salt Application period (IN stdev = 529 mg/L and OUT stdev = 442 mg/L), while the Non-Salt Application period storm events were more relatively similar (IN stdev = 57

and OUT stdev = 55). For an individual storm event, however, there was also variation between individual samples taken at each separate location in the CSW (IN, M1, M2, M3, and OUT).

Figure 3.4 displays the average concentration of all samples on each storm sampling day. Error bars display the range of concentrations for each particular sampling day.

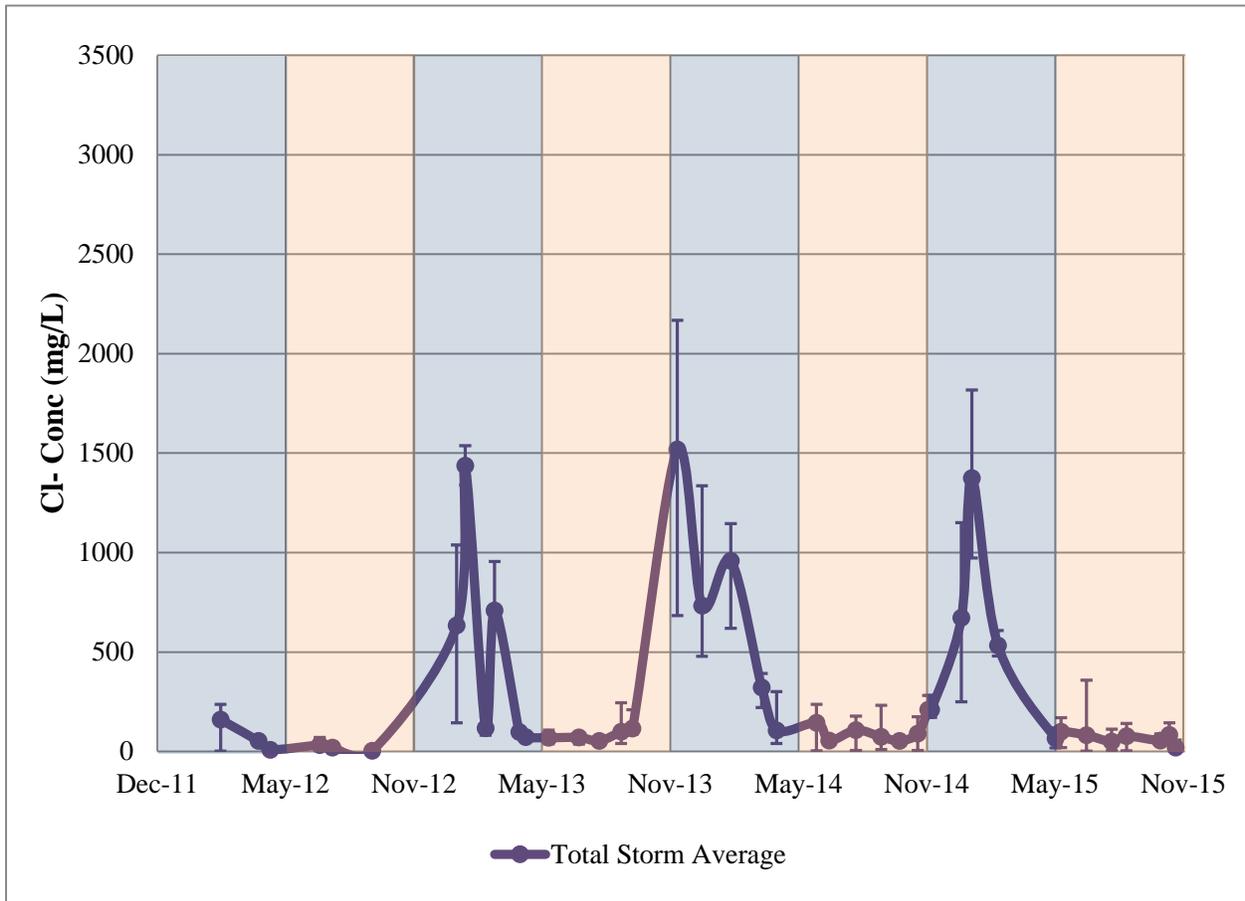


Figure 3.4: Total Averaged CSW Samples for Storm, including IN, OUT, M1, M2, and M3: Chloride Concentration over Time; Range shown in bars; n =41

In Non-Salt Application periods, inlet and outlet concentrations are similar with only a small range, however, during many of the Salt Application period storms, the inlet and outlet have different values with a large range for all samples. These large ranges include: 1/30/13 (~800 mg/L range), 12/10/13 (~1,500 mg/L range), 1/14/14 (~800 mg/L range), 1/18/15 (~900

mg/L range), and 2/2/15 (~1,800 mg/L range). Figure 3.4 shows that there can be a large range of chloride concentrations throughout the wetland during a storm event in the Salt Application period, but that the same phenomenon is not seen in the Non-Salt Application period. Looking more closely at the autosampler samples taken since April 2014, when 4 samples were taken at each location over the course of the storm, it is apparent that concentrations can change significantly over the course of the storm.

Figure 3.5 shows inlet and outlet chloride concentrations for several dates from 2015 that had autosampler samples instead of grab samples, including both Salt Application and Non-Salt Application periods. Some dates had incomplete data sets which is due to malfunctioning of equipment or lack of sample.

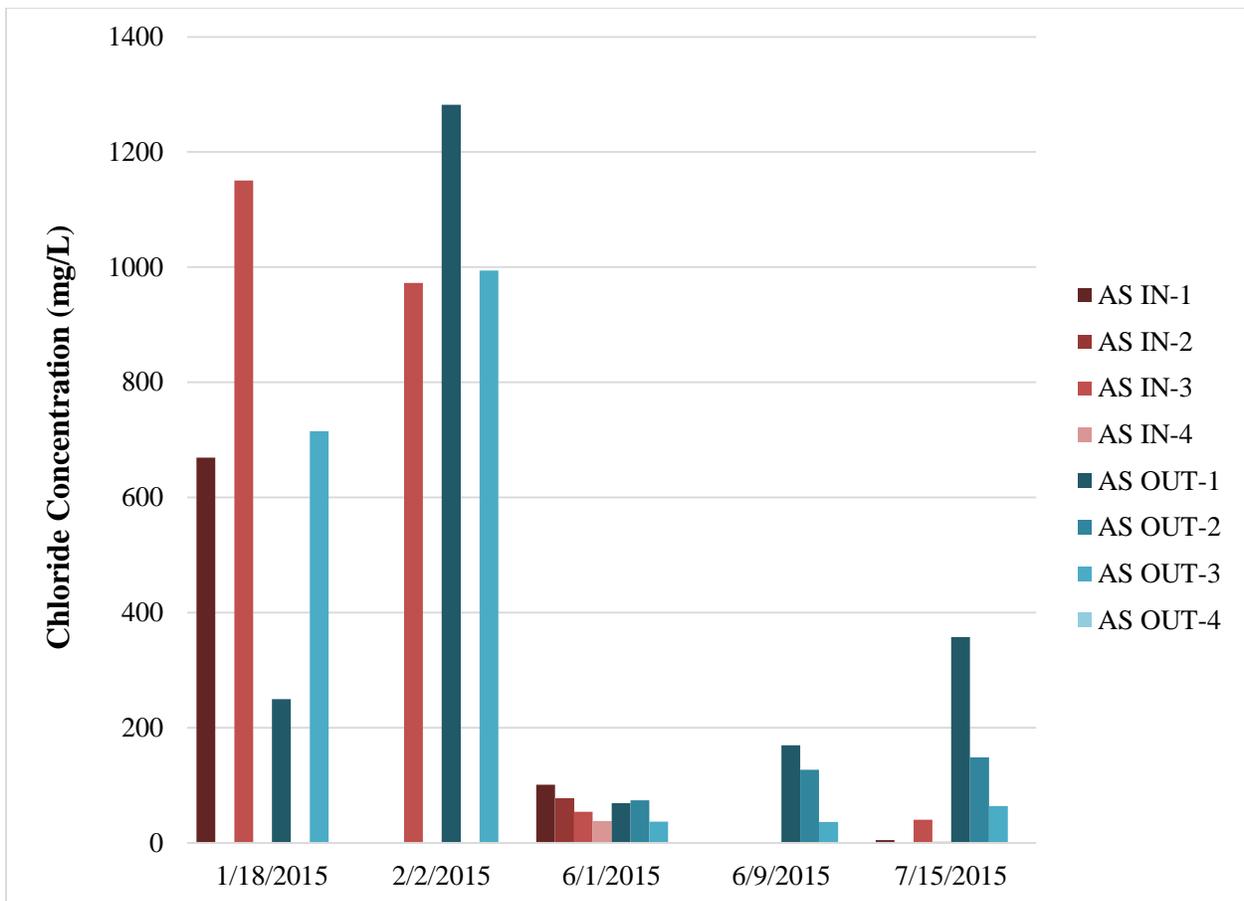


Figure 3.5: Chloride Concentration during Several Autosampler Storm Sampling Days in 2015

Specific information on the sample names and when they were taken is available in Figure 2.2 and Table 2B. Chloride concentrations may change significantly over the course of the storm, as seen especially on 1/18/15. On 1/18/15 inlet concentrations fluctuate from 670 mg/L to 1,151 mg/L (a difference of ~500 mg/L) and outlet concentrations from 250 mg/L to 715 mg/L (also a difference of ~500 mg/L). On 2/2/15 the only inlet concentration taken was 973 mg/L and at the outlet concentrations fluctuated from 1,282 mg/L to 994 mg/L. In Non-Salt Application months, a dilution effect over the course of the storm is seen for 6/1/15, 6/9/15, and 7/15/15 samples. This shows that there may be significant changes in chloride concentration over the course of a storm, and this supports the data shown earlier in Figure 3.4 that shows a large range of chloride concentrations within the wetland itself during a storm event.

Baseflow chloride concentrations for both IN and OUT are shown here in Figure 3.6 so that any patterns may be found as chloride flows through the CSW during baseflow conditions. Comparing IN and OUT baseflow datasets together can give some insight into the movement of chloride through the wetland, specifically how concentrations may change from the inlet to the outlet as well as overall trends in the wetland during baseflow events.

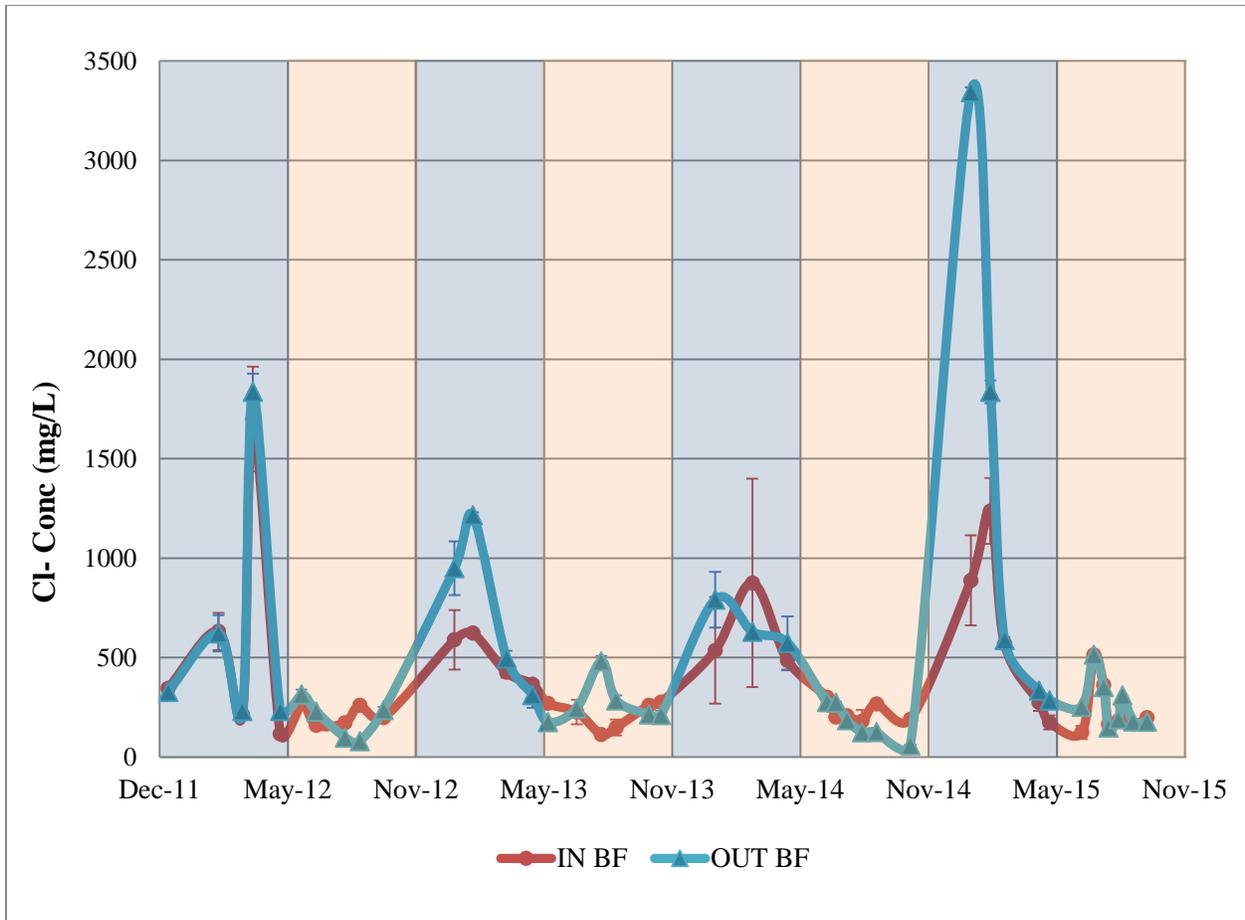


Figure 3.6: Average Baseflow Chloride Concentration over Time: IN and OUT; IN is a continuous blue line and OUT is a continuous red line; standard deviation is shown in bars; IN $n = 42$, OUT $n = 42$

A baseflow event was only sampled for water quality if outlet flow was equal to or less than $0.1 \text{ ft}^3/\text{s}$ or if it had not rained in a 72 hour period previous, in order to make the assumption that a previous storm event had not affected the flow in the CSW. Chloride that was flushed into the wetland during a storm event would be flushed out within approximately $49 \text{ hours} \pm 19 \text{ hours}$ (the mean residence time during storm conditions based on tracer test studies) (Komlos et al. 2016). This means that during the baseflow sampling there should be no additional flow from a rain event and therefore that there are no additional inflows of chlorides directly from impervious

surfaces. This assumption that there is no additional chloride from impervious surfaces entering the CSW is important, because the highest chloride spikes for both storms and baseflows are seen around February and March, but inlet and outlet baseflow concentrations remain above the summer median (~225 mg/L) until June or July, a 5 month delay. Because both inlet and outlet concentrations have an elevated summer median even though inlet storm concentrations are low, this suggests a similar conclusion as in research done by Demers and Sage (1990), Brown and Scorca (1995), Gardner and Royer (2010), Sadowski (2002), Kaushal et al. (2005), and Corsi et al. (2014) that there is an initial inflow of chloride mass into the CSW from the upstream drainage basin, retention of chloride within that drainage basin, and slow release of chloride mass possibly from groundwater flow from the drainage basin and into the CSW late into the summer months.

Table 3B shows the average IN and OUT baseflow chloride concentrations for the Salt Application period for each year, as well as the maximum concentration for that year and the standard deviation. Table 3C shows the average IN and OUT baseflow chloride concentrations for the Non-Salt Application period for each year, as well as the maximum concentration for that year and the standard deviation. Salt Application and Non-Salt Application period baseflow concentrations are separated in order to compare any trends that may be observed concerning how road de-icing salt application may affect baseflow concentrations.

Table 3B: Salt Application Period Average, Standard Deviation, Median, and Maximum Chloride Concentration for Each Year: Baseflow; units are mg/L

	INLET			OUTLET		
	avg ± stdev	med	max	avg ± stdev	med	max
2012 Salt Application (n=5)	601 ± 644	346	1699	650 ± 683	328	1837
2013 Salt Application (n=4)	501 ± 125	508	623	743 ± 413	723	1215
2014 Salt Application (n=3)	633 ± 211	536	875	665 ± 113	630	791
2015 Salt Application (n=5)	629 ± 439	569	1237	1277 ± 1316	588	3343
2012-2015 TOTAL (n=17)	591 ± 404	536	1699	859 ± 814	588	3343

Table 3C: Non-Salt Application Period Average, Standard Deviation, Median, and Maximum Chloride Concentration for Each Year: Baseflow; units are mg/L

	INLET			OUTLET		
	avg ± stdev	med	max	avg ± stdev	med	max
2012 summer (n=5)	199 ± 50	212	269	228 ± 100	191	315
2013 summer (n=6)	216 ± 69	244	276	268 ± 111	229	481
2014 summer (n=6)	225 ± 48	205	301	174 ± 87	155	276
2015 summer (n=8)	246 ± 131	190	513	265 ± 124	221	515
2012-2015 TOTAL (n=25)	227 ± 84	202	513	229 ± 110	213	515

Chloride concentrations are on average much lower in Non-Salt Application periods (IN median = 202 mg/L and IN average = 227 mg/L, OUT median = 213 mg/L and OUT average = 229 mg/L) than in Salt Application periods (IN median = 536 mg/L and IN average = 591 mg/L, OUT median = 588 mg/L and OUT average = 859 mg/L), however the outlet average of 229 mg/L chloride concentration is still at the higher end of what meets national freshwater standards

(230 mg/L chronic criterion and 860 mg/L acute criterion), and what is found naturally in freshwater, typically less than about 300 mg/L chloride (Kaushal 2009). While there is not sufficient evidence from this data, it is likely that the Villanova CSW, despite large volumes that dilute chloride to low levels in the summer, does not currently achieve pre-urbanization chloride levels during Non-Salt Application period baseflow, the national baseflow median being 81 mg/L in urban areas, and 3.5 mg/L in forested basins (Mullaney et al. 2009).

There is not a large difference between the inlet and outlet for most of the baseflow events especially in Non-Salt Application periods, but in Salt Application months, there are several large gaps between the inlet and outlet. The most extreme example of this is in 2015, on 1/29/15, there is an approximately 2,500 mg/L difference between IN and OUT concentrations during the first Salt Application baseflow event (IN at 888 mg/L and OUT at 3,343 mg/L). This phenomena did not occur on any of the other sampling days, and it is not possible with this data to determine why this day in particular had such high chloride concentrations or why there was such a large range of concentrations throughout the CSW, but it does serve as an indication that chloride concentrations may be extremely variable and it serves to put the dataset into perspective. It indicates that chloride concentrations in the CSW may have been this high or been fluctuating between locations with a high range at other times during the study period but were not sampled at that time. With this in mind it is difficult to discern any consistent patterns because the dataset is so small, however one notable point is that when IN and OUT samples were not close in range to each other, outlet concentrations were greater than inlet. This can be seen on 2/19/13 (IN = 623 mg/L, OUT = 1,215 mg/L), 1/29/15 (IN = 888 mg/L OUT, = 3,343 mg/L), and 2/26/2015 (IN = 1,237 mg/L, OUT = 1,836 mg/L). This would be an indication that

more chloride is leaving the wetland than entering during baseflow conditions, and could point towards retention of chloride in the CSW, that slowly releases over time.

One interesting point of the data is the 8/21/13 event, when the baseflow outflow concentration (481 mg/L) was higher than the inflow concentration (113 mg/L), which may be due to a concentration of chloride related to evaporation in the CSW during a dry period. While this shows that evaporation may have a role in increasing chloride concentration as it moves through the CSW, it was the only baseflow event in which this phenomena occurred, and therefore it is assumed that in this regard, evaporation generally does not play a large role in changes in chloride concentrations as they pass through the wetland in Non-Salt Application periods. It is assumed that evaporation would have a negligible role during Salt Application periods, because this is not a period when high temperatures are observed.

As with storm events, a similar pattern occurred in baseflow event samplings where large ranges of chloride concentrations were found at different locations in the CSW for a specific event. Figure 3.7 shows a graph of the total average of CSW baseflow event samples (average of all IN, OUT, M1, M2, and M3 duplicates for each storm date) with bars showing the respective

ranges for each storm date.

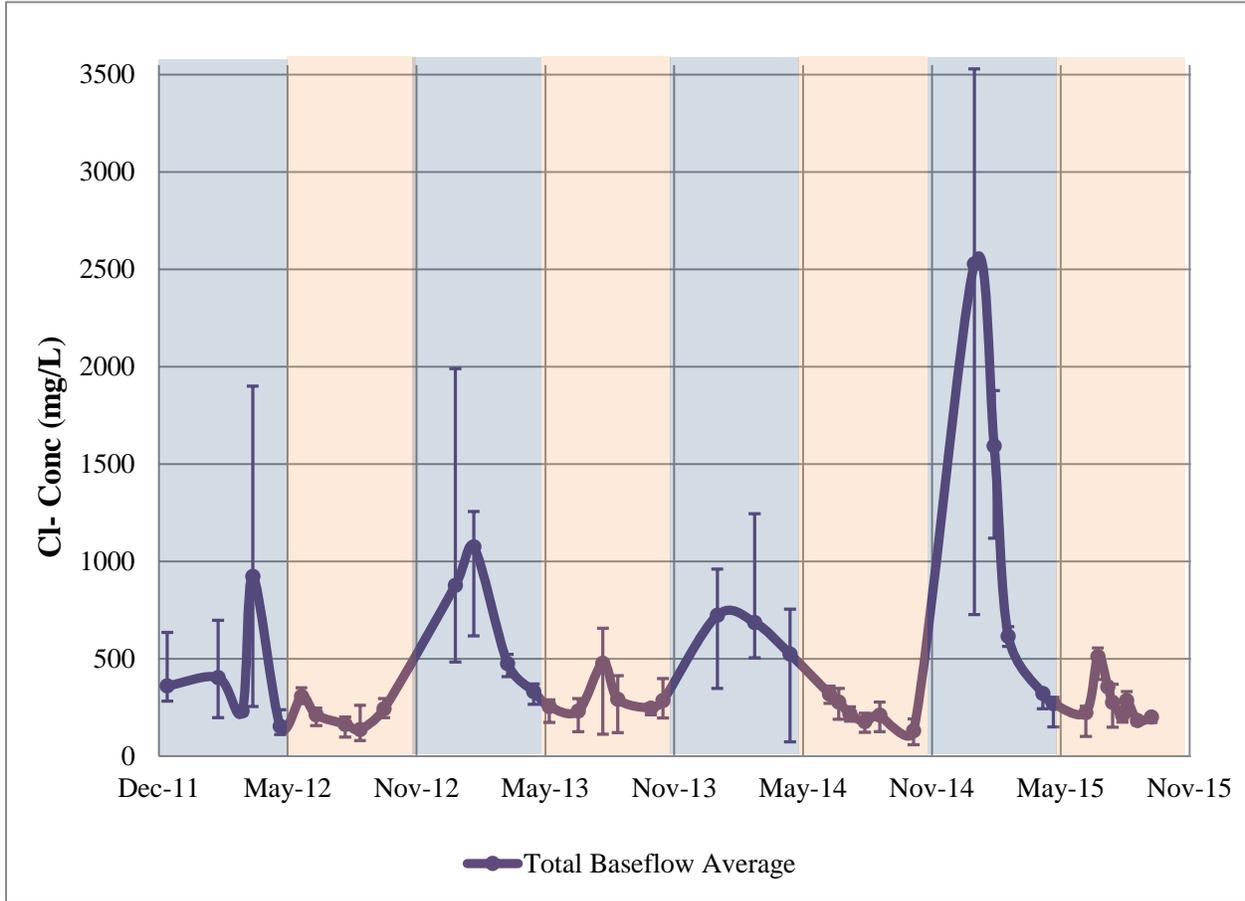


Figure 3.7: Total Averaged CSW Samples for Baseflow, including IN, OUT, M1, M2, and M3: Chloride Concentration over Time; Range shown in bars; n = 42

The ranges for events with high average concentrations are larger than the ranges for events with low average concentrations. Generally, this results in baseflow events during Non-Salt Application period events with relatively small ranges, and Salt-Application period events with large ranges. This includes: 4/12/12 (~ 1,700 mg/L), 1/24/13 (~1,500 mg/L range), 2/19/15, 1/30/14, 3/24/14, and 5/13/15 (all ~ 500 mg/L range), 1/29/15 (~2,700 mg/L range), and 2/26/15 (~500 mg/L range). Again, the most notable exception is the 1/29/15 baseflow event, which not only had the highest data point of the dataset of approximately 3,500 mg/L, but the largest range, 2,700 mg/L, with the lowest concentration that day being approximately 800 mg/L. One factor

that may affect the large ranges that are observed in baseflow is residence time, which for baseflow is approximately twice as much as for a storm event (96.0 ± 13.5 hours), and therefore slowly moving volumes may move chloride through the CSW unevenly (Komlos et al. 2016). This shows that there is a lot of variability in chloride concentrations throughout the CSW during baseflow conditions.

All IN and OUT storm chloride concentrations were graphed alongside all IN and OUT baseflow concentrations in order to view all datasets on the same axis (Figure 3.8). The overall trend is that there is a large amount of variability in chloride concentrations through the CSW in Salt Application periods for both storms and baseflow events, while Non-Salt Application periods have much lower chloride concentrations and much less variability.

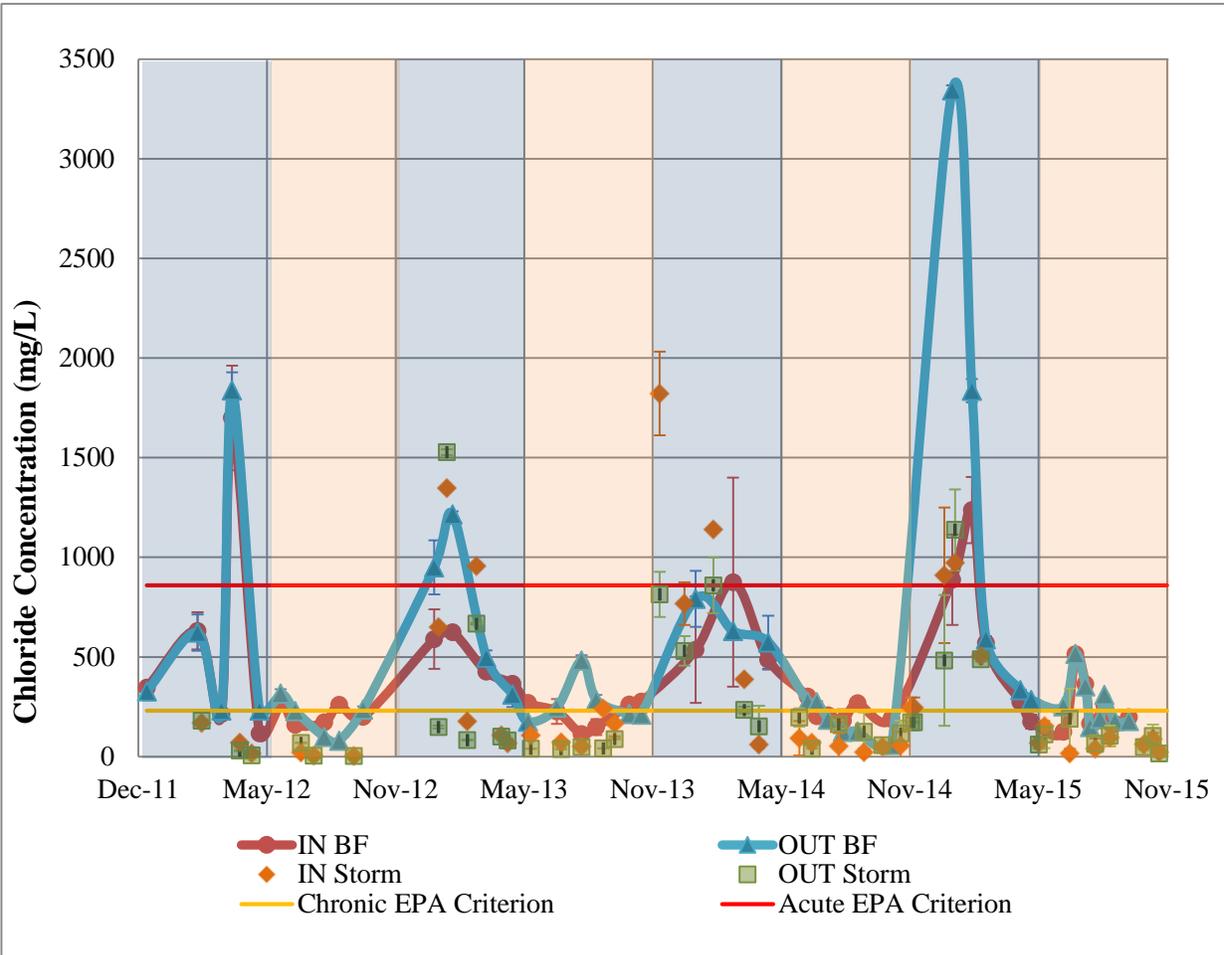


Figure 3.8: IN and OUT Baseflow and Storm CSW Samples; Chloride Concentration over Time; standard deviation shown in bars; Chronic criterion (230 mg/L) in yellow line and Acute Criterion (860 mg/L) in bright red line); IN Baseflow in dark red line $n = 42$, OUT Baseflow in blue line $n = 42$, IN Storm in orange triangles $n = 41$, OUT Storm in green squares $n = 41$

Because of the small dataset size, no direct correlation can be observed between the influent loading of chloride seen during storm events and immediately following baseflow concentrations, although spikes in baseflow chloride concentrations occur just as the storm concentrations do during the Salt Application periods. This means that no clear correlation was observed that showed that a high spike of chloride in a storm event resulted in a spike in chloride in the following baseflow event. However, both storm and baseflow spikes were observed only during the Salt Application period, while Non-Salt Application experienced no high spikes. Non-

Salt Application baseflow and storm event chloride concentrations were low, but storm event concentrations were lower, probably due to dilution. Because Non-Salt Application period baseflow chloride concentrations remain elevated through the summer while storm chloride concentrations achieve low levels, this implies retention of chloride in the area draining to the CSW, which may enter the CSW through groundwater flow. Retention of chloride in the watershed would explain the heightened chloride concentrations that are delayed after the Salt Application period in the summer months. Storm concentrations are possibly low due to dilution from rainwater.

Exceedance probability plots were made in order to compare all seasons and event types. Figure 3.9 is an exceedance probability plot of all samples in the 4 year study period from Dec 2011 – Nov 2015 separated by Salt Application period and Non-Salt Application period.

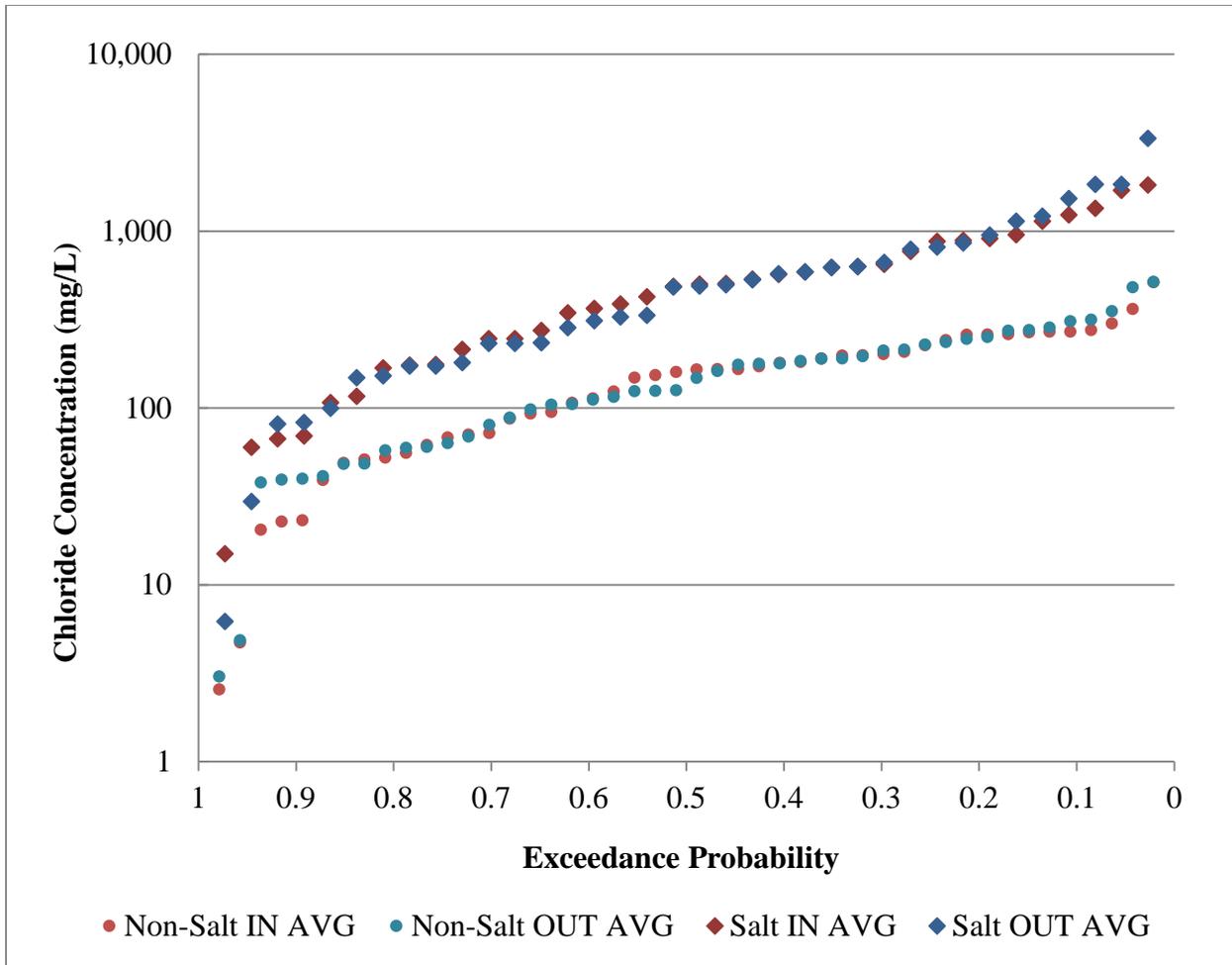


Figure 3.9: Chloride Exceedance Probability Distribution Salt and Non-Salt Application Period IN and OUT samples over the full 4 year study period; y-axis on a base 10 log scale

Overall, the Salt Application chloride concentrations (Salt Application IN median = 569 mg/L, stdev = 460 mg/L, n = 31 and OUT median = 530 mg/L, stdev = 683 mg/L, n = 31) are higher than the Non-Salt Application concentrations (Non-Salt Application IN median = 160 mg/L, stdev = 107 mg/L, n = 47 and OUT median = 126 mg/L, stdev = 116 mg/L, n = 47). The maximum value for the Salt Application period was 3,343 mg/L and for Non-Salt Application it was only 515 mg/L. Inlet and outlet patterns are similar to each other for both the Salt Application and Non-Salt Application periods and both periods have a similar slope.

The same exceedance probability plot was made again for the full 4 year study period, but with a separation between storm and baseflow events (Figure 3.10). Generally, storm events had lower chloride concentrations (Storm IN median = 90 mg/L, stdev = 452 mg/L, n = 36 and OUT median = 105 mg/L, stdev = 350 mg/L, n = 36) than did baseflow events (Baseflow IN median = 264 mg/L, stdev = 317 mg/L, n = 42 and OUT median = 280 mg/L, stdev = 603 mg/L, n = 42) and storms dominated the lowest values, however the curves converge at the highest values, where baseflow and storm concentrations are similar.

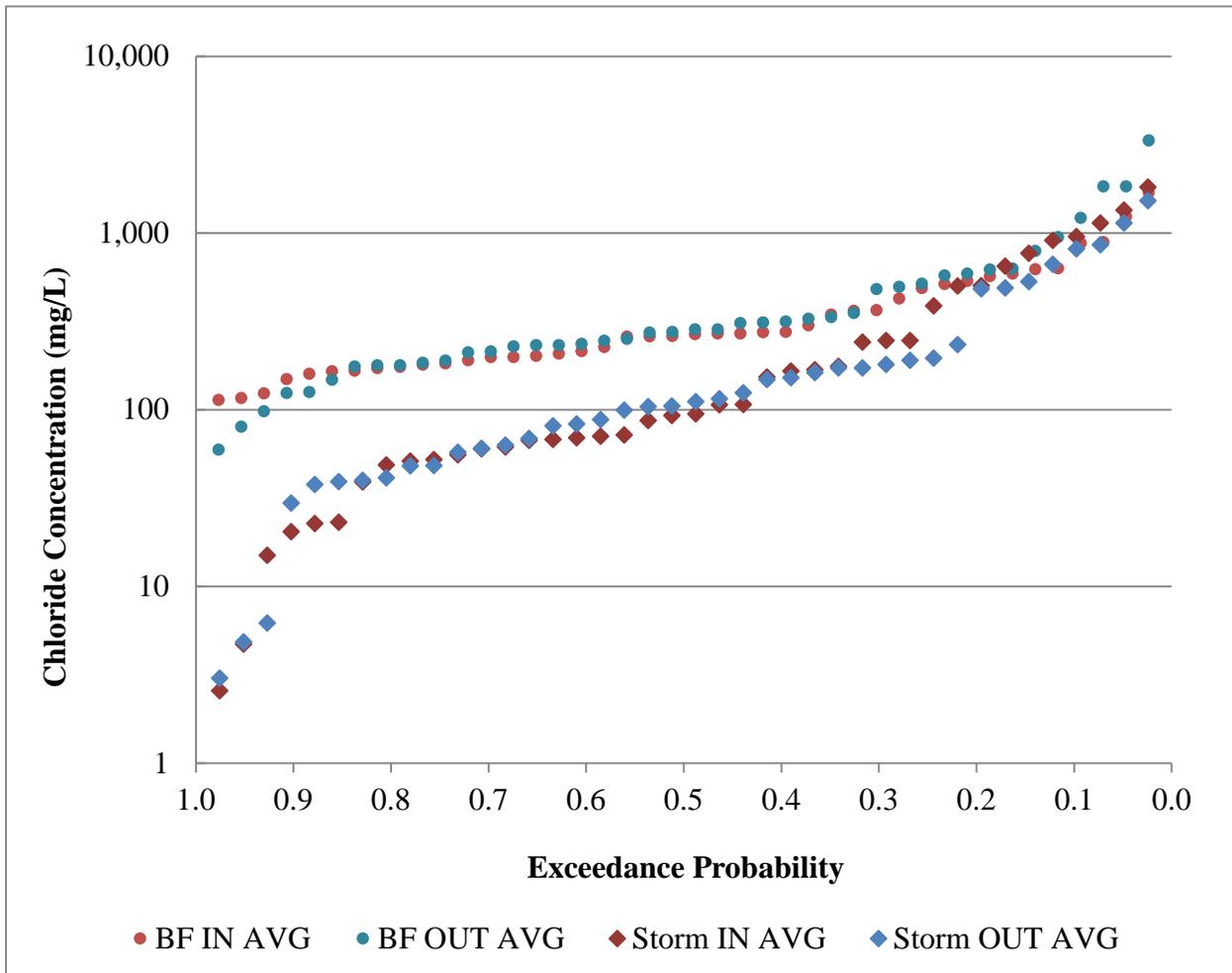


Figure 3.10: Chloride Exceedance Probability Distribution Baseflow and Storm IN and OUT samples over the full 4 year study period; y-axis on a base 10 log scale

The storm maximum was 1,528 mg/L and the baseflow maximum was 3,343 mg/L. The storm minimum was 3 mg/L, while the baseflow minimum was 59 mg/L. The slopes were different for each event type, with storm events encompassing some of the highest and the lowest values, but with baseflow staying relatively higher in concentration.

3.2 EPA Water Quality Criteria

Constructed stormwater wetlands (CSWs) have substantive benefits in terms of water quality improvement for influent stormwater runoff (Carlisle and Mulamootil 1991). One of the main goals of this study was to determine if chloride concentrations passing through the CSW have a negative effect on the surrounding watershed in terms of water quality and its effect on freshwater ecosystem health. The focus of this chloride concentration analysis is on the downstream waters of Mill Creek, since it is a natural freshwater body with the CSW as its headwaters. While the ecosystem structure of the CSW itself would certainly also be affected by concentrations of chloride within the CSW, concentrations within the wetland itself are of less concern because one of the primary purposes of the CSW is to improve water quality from the inlet to the outlet before releasing effluent flow to Mill Creek. Because of this, whether or not the CSW itself between the inlet and outlet is affected by high chloride concentrations is irrelevant to this study. However, any indication that chloride is moving vertically within the CSW itself rather than horizontally *would* relate to this study, as this would suggest that infiltration may be occurring and that groundwater chloride concentrations would therefore be affected, which would also affect the surrounding ecosystem. However, this question will be addressed later in the report.

The way that chloride concentration downstream of the CSW will be assessed for water quality is by comparison to EPA recommended water quality criteria for fresh water. The

national criteria for chronic and acute toxicity is defined under the terms that "...the four-day average concentration of dissolved chloride, when associated with sodium, does not exceed 230 mg/L more than once every three years on average and if the one-hour average concentration does not exceed 860 mg/L more than once every three years on average" (USEPA 1988). While this study does not assess data against these criteria in their exact four-day and one-hour definitions, these criteria are used as a benchmark to estimate how often the CSW may potentially meet criteria in the effluent. Chloride data at the outlet during the time of the study (Dec 2011 - Nov 2015) were compared to these guidelines in Figure 3.11.

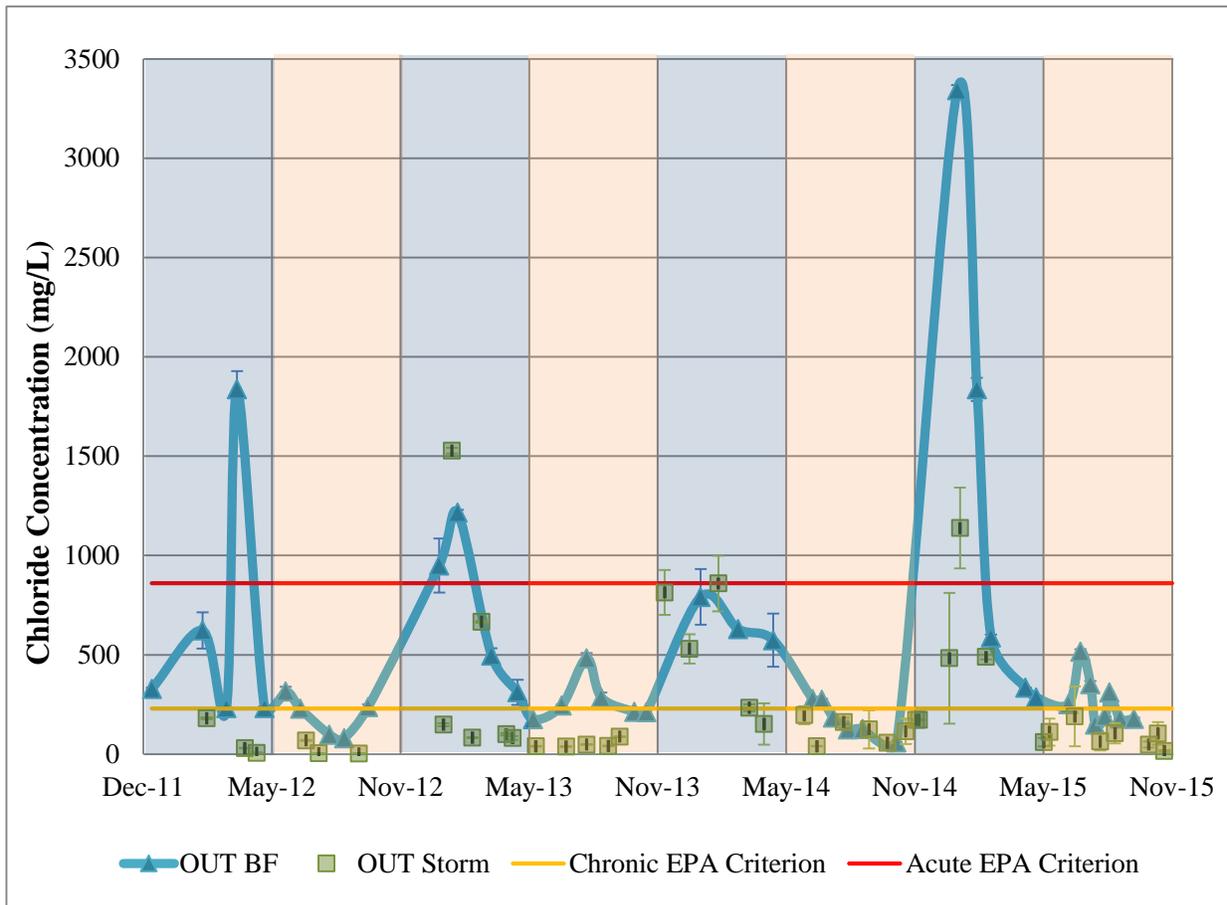


Figure 3.11: Chloride Concentrations for Baseflows and Storms at the CSW outlet against EPA Chronic and Acute Criteria; OUT baseflow in blue line; OUT Storm in green squares; Chronic Criteria (230 mg/L) in yellow line; Acute Criteria (860 mg/L) in red line

As shown in Figure 3.11, chronic criterion, 230 mg/L, appears low in the data range, and acute criterion, 860 mg/L, while also relatively low in the range is only exceeded by seven points of data. Maximum concentrations of chloride are high compared to these criteria; even reaching 2,000 and 3,000 mg/L. These high spikes occur infrequently, however values between 230 and 860 mg/L do occur quite frequently, especially during baseflow conditions. In order to assess how often the EPA recommended freshwater criteria is met, a simple calculation based on the number of events was made. The average outlet chloride concentrations were separated for storms and baseflows and each data set was sorted in ascending order. Data was divided into three categories: under 230 mg/L, between 230-860 mg/L, and over 860 mg/L, and number of events (n) was determined for each category. The number of events (n) in each category were then divided by the total number of events and the percentage of events in each category was found (Tables 3D and 3E).

Table 3D: CSW Storm Criteria Assessment; % of Events Meeting/Exceeding Criteria

	Number of Events (n)	Percentage of Events
Meets both Criteria	31	77%
Exceeds Chronic Criterion	9 (*5)	23% (*13%)
Exceeds Both Chronic and Acute Criteria	4	10%
TOTAL:	40	<i>*between chronic/acute</i>

For storms during the study period, there was a total of 40 events. The average outlet chloride concentration for 77% of these events met both EPA criteria, while 23% exceeded the EPA chronic criterion. Of those events that exceeded the chronic criterion, 10 of that 26% exceeded the acute criterion as well. Data was collected about as frequently during both the Salt Application period (n = 18) and the Non-Salt Application period (n = 22) Storms only affect the

CSW approximately 13% of the year, however, so baseflow values will be more indicative of an overall trend for the majority of the year.

Table 3E: CSW Baseflow Criteria Assessment; % of Events Meeting/Exceeding Criteria

	Number of Events (n)	Percentage of Events
Meets both Criteria	14	33%
Exceeds Chronic Criteria	28 (*23)	67% (*55%)
Exceeds Both Chronic and Acute Criteria	5	12%
TOTAL:		
	42	<i>*between chronic/acute</i>

The Villanova CSW was sampled a total of 42 times during baseflow conditions over the study period. The average outlet chloride concentration for only 14% of these events met both EPA criteria, while 67% exceeded the EPA chronic criterion. Of those events that exceeded the chronic criteria, 12 of that 67% exceeded the acute criterion as well. Data is less frequently collected in the winter, so there is more variation and less accuracy in this Salt Application period (n = 17) than the Non-Salt Application period (n = 25) If more data had been collected in the winter months, perhaps the number of storm events exceeding EPA criteria would be higher. Baseflow constitutes a majority of the year, and therefore is much more influential on downstream water quality in terms of concentration, although storms have greater volumes over the course of the year.

Over the course of the study, approximately 184 days of the 4 year study period were storm events (See Tables A14-A17 in the Appendix). Using this information, a total estimate for the year was made based on the assumption that all other days in the study period were baseflow. This would mean that of the 4 year study period, 13% of the time would be defined as a storm

event, and that the remaining 87% was defined as baseflow. Under this assumption, estimates were made for criteria exceedance in Table 3F.

Table 3F: CSW Criteria Assessment; % of Time (Estimated) Meeting/Exceeding Criteria

n = 69	Percentage of Time, estimated
Meets both Criteria	39%
Exceeds Chronic Criteria	61%
Exceeds Both Chronic and Acute Criteria	12%

Using these assumptions, it is estimated that the Villanova CSW meets both criteria 39% of the time under all conditions, exceeds chronic criteria 61% of the time, and exceeds acute criteria 12% of the time. Again, this serves as only an estimate of the CSW’s performance, since this study was unable to assess the precise EPA criteria definitions, and can be used as a benchmark estimate.

CHAPTER IV: TDS, CONDUCTIVITY, AND CHLORIDE CORRELATIONS

4.1 Stormwater Wetland Correlations

Chloride is the negative ion in NaCl, the main ingredient in most road de-icing salts, and a naturally occurring mineral. It is one of many ions that are commonly present in stormwater samples and the contaminant of concern in this study. TDS, or Total Dissolved Solids, is a weight measurement of particles less than 0.45 micron diameter, and so includes both positive and negative ions and molecules or molecule agglomerations. TDS, therefore, is directly related to chloride concentration because the mass of chloride ions in solution added to the mass of the other ions present in solution would add up to the total TDS mass. Chloride concentration and TDS concentration are both measured in mg/L, and so are directly correlated. Conductivity, however, is not a weight measurement; it is a measure of the electrical conductivity of a sample,

and so is proportional to the number of charged particles in solution. Conductivity measurements are therefore proportional to TDS. Using TDS and conductivity values in comparison to chloride concentrations, correlations can be created in the following combinations: chloride and TDS, chloride and conductivity, and TDS and conductivity. Using these three parameters, the chloride data can be checked against TDS and conductivity to ensure the accuracy of the data set. Each correlation can also be used to estimate other parameters from one parameter, especially in estimating TDS from conductivity measurements (Williams 1966).

4.1.1 Chloride versus TDS Correlation at the CSW

A chloride vs TDS curve was graphed using data over the four year study period from December 2011 to November 2015 (Figure 4.1). For this and for all of the CSW correlations, the duplicate samples were averaged for chloride concentration, TDS, and conductivity and then plotted in order to maintain the integrity of the data. Individual duplicate samples (ex. IN 1 and IN 2) were not plotted separately because these are not independent of each other.

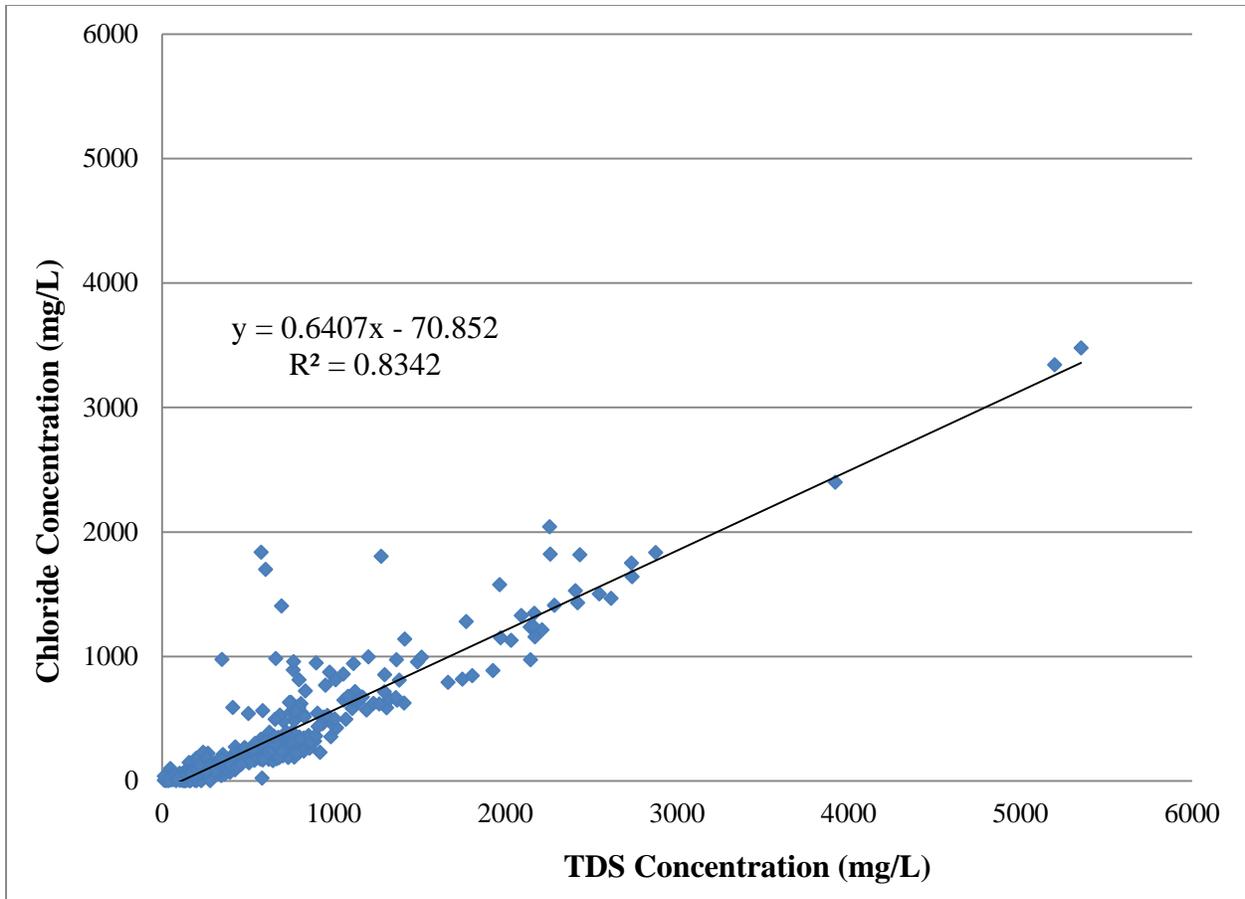


Figure 4.1: Chloride vs. TDS Correlation at the CSW with linear trend line; $n = 421$

TDS has a range between non-detect (< 10 mg/L) and approximately 5,500 mg/L. Chloride concentration has a range between non-detect (< 2 mg/L) and approximately 3,500 mg/L. The equation of this line is $y = 0.6407x - 70.582$ and the R^2 is 0.8342. The x-intercept lies at approximately 70 mg/L, which may be due to the fact that TDS is comprised of other particles besides chloride, and therefore, although chloride concentration may be non-detect, the other particles still make up TDS have a baseline of approximately 70 mg/L. The slope is 0.64 mg Cl^- /mg TDS, meaning that chloride is approximately 0.64 of the TDS. Therefore, TDS is greater than chloride in most instances (besides several points that lie closer to the y-axis). This

correlation only has an R^2 of 0.8342, so it is not entirely reliable as a way to directly correlate chloride and TDS, but can serve as a basic estimate to confirm the accuracy of a data set.

4.1.2 Chloride versus Conductivity Correlation at the CSW

A chloride vs conductivity curve was graphed using data over the four year study period from December 2011 to November 2015 (Figure 4.2). Conductivity has a range between non-detect ($< 1 \mu\text{S}/\text{cm}$) and approximately 10,000 $\mu\text{S}/\text{cm}$. Chloride concentration has a range between non-detect ($< 2 \text{ mg}/\text{L}$) and approximately 3,500 mg/L . The trend is linear and the equation of the line is $y = 0.3499x - 30.27$ and the R^2 is 0.8548.

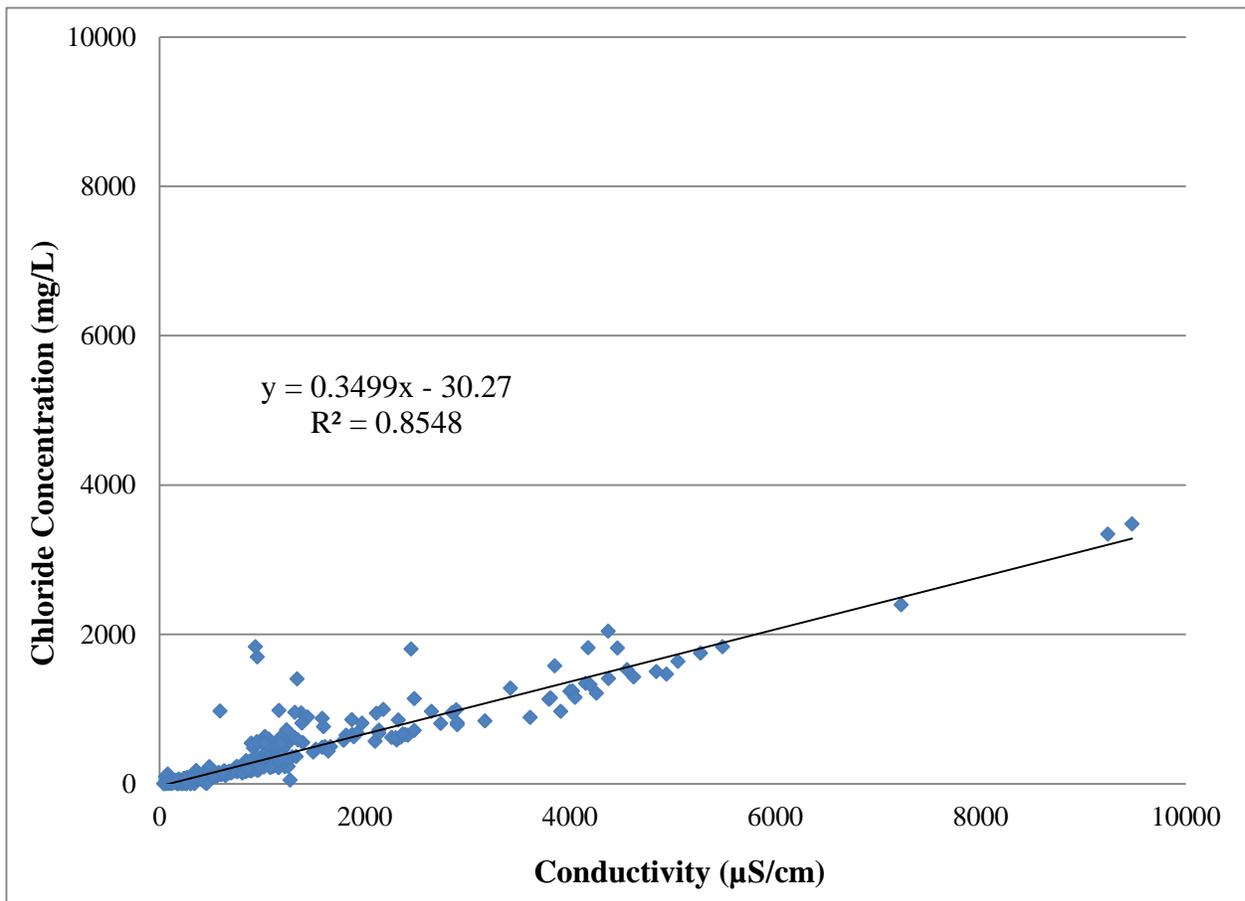


Figure 4.2: Chloride vs. Conductivity Correlation at the CSW with linear trend line; $n = 421$

The positive correlation between conductivity and chloride was expected as well. The slope is 0.35 (mg/L Cl⁻)/(μS/cm), meaning that chloride is approximately 0.35 times the conductivity. This correlation has an R² of 0.8548, so same as with the chloride/TDS correlation, it also is not entirely reliable as a way to directly correlate chloride and conductivity, but can serve as a basic estimate to confirm the accuracy of a data set.

4.1.3 TDS versus Conductivity Correlation at the CSW

TDS and conductivity correlations are common equations used to compare data and gain valuable insights into the molecular makeup of a specific waterway. Some researchers may use TDS vs conductivity equations to calculate TDS from a conductivity measurement, since conductivity is a much cheaper, easier, and more reliable test. The equation is

$$TDS = k * conductivity$$

where k is a constant usually between 0.55 and 0.7 (American Public Health Assoc. 1999). TDS values were plotted against conductivity values for the CSW in order to determine the TDS/conductivity equation (Figure 4.3).

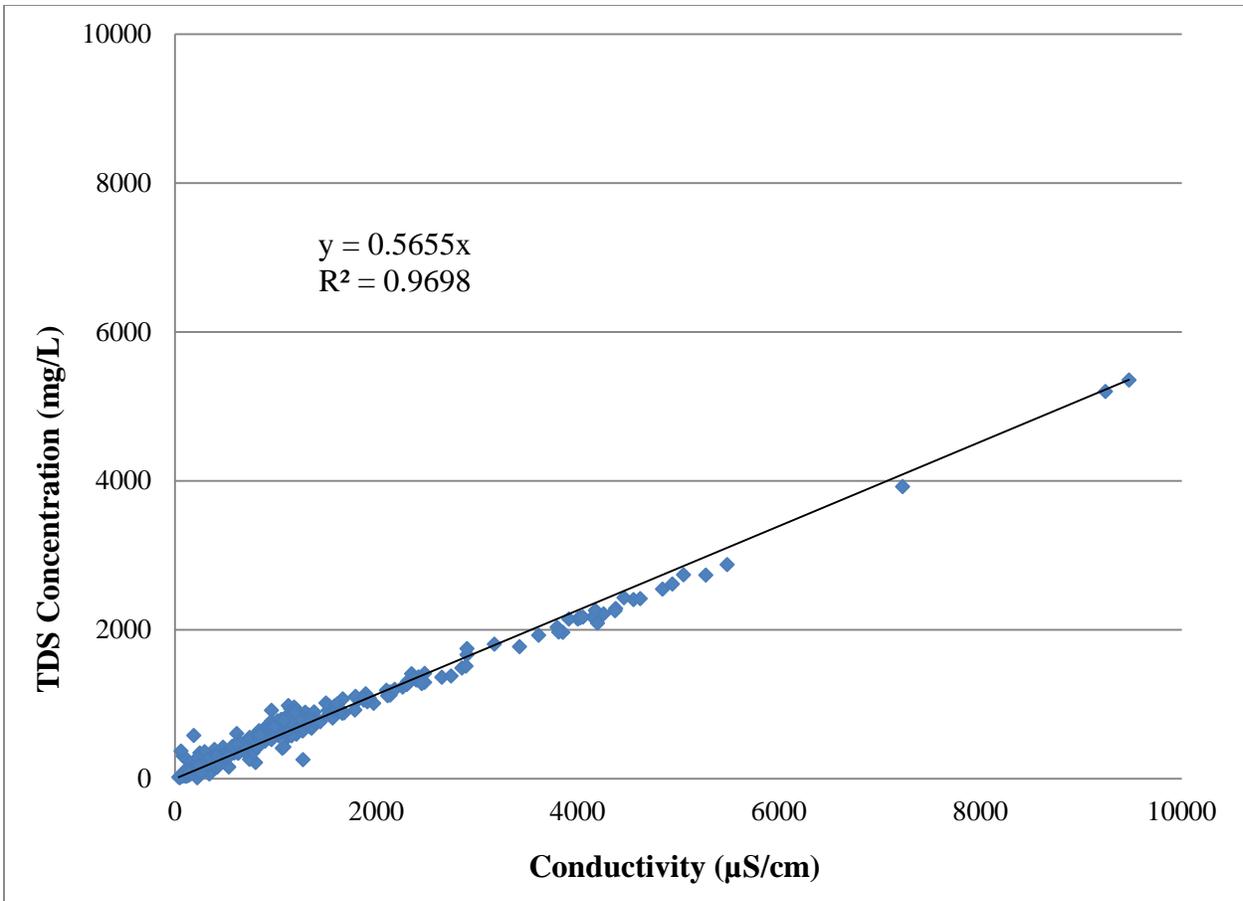


Figure 4.3: TDS vs. Conductivity Correlation at the CSW with linear trend line; $n = 454$

There is a linear correlation, with an equation of $y = 0.57x$, and an R^2 of 0.9698. The correlation is strong, with few outliers and the R^2 is high at 0.9698. This correlation works well and could be used as a calculation of TDS from conductivity. This correlation is more reliable than the chloride/TDS or the chloride/conductivity curves.

4.1.3.1 TDS versus Conductivity Correlation for values above 1,000 mg/L

Because the dataset was so large and the ranges for TDS and conductivity were so large, averaged values were separated into those above 1,000 mg/L TDS and those below 1,000 mg/L TDS in order to determine if there was a different correlation for the higher range of values than

for the lower range. Each range was graphed separately. Values above 1,000 mg/L TDS were graphed against conductivity (Figure 4.4). The equation obtained was $y = 0.54x$, with an R^2 of 0.9896.

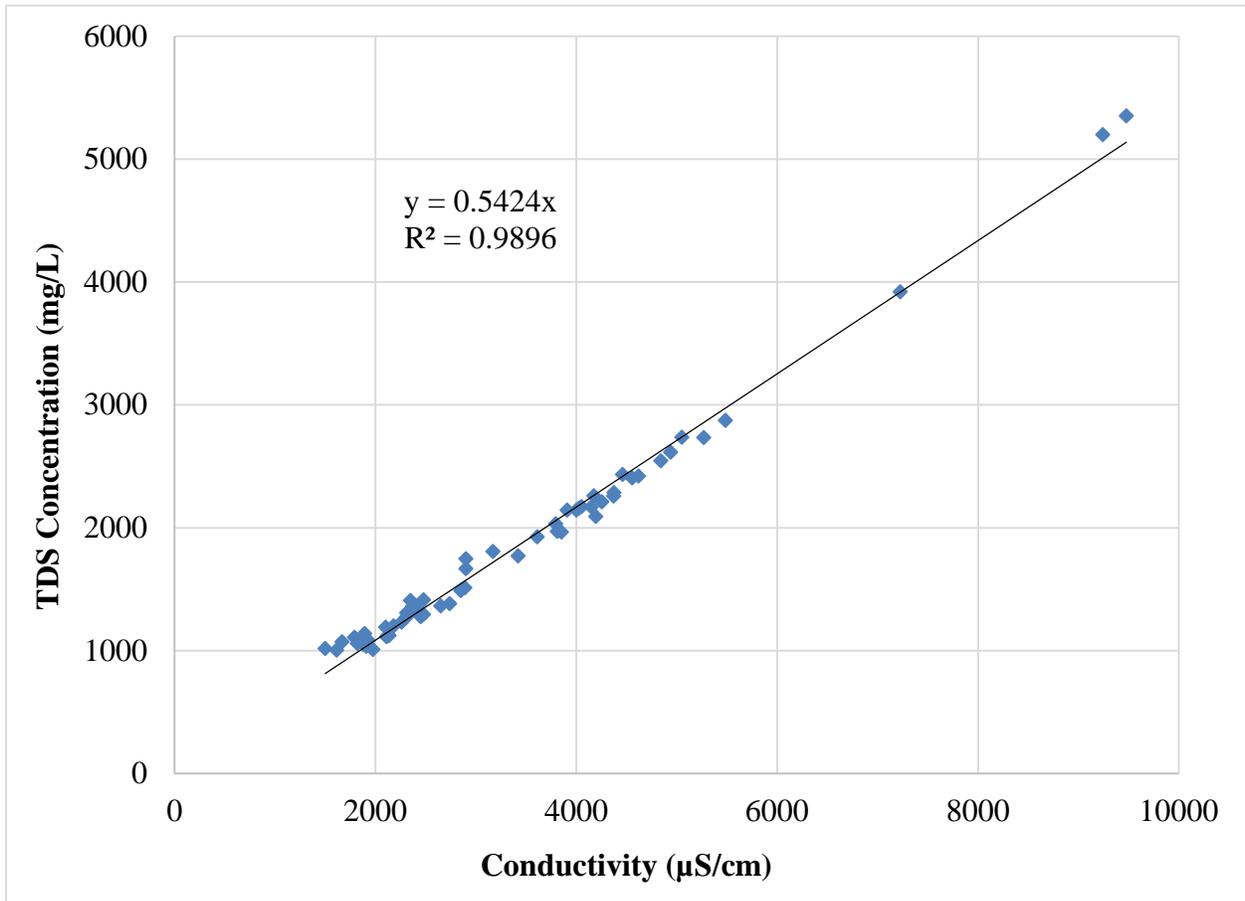


Figure 4.4: TDS vs. Conductivity Correlation for TDS > 1,000 mg/L with linear trend line, $n = 60$

The R^2 (0.9896) for this correlation is better than that of the correlation including the entire range (0.9698), and the slope is similar. The slope for the high range shown in Figure 4.4 is 0.54 (mg/L)/(µS/cm) and for the correlation including the entire range (Figure 4.3) it is 0.57 (mg/L)/(µS/cm).

4.1.3.2 Linear Relationship for TDS Values below 1000 mg/L

While the slopes were similar for the correlation for high range samples (> 1,000 mg/L TDS) and the correlation including the entire range, the slope for low range samples (< 1,000 mg/L TDS) was less similar and may point to a different trend in lower range samples. The low range samples less than 1,000 mg/L TDS are plotted in Figure 4.5.

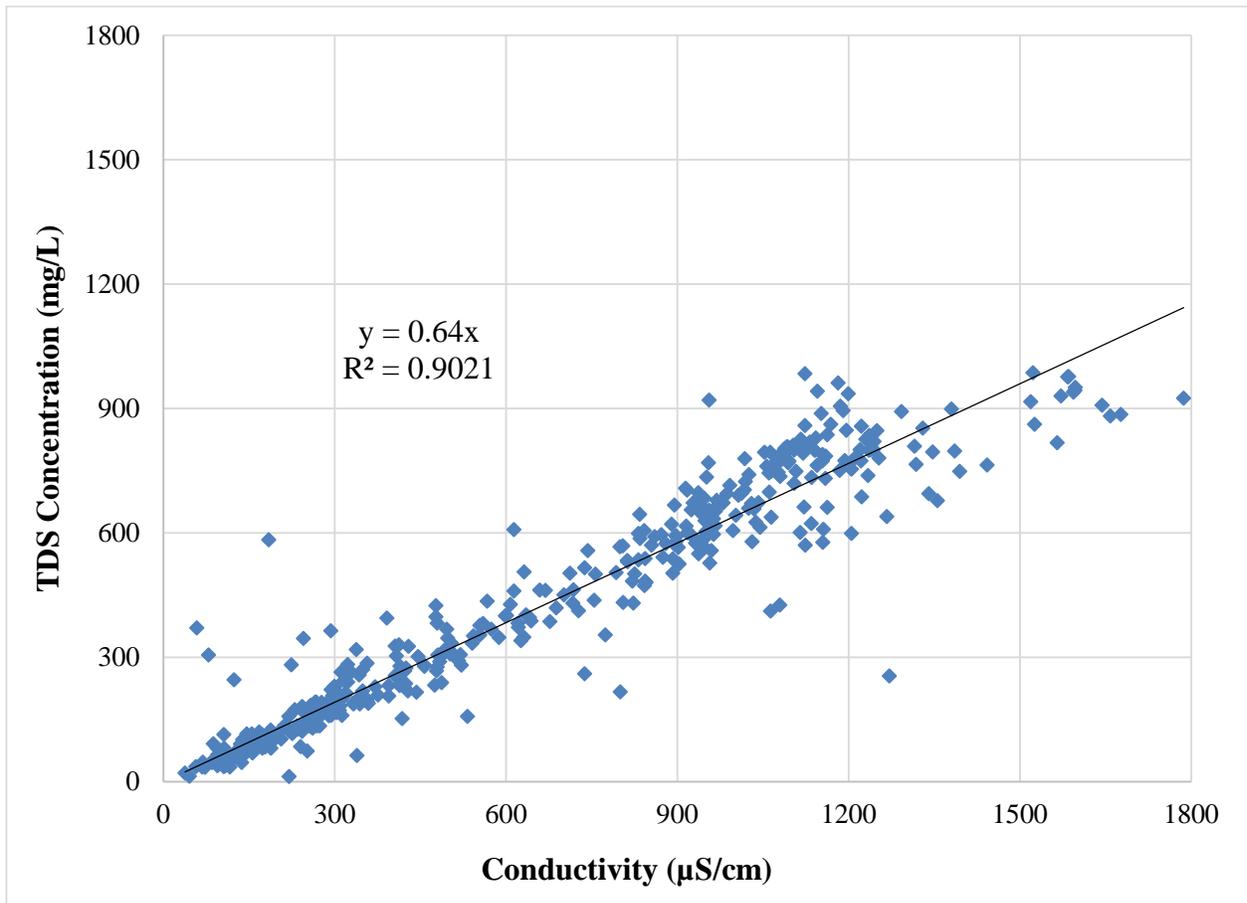


Figure 4.5: TDS vs. Conductivity Correlation: Values below 1,000 mg/L with linear trend line; $n = 393$

The correlation is still linear, with an equation of $y = 0.64x$, and has some scatter, with an R^2 of 0.9021. The R^2 of this correlation (0.9021) is not as high as either the high range correlation (0.9896) or the full range correlation (0.9698), and this is due to the fact that the

lower values are more scattered relative to the range, as deviation carries more weight in this range. The slope for this low curve (0.64 (mg/L)/(μS/cm)) is higher than that for the high curve (0.54 (mg/L)/(μS/cm)) or for the full range curve (0.5655 (mg/L)/(μS/cm)). Because the higher values carry more weight in the correlation, it makes sense that the full range and high range curves would have similar slopes, because the full curve linear correlation would be influenced more by the high range data points. To be more accurate, the lower range correlation could be used for lower values, and the higher range correlation for high values. These correlations can be used if either TDS or conductivity data is sampled without the other, using the equations to calculate one parameter from the other. In cases where chloride concentration was not sampled but either TDS or conductivity had been sampled, and an estimation of chloride concentration needs to be made, the previous Chloride/TDS and Chloride Conductivity equations may be used for a rough estimate, but these datasets are not refined enough to be used with accuracy.

4.2 Bio-infiltration Traffic Island Correlations

4.2.1 Chloride versus TDS Correlation at the BTI

In order to have a comparison to the CSW TDS-Conductivity correlations, the Bio-infiltration Traffic Island (BTI) was also analyzed in order to create a TDS-Conductivity correlation, for both surface samples and subsurface samples. The BTI sample locations are listed in Table 2C and shown in Figure 2.4. Surface (i.e. first flush/ponded/overflow) samples and subsurface (i.e. lysimeter) samples were separated because there was a different trend for subsurface samples compared to the trend seen for surface samples. Figure 4.6 shows a comparison of the surface sample trend chloride-TDS curve and the subsurface sample trend chloride-TDS curve.

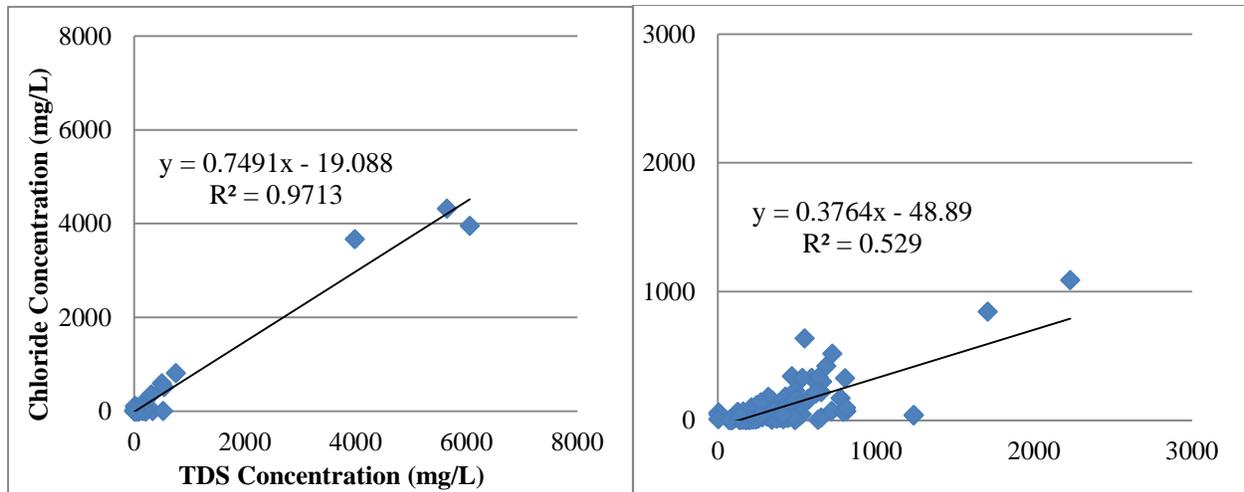


Figure 4.6: Chloride versus TDS Linear Correlation for Surface Samples $n = 196$ (left side) and Subsurface Samples $n = 129$ (right side) from the BTI

The surface sample chloride-conductivity curve has a slope of 0.75 mg Cl/mg TDS, while the subsurface chloride-conductivity curve has a slope of 0.38 mg Cl/mg TDS, approximately half of the surface sample slope. In the subsurface water, there is a much greater concentration of ions that are not chloride that increase the TDS. This is why the chloride only comprises approximately 30% of the TDS for subsurface samples, while it comprises about 70% of the surface sample TDS.

4.2.2 Chloride versus Conductivity Correlation at the BTI

The same phenomena occurs in regards to the chloride-conductivity curve. Figure 4.7 shows a comparison of the surface sample trend chloride-conductivity curve and the subsurface sample trend chloride-conductivity curve. The slope for the subsurface correlation was 0.26 (mg/L)/(μ S/cm), which is only half of the surface chloride-conductivity correlation slope (0.43 (mg/L)/(μ S/cm)). Again, because there would be significant concentrations of ions other than chloride in the subsurface, it makes sense that the ratio of chloride to conductivity would be less in the subsurface than in the surface.

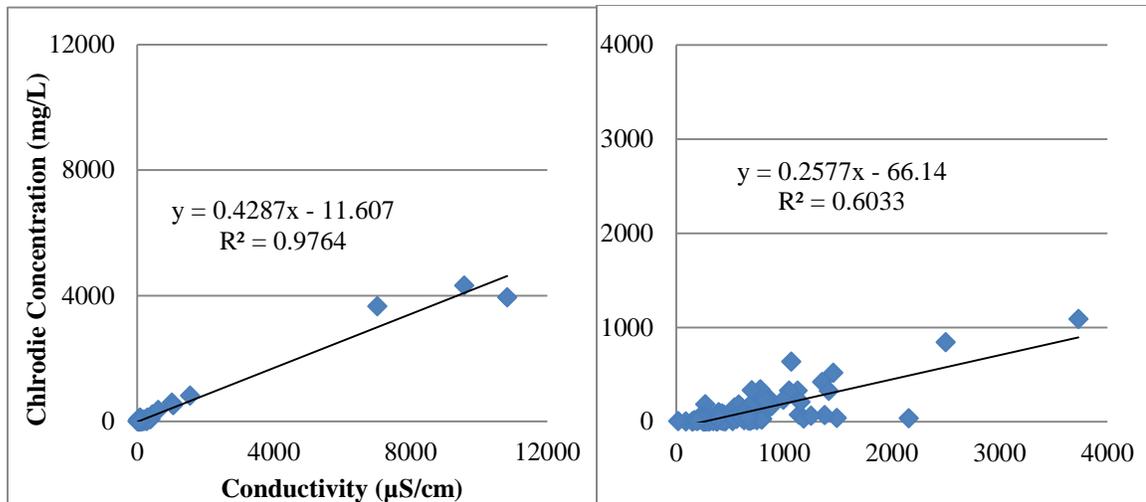


Figure 4.7: Chloride versus Conductivity Linear Correlation for Surface Samples $n = 201$ (left side) and Subsurface Samples $n = 145$ (right side)

Chloride exerts a much smaller influence on the subsurface conductivity readings than it does on the surface water readings. These interesting correlations may be of use in future studies if chloride movement through soils and groundwater is studied in conjunction with current research on how chloride may be retained in soils (Bastviken et al. 2006, Svensson et al. 2007).

4.2.3 TDS versus Conductivity Correlation at the BTI

TDS was plotted against conductivity for surface samples in order to determine the TDS-Conductivity curve, shown in Figure 4.8. The TDS versus Conductivity correlation has a linear fit with an equation of $y = 0.56x$ and an R^2 of 0.9908.

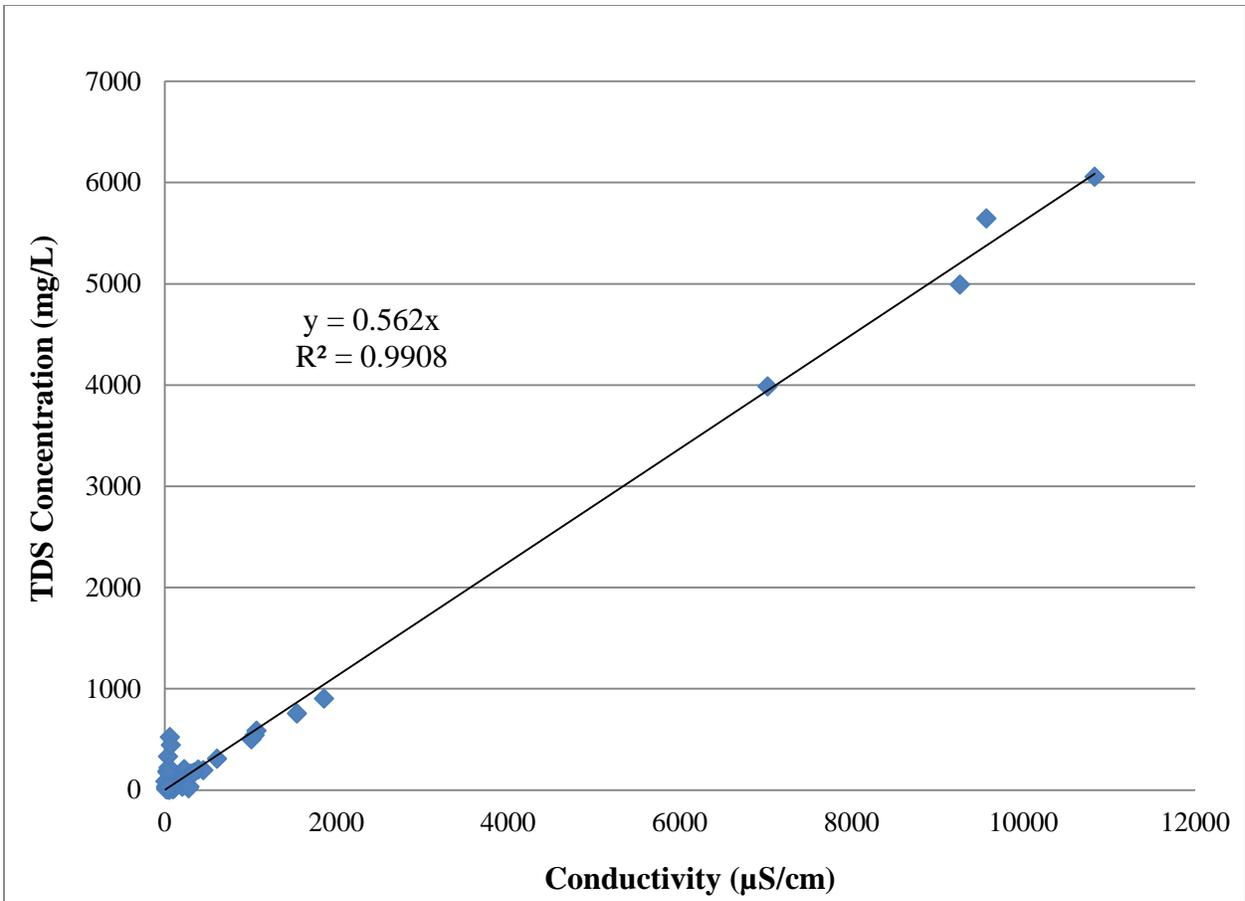


Figure 4.8: TDS vs. Conductivity Correlation – Surface Samples BTI with linear trend line; $n = 229$

This curve is similar to the TDS versus Conductivity curve calculated for the CSW, although there are far less points in the middle range, between approximately 2,000 and 8,000 mg/L. This is due to the fact that in the winter months, snow is piled on top of the BTI and then melts and infiltrates through the soil when temperatures rise. The highest values are attributed to a few first flush samples (FF02: Table 2C and Figure 2.4) in the Salt Application period which captures runoff that flows directly from the parking lot drainage area carrying high loading of TDS and the low values occur after road de-icing salts have already been flushed through the BTI at the end of the Salt Application period and in the Non-Salt Application

period. This results in a small number of high concentrations in the Salt Application periods only once or twice a year and data points low in the range for the rest of the year.

The TDS versus Conductivity correlation for subsurface samples is shown in Figure 4.9. The linear correlation that was found has an equation of $y = 0.6138x$ and an R^2 of 0.7969. The pattern seen in surface samples at the BTI for TDS versus conductivity is somewhat different than that seen for surface samples. The range is only from non-detect ($< 1 \mu\text{S/cm}$) to about 4,000 $\mu\text{S/cm}$, while the surface samples have a range from non-detect to about 12,000 $\mu\text{S/cm}$, because of those few high points of data.

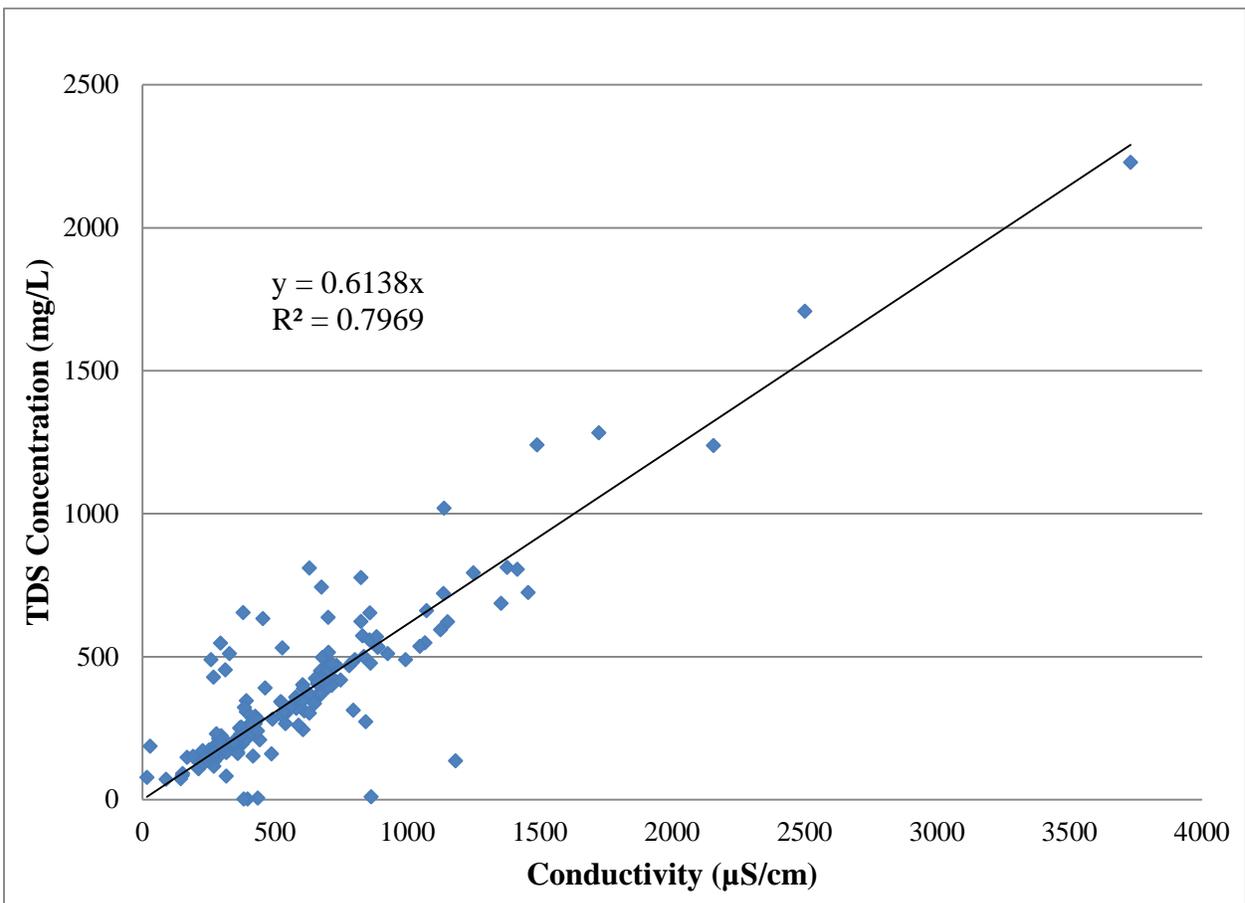


Figure 4.9: TDS vs. Conductivity Correlation – Subsurface Samples BTI with linear trend line; $n = 163$

The subsurface correlation has significantly more scatter than the surface correlation, but this may be due to the fact that the range is much lower. The equations of both surface and subsurface correlations are similar given that the slopes are close in value. The slope of the TDS versus Conductivity correlation for surface samples was 0.56 (mg/L)/(μS/cm) and for subsurface samples it was 0.61 (mg/L)/(μS/cm). The chloride vs TDS and chloride vs conductivity correlations were different, because chloride is only one ion that attributes to both TDS and conductivity. Because TDS and conductivity are much more directly related, it makes sense that these two TDS vs conductivity curves are similar.

4.3 Comparison of Constructed Stormwater Wetland and Bio-infiltration Traffic Island Correlations

Chloride versus TDS correlation equations for the CSW as well as the BTI surface and subsurface samples are shown in Table 4A. The slopes of the correlations for chloride versus TDS had a range between approximately 0.4 and 0.8, and curves for each location were unique.

Table 4A: Slope (m), R², and number of samples (n) from the chloride and TDS correlation curve equations; slope has units of mg Cl⁻/mg TDS

Location	m, y = mx +b	R²	n
Constructed Stormwater Wetland (CSW)	0.64	0.8342	421
Bio-infiltration Traffic Island (BTI) Surface	0.75	0.9713	196
Bio-infiltration Traffic Island (BTI) Subsurface	0.38	0.5290	129

The BTI subsurface correlation has the lowest slope (0.38 mg Cl⁻/mg TDS), showing that chloride has the lowest influence on TDS for these samples. The BTI surface sample correlation has the highest slope (0.75 mg Cl⁻/mg TDS), which shows that chloride has the most influence on these samples as a part of TDS. The CSW equation has the highest R² value, most likely because there is a smaller range of samples and no large gaps between high concentrations and

low concentrations than for the BTI surface samples. The BTI subsurface sample correlation had a large amount of scatter, especially for data points that sat close to the x-axis, therefore the low R^2 coefficient is not surprising.

The chloride versus conductivity correlation equations are listed in Table 4B. The slopes of the correlations for chloride versus conductivity had a range between approximately 0.25 and 0.45, and as with chloride versus TDS, curves for each location were unique.

Table 4B: Slope (m), R^2 , and number of samples (n) from the chloride and conductivity correlation curve equations; slope has units of (mg Cl⁻/L)/(μ S/cm)

Location	m, $y = mx + b$	R^2	n
Constructed Stormwater Wetland (CSW)	0.35	0.8548	421
Bio-infiltration Traffic Island (BTI) Surface	0.43	0.9764	201
Bio-infiltration Traffic Island (BTI) Subsurface	0.26	0.6033	145

Similar patterns exist with this chloride versus conductivity correlation equations as what was seen with the chloride versus TDS data. The lowest slope (0.26 (mg Cl⁻/L)/(μ S/cm)) occurs in the BTI subsurface equation and the highest in the BTI surface equation (0.43 (mg Cl⁻/L)/(μ S/cm)). Chloride has more of an effect on the conductivity in the surface sample dataset than in subsurface. The R^2 for the subsurface samples is again relatively low, most likely due to scatter around the x-axis.

The TDS versus conductivity equations, of most interest to this research, is shown below in Table 4C. All equations have similar slopes in the range of 0.54-0.64 (mg TDS/L)/(μ S/cm), and all three CSW and the BTI surface correlations have a high R^2 value (0.9698, 0.9896, 0.9021, and 0.9908, respectively).

Table 4C: Slope (m), R², and number of samples (n) from the TDS and conductivity correlation curve equations; CSW correlation equation uses the original linear curve with the entire range included for comparison purposes; slope has units of (mg TDS/L)/(μS/cm)

Location	m, y = mx +b	R²	n
Constructed Stormwater Wetland (CSW) full range	0.57	0.9698	454
Constructed Stormwater Wetland (CSW) high range	0.54	0.9896	393
Constructed Stormwater Wetland (CSW) low range	0.64	0.9021	60
Bio-infiltration Traffic Island (BTI) Surface	0.56	0.9908	229
Bio-infiltration Traffic Island (BTI) Subsurface	0.61	0.7969	163

The BTI subsurface R² was lower (0.7969), and again expected due to scatter of data, although it is interesting to note that the TDS/conductivity correlation in the subsurface is not as reliable as in surface water, although the correlation itself was similar to what was seen for both the CSW and the BTI surface samples. In fact, the BTI subsurface sample correlation was most similar to the CSW low range correlation. The similarity in slope with the CSW low range (TDS < 1,000 mg/L) may be due to the fact that the range is low for the subsurface sample correlation as well (TDS < 2,500 mg/L). The low R² value may be due to the fact that the range is low, but the CSW low range correlation has an R² of 0.9021, indicating that there are other reasons for the subsurface correlation to be less reliable. Perhaps this is because the sample size is smaller, or because subsurface samples have a more complex relationship between TDS and conductivity than do surface samples. Due to the similarity in the correlations, it seems that generally the TDS loadings at the two sites are comparable, and that ionic compositions are similarly balanced.

Calculating the TDS versus conductivity equation specifically for the Villanova CSW and the BTI may prove to be a valuable tool in monitoring water quality at these locations and in conducting future research. Graphing each individual correlation: chloride vs TDS, chloride vs conductivity, and TDS vs conductivity, and making a comparison to the BTI correlations serves to give perspective to the CSW chloride loading as part of the ionic composition of the system.

CHAPTER V: FATE OF CHLORIDE

5.1 Chloride Mass Balance: De-Icing Salt Application

Looking at chloride concentrations alone in the Villanova CSW does not give a full picture of chloride transport through the CSW. The volume of water passing through the CSW is equally important as the concentration of chloride, because the concentration applied over the volume reveals the mass of chloride moving through the system. A small concentration of chloride over a large volume may still be a large mass, due to dilution. Likewise, a large concentration of chloride in a small volume may turn out to be a small mass. A mass balance of chloride was performed at the inlet and the outlet of the CSW in order to determine how much chloride is moving into and out of the CSW, and to see if chloride is being retained within the CSW itself. In order to compare the mass seen entering the CSW to expected values based on how much chloride was applied to impervious surfaces upstream of the CSW, estimates of the road de-icing salt usage was provided by Villanova facilities and drainage area to the CSW was combined with these salt purchase numbers in order to estimate what the loading of road de-icing salt was in Salt Application season. The salt purchase numbers from facilities is provided in the Appendix in Table A1. These purchases included a number of different companies and products, with a few different chemical compositions. Most of the road de-icing salt applied was NaCl, and there was a small amount of CaCl₂ purchased as well. A graph displaying the tons of all salt products purchased per year is shown below in Figure 5.1.

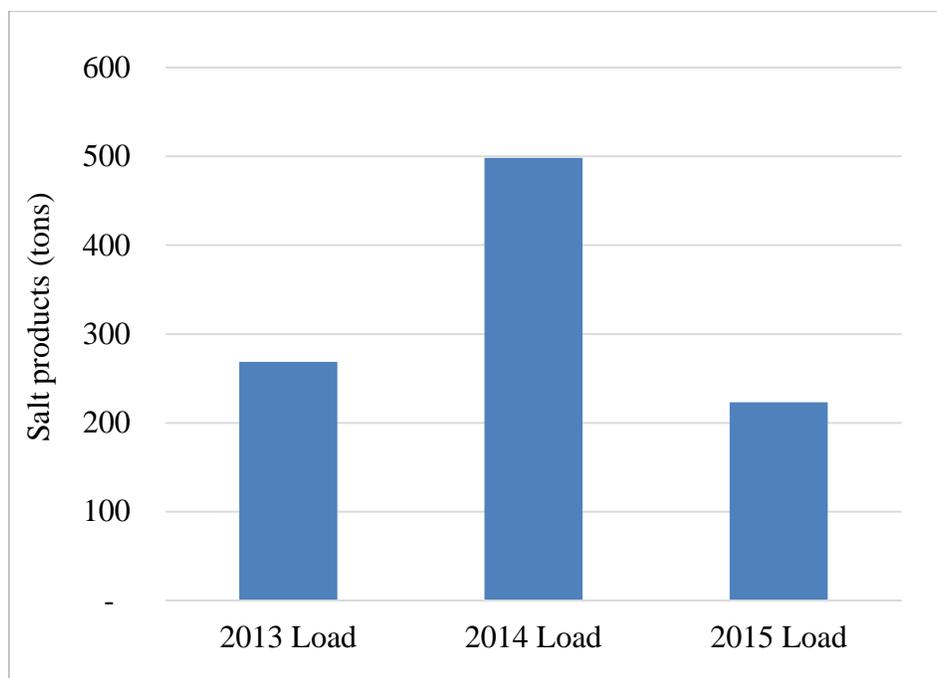


Figure 5.1: Tons of Salt Products Purchased over the Study Period; including all types; 2012 data was not available

It was assumed that all salt products were used in each year's Salt Application season, although it is probable that a small quantity remains left over each year and is kept in storage for the next year. It was assumed that this amount was negligible compared to the total amount of product applied each year. Looking at Figure 5.1, it is apparent that the 2014 salt usage was twice as much as either 2013 or 2015 years. This year there had been many ice storms resulting in a long-term power outage in the Philadelphia area and 67.6 inches of snow (Kuhne, accuweather.com). With this in mind, the fact that much more salt was used that year is not surprising, and this will bring an interesting dimension to the mass calculations done for that year.

Because there were several different de-icing products used, each purchase was identified for its main ingredient, either NaCl or CaCl₂, and respective calculations were done to determine the weight of chloride in each purchase in order to calculate the total amount of chloride applied

to Villanova’s campus per yearly Salt Application season. Full calculations are in Table A1 in the Appendix, and the summary is below in Table 5A.

Table 5A: Tons of Salt, Kilograms of Salt, and Kilograms of Chloride Purchased per Year

Year	Salt Purchased (tons)	Salt Purchased (kg)	Cl⁻ Purchased (kg)
2013	270	244,000	142,000
2014	500	452,000	273,000
2015	220	202,000	121,000

The amount of chloride that makes up the salt purchases per Salt Application season was calculated according to the composition of each product, however this is the amount of chloride used on the entirety of Villanova’s campus per year, not only on the CSW. In order to estimate how much of the road de-icing salt would have been applied to the CSW drainage area alone, Villanova facilities was consulted. Facilities estimated that approximately 40% of the salt was applied to the main campus, 20% to the west campus, 10% to the law school area adjoining the wetland, 10% to athletics, 10% to south campus, and 10% to the main parking lot. The CSW drainage area captures approximately half of the main campus (20%), a majority of the law school area (10%), and a large portion of the west campus area (10%), which could be roughly estimated at 40% of the total area. (See Figure 5.2).

In order to check this general estimate, an AutoCAD drawing of the CSW drainage area within a full map of the drainage areas of Villanova’s campus was also consulted (Figure 5.2).

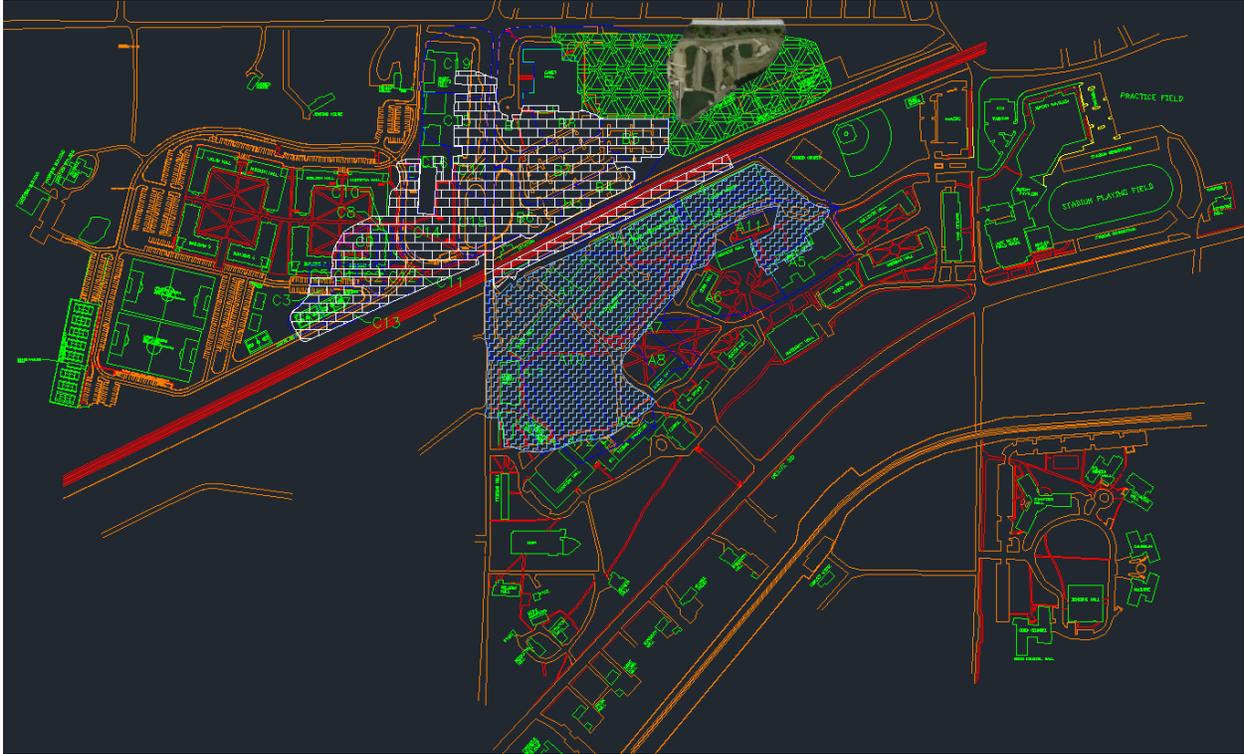


Figure 5.2: Villanova Campus AutoCAD Drawing of Drainage Areas to the CSW within a full drawing of Villanova campus drainage areas; Main (small blue pattern), West (light blue brick pattern), and Wetland (etched green pattern) drainage areas are shown; Credit James Pittman 2011

This AutoCAD drawing shows that there are three distinctive drainage areas to the Villanova CSW: the Main Campus drainage area, the West campus drainage area, and the Wetland drainage area. These cover a sizable portion of Villanova's campus. The map of these drainage areas is helpful in determining the full drainage area of the CSW, however, it is less helpful in determining the percent that is impervious vs pervious within each watershed as compared to the entire campus area.

In order to make the best estimate of how much road de-icing salt may drain directly to the CSW, it is imperative to have an estimate of the percent of the impervious area that drains to the CSW, not just the full drainage area. There is an uneven spread of grassy fields, gardens, athletic fields, and buildings across campus that makes the drainage area non-uniform in terms of

salt-application. In order to make a second estimate of road de-icing salt distribution, a Google Earth image of Villanova's campus was used in conjunction with Figure 5.2, so that the CSW drainage areas were superimposed on the campus map (Figure 5.3).



Figure 5.3: Villanova Campus Google Earth Map with AutoCAD Drawing of Drainage Areas to the CSW superimposed: Main drainage area in red, West drainage area in blue, Wetland drainage area in green; large fields and other non-salted areas in yellow

The drainage areas were superimposed onto the Villanova Campus and then the large grassy areas, fields, etc. were marked in yellow. The area for each of these yellow areas was calculated and the sum of these areas was subtracted from the total area of campus (9,490,000 ft²), and each of the three drainage areas were modified in the same way. Any large fields and green spaces in the drainage areas were added together and then subtracted from the respective drainage area. The summary of these calculations is listed in Table 5B.

Table 5B: Estimate of Campus Area, CSW Drainage Areas, and Subtracted Areas; in square feet

TOTAL CAMPUS AREA	9,490,000
SUM OF YELLOW SECTIONS	3,530,000
NEW CAMPUS AREA	5,960,000
MAIN CAMPUS: DRAINAGE AREA	662,000
WETLAND: DRAINAGE AREA	172,000
WEST CAMPUS: DRAINAGE AREA	811,000
TOTAL DRAINAGE AREA	1,650,000
% OF CAMPUS DRAINING TO WETLAND	28%

These calculations result in the total campus area excluding large non-salted areas being 5,960,000 ft² and the total CSW drainage area excluding large non-salted areas being 1,650,000 ft². The CSW drainage area under this estimation is approximately 28% of the total campus area. These calculations were not exact determinations of the precise area of all impervious surfaces that would have salt applied to them, but a general estimate excluding large obviously non-salted areas. It was assumed that the density of impervious cover in the modified CSW drainage area was the same as that in the modified Villanova campus area and that salt application would have been uniform regardless of the surface it was being applied on, the timing of salting, or any other factors.

Using the estimations from the Google Earth image, the percentage of Villanova's campus draining to the CSW was estimated to be 28%. Using this, the percent of chloride applied only to the CSW drainage area can be estimated by multiplying 28% times the total amount of chloride applied. These calculations are summarized in Table 5C.

Table 5C: Kilograms of Road De-Icing Salt and Kilograms of Chloride Applied to the CSW Drainage Area per Salt Application Year

Year	Salt Purchased (kg)	Salt Applied to CSW Drainage Area (28% of the total) (kg)	Cl⁻ Applied to CSW Drainage Area (kg)
2013	243,800	68,300	39,800
2014	452,100	126,600	76,400
2015	202,300	56,700	34,000

According to these road de-icing salt application numbers, approximately twice as much chloride was applied to the CSW drainage area in 2014 than in either 2013 or 2015. These masses of chloride will be compared to what is seen entering the inlet of the CSW in each Salt Application season.

5.2 Chloride Mass Balance through the Wetland

In order to understand the movement of chloride through the CSW, the inlet and outlet were analyzed for the 2013 and 2014 years to make a comparison between how much mass entered and how much mass left the CSW and then entered Mill Creek. Chloride concentrations were separated into baseflow and storm events as well as into Salt Application and Non-Salt Application periods and the same was done for volume data at the inlet and the outlet, which was calculated using a MATLAB code and summed to get a total volume for each season and flow condition. The complete chloride concentration data with averages and medians for each year are shown in Tables A2 through A9 in the Appendix and the complete flowrate and volume data are in Tables A10 through A17 in the Appendix. The summary is of volume data for 2013 and 2014 are listed respectively in Tables 5D and 5E below.

*Table 5D: 2013 Summary of Baseflow and Storm Volumes, Rainfall Totals, and Durations;
Lower table shows total flow volumes for 2013 and the calculation for interflow*

	Duration (days)	Rainfall (in)	Inlet Volume (m³)	Outlet Volume (m³)	% Retained
2013 Winter Baseflow	54		19,500	10,200	48%
2013 Winter Storm	36	23	58,800	35,000	41%
2013 Summer Baseflow	92		24,800	13,400	46%
2013 Summer Storm	36	34	87,100	52,900	39%
2013 BF + Storm	219	56	190,200	111,500	41%

	Duration (days)	Rainfall (in)	Inlet Volume (m³)	Outlet Volume (m³)	% Retained
2013 TOTAL	365	56	262,800	130,400	50%
2013 BF + Storm	219	56	190,200	111,500	41%
2013 Interflow (TOTAL - (BF + Storm))	146		72,600	18,900	74%
Baseflow + Interflow	292		116,900	42,500	64%

In 2013, there was a total of 56 inches of rain, occurring on a total of 36 days during the Salt Application period and 36 days during the Non-Salt Application period. Influent volumes totaled 262,800 m³ for the year, with effluent volumes totaling 130,400 m³. Volume retention for each season fluctuates around 40-74%, with an overall retention of 50% for the year. Due to the definition of baseflow conditions written in the baseflow code which was used to calculate flowrates and volumes in the CSW, the total duration of baseflow and storm events does not add up to the full 365 day year. In 2013, baseflow and storm durations totaled 219 days. The baseflow code is written with a rule that baseflow conditions may not be defined until 72 hours after a storm event has ended. This intermediary time is separated from baseflow to ensure that storm flows do not affect baseflow. For the purposes of this study it was determined that interflow must be accounted for, since it comprises such a large portion of the year, and that it was most appropriate to include it with baseflow in order to best estimate mass transport through

the CSW over the full year. The total volume passing through the CSW at the inlet and the outlet for each year was summed and interflow was estimated by subtracting baseflow and storm event volumes from the total to obtain the missing volume. In mass balance calculations, baseflow volume and interflow volume are added together to obtain mass estimates for baseflow periods.

The largest volume passing through the CSW in 2013 was during Non-Salt Application storms, with 87,100 m³ entering and 52,900 m³ leaving, while the lowest volume occurred during the Salt-Application period baseflow with 19,500 m³ entering and 10,200 m³ leaving. Interflow was estimated to account for the missing 146 days with 72,000 m³ of influent and 18,900 m³ of effluent. The sum of baseflow and interflow volumes results in a total of 116,900 m³ of mixed baseflow/interflow influent and 42,500 m³ effluent. With a total influent volume for the 2013 year of 262,800 m³, a total effluent volume of 130,400 m³, and an overall volume retention rate of 50%, it is expected that this volume retention seen in 2013 will in a significant way affect the retention of chloride within the CSW.

There are some interesting differences between the flows and resulting volumes occurring in 2013 and those in 2014. The 2014 volumes and interflow calculation summary is shown below in Table 5E.

*Table 5E: 2014 Summary of Baseflow and Storm Volumes, Rainfall Totals, and Durations;
Lower table shows total flow volumes for 2014 and the calculation for interflow*

	Duration (days)	Rainfall (in)	Inlet Volume (m³)	Outlet Volume (m³)	% Retained
2014 Winter Baseflow	78		68,800	45,100	34%
2014 Winter Storm	79	32	224,900	123,200	45%
2014 Summer Baseflow	75		31,300	11,600	63%
2014 Summer Storm	33	16	53,600	48,400	10%
2014 Calculated Total	264	48	378,500	228,300	40%

	Duration (days)	Rainfall (in)	Inlet Volume (m³)	Outlet Volume (m³)	% Retained
2014 TOTAL	365	48	431,000	257,300	40%
2014 BF + Storm	264	48	378,500	228,300	40%
2014 Interflow (TOTAL - (BF + Storm))	101		52,500	29,000	45%
Baseflow + Interflow	253		152,600	85,700	44%

In 2014, there was a total of 48 inches of rain, less than the 56 inches in 2013. Storm events during the Salt Application period between December and May totaled 32 of those inches, while the Non-Salt Application period had 16 inches. The total duration of baseflow and storm events is 264 days and, as stated above, a considerable amount of the time conditions in the CSW do not meet either the baseflow or storm conditions, but are considered interflow. Interflow was estimated to account for the 101 missing days with 52,000 m³ of influent volume and 29,000 m³ of effluent volume. Volumes for all seasons are comparable to what was seen in 2013, however, volumes observed in the Salt Application period storms are much larger, and in fact the volumes seen in this storm season alone (224,900 m³ influent and 123,200 m³ effluent) are greater than the total flow observed for the entire 2013 year (190,200 m³ influent and 111,500 m³ effluent). A likely explanation for this unexpectedly high volume is that during the 2014 winter season, the Philadelphia area experienced approximately 67.6 inches of snow, about three times the average,

which could have contributed to the large volumes seen during this time period (Kuhne, accuweather.com). The lowest volume entering the wetland was during the Non-Salt Application period baseflow (31,300 m³ influent and 11,600 m³ effluent). Retention rates fluctuate between 10-63%, a larger range than 2013, with the greatest amount of retention occurring during the Non-Salt Application period baseflow (63%). The total influent volume for the year is 431,000 m³ and the total effluent volume is 257,300 m³, (both approximately twice as much as the 2013 volumes), resulting in an overall 40% volume retention for the year (similar to the 50% estimated for 2013). 2014 is a unique year because of the large loading of snow and ice resulting in unusually high volumes, and because of the also abnormally large mass of road de-icing salt applied to the CSW drainage area.

Using these volumes from the tables above, as well as the median chloride concentrations from Tables A2 through A9 in the Appendix, the mass of chloride for each season was determined by multiplying the median chloride concentrations by the volumes and then accounting for units. Summaries are shown for 2013 and 2014 mass balance calculations in Tables 5F and 5G, respectively.

Table 5F: 2013 Summary of Baseflow and Storm Mass of Chloride; Entering from Inlet and Leaving from Outlet; Mass Retained in kilograms and in percentage; % Volume Retained was included for comparison

	Median Mass Entering (kg)	Median Mass Leaving (kg)	Mass Retained (kg)	% Mass Retained	% Volume Retained
2013 Winter Baseflow	43,700	15,200	28,500	65%	48%
2013 Winter Storm	24,300	4,300	20,000	82%	41%
2013 Summer Baseflow	7,500	4,900	2,600	35%	46%
2013 Summer Storm	9,300	2,200	7,100	77%	39%

	Total Median Mass Entering (kg)	Total Median Mass Leaving (kg)	Total Median Mass Retained (kg)	% Mass Retained	% Volume Retained
2013 Winter Totals	68,000	19,500	48,400	71%	61%
2013 Summer Totals	16,800	7,100	7,800	46%	37%
2013 TOTAL	84,800	26,600	56,200	66%	50%
<i>Cl- Load (kg) for 2013</i>	<i>39,800</i>				

In 2013, the largest mass of chloride entered the CSW in the Salt Application season during baseflow (43,700 kg), and the mass leaving the CSW during that period was low in comparison (15,200 kg). The total Salt Application period mass was 68,000 kg influent and 19,500 kg effluent, which is higher than the total Non-Salt Application period mass of 16,800 kg influent and 7,100 kg effluent. This is expected, since road de-icing salts are applied in the winter months, so more mass of chloride is expected during the Salt Application period. Salt Application period baseflow and storm mass retention was high, 65% for baseflow and 82% for storm, and this is significant considering that the largest masses were retained during this period (48,400 kg retained total). The Non-Salt Application storms also had a large percentage of chloride retention (77%), however, the mass was much smaller (9,300 kg influent and 2,200 kg effluent), and therefore is not as significant (7,100 kg retained). One interesting observation is that chloride mass retention rates are higher than volume retention rates for all seasons except the

summer baseflow. Overall, mass retention rates are higher in the Salt Application period (Salt period: 71 % chloride retention and 61% volume retention; Non-Salt period: 46% chloride retention and 37% volume retention), which may be evidence towards the hypothesis of retention of chloride in winter months followed by release in summer months. Approximately four times as much chloride entered and left the CSW in the Salt Application period (68,000 kg entering, 19,500 kg leaving) than in the Non-Salt Application period (16,800 kg entering, 7,100 kg leaving), and in total 84,800 kg of chloride entered the wetland over the 2013 year and 26,600 kg left, with an overall 66% mass retention rate. Volume retention over all of 2013 was 50% and the estimated chloride loading from applied road de-icing salts was 39,800 kg. Approximately twice as much of that estimated 39,800 kg of road de-icing salt chloride is being observed for 2013, which points to an additional source of chloride entering the CSW other than that from impervious surfaces.

Table 5G summarizes mass and volume data for the 2014 year. As with large differences in volume from season to season in the 2014 year, so too are there large differences in the mass moving through the wetland in 2014.

Table 5G: 2014 Summary of Baseflow and Storm Mass of Chloride; Entering from Inlet and Leaving from Outlet; Mass retained in kilograms and in percentage; % Volume Retained was included for comparison

	Median Mass Entering (kg)	Median Mass Leaving (kg)	Mass Retained (kg)	% Mass Retained	% Volume Retained
2014 Winter Baseflow	45,021	33,270	11,751	26%	34%
2014 Winter Storm	172,752	65,321	107,431	62%	45%
2014 Summer Baseflow	14,050	5,103	8,947	64%	63%
2014 Summer Storm	2,893	5,822	-2,930	-101%	10%

	Total Median Mass Entering (kg)	Total Median Mass Leaving (kg)	Total Median Mass Retained (kg)	% Mass Retained	% Volume Retained
2014 Winter Totals	217,772	98,590	119,182	55%	43%
2014 Summer Totals	16,943	10,926	6,017	36%	33%
2014 TOTAL	234,716	109,516	125,200	53%	40%
<i>Cl- Load (kg) for 2014</i>	76,400				

In the Salt Application months, in comparison to the 2013 data, the mass of chloride is much higher. In the Salt Application baseflow, 45,000 kg entered and 33,300 kg flowed out of the wetland, with a 26% mass retention rate and a 34% volume retention rate. The largest mass of chloride entered the wetland in the Salt Application season during storm events (172,752 kg), and the mass leaving the wetland during that period was relatively low (65,320 kg). This results in mass retention of 62%, with a volume retention for that storm period of 45%. This mass is more than twice the mass observed in the CSW for the entire 2013 year (84,800 kg entering, 26,600 kg leaving). For the Non-Salt Application period, storms and baseflows both had a much smaller mass of chloride entering and leaving, but different retention rates. Non-Salt Application baseflow had 14,050 kg entering and 5,103 kg leaving, with mass retention of 64% and volume

retention of 63%. Non-Salt Application storms had only 2,893 kg entering but 5,822 kg leaving, with the only case of mass export, with mass retention of -101% and volume retention of only 10%. This is interesting to note, and most likely the mass export is due to the fact that so little volume retained. However, it is still curious that twice as much chloride was exported from the CSW than what had entered. This may be due to the fact that large masses of chloride were stored in the CSW and then released during Non-Salt Application period storms.

Far more chloride entered and left the CSW in the Salt Application period (217,800 kg entering, 98,600 kg leaving) than in the Non-Salt Application period (16,900 kg entering, 10,900 kg leaving), and the Salt Application and Non-Salt Application seasons had different mass retention rates, 55% and 36%, respectively. As seen in 2013, the chloride retention rates are generally higher than the volume retention rates (Salt period: 55 % chloride retention and 43% volume retention; Non-Salt period: 36% chloride retention and 33% volume retention). In total 234,700 kg of chloride entered the wetland over the 2014 year and 109,500 kg left, with an overall 53% mass retention rate. Volume retention over all of 2014 was 40% and the estimated chloride loading from applied road de-icing salts was 76,400 kg. The total amount seen entering the CSW was three times higher than the estimated road de-icing salt loading for the year. This again points to the possibility that there is another source of chloride to the CSW.

One of the concerns in calculating mass in this way is that there are only approximately 12 sampling events for baseflow each year, and more importantly only about 12 sampling events for storms each year. As discussed in section 3.1, storm events can be extremely variable in concentration and they fluctuate in intensity. This provides a challenge for accurately estimating mass of chloride through the CSW during storm events. Of special concern was the chloride mass estimate for the Salt Application storm events in the 2014 year, when chloride influent was

estimated to have carried in 172,800 kg of chloride and to have released 65,300 kg of chloride in the effluent. This season had a large amount of flow (224,900 m³ influent and 123,200 m³ effluent), which would have contributed to the large mass which was calculated, however, there is a possibility that a high median concentration, calculated with only five points of data may also have skewed mass estimations as well.

In order to check these estimations, storm event concentrations were matched to their respective storm event volumes in order to estimate how much chloride mass may have been contributed by each individual event. This mass could then be compared to the total in order to determine if these data points contributed in a large way to the total mass estimation. Table 5H shows the individual calculations of mass for each of the five storm sampling events that took place during the 2014 Salt Application period.

Table 5H: 2014 Comparison of 5 Individual 2014 Salt Application Period Storms in Calculating Mass of Chloride

Storm Start	Duration (hrs)	Rainfall (in)	Inlet Volume (m³)	Outlet Volume (m³)	Average In Conc (mg/L)	Average Out Conc (mg/L)	Mass In (kg)	Mass Out (kg)
12/9/13	51	0.48	3,119	3,035	1,822	814	5,683	2,470
1/10/14	91	1.52	8,560	6,589	768	530	6,574	3,492
2/21/14	75	0.59	18,037	5,350	1,139	859	20,544	4,596
4/7/14	80	0.38	6,873	4,051	338	234	2,323	948
4/25/14	78	0.64	9,496	3,330	60	152	570	506
Total:	16 days	3.61	46,100	22,400			35,700	12,000
Season Total:	79 days	32	224,900	123,200	768	530	172,800	65,300

As shown, these five data points only account for 3.61 of the 32 days and only 16 inches of the 79 total inches of rainfall. The volume calculated from these five events (46,100 m³ influent and 22,400 m³ effluent) accounts for approximately one fifth of the total calculated for

the 2014 Salt Application season (224,900 m³ influent and 123,200 m³ effluent). These events (35,700 kg influent and 12,000 kg effluent) also account for one fifth of the mass calculated over the entire period (172,800 kg influent and 65,300 kg effluent). This shows that these five data points only account for a small portion of the total mass estimated for that period of time using the median chloride concentration. These median concentrations are high (IN median = 768 mg/L, OUT median = 530 mg/L), and therefore may be unfairly weighing the large volume of stormwater seen during this period towards calculation of a much higher mass of chloride.

One final check is to take the total volumes and medians of chloride over both 2013 and 2014 for both storms and baseflow events as well as for the Salt Application period and the Non-Salt Application period to see if a larger set of data considering these groups separately will give a more accurate comparison for the mass balance. Table 5I presents this separated seasonal and storm type data along with the total for 2013-2014 and the road de-icing salt chloride application masses.

Table 5I: 2013 and 2014 Sum Baseflow and Storm Comparison in Calculating Mass of Chloride; Total Calculation over both years is included as well as total road de-icing salt chloride estimate

	Volume in (m³)	Volume out (m³)	Vol Retention	Median In (mg/L)	Median Out (mg/L)	Mass In (kg)	Mass Out (kg)	Mass Retention
All Salt	453,600	232,000	49%	523	552	237,400	128,100	46%
All Non-Salt	240,200	155,700	35%	149	125	35,700	19,500	45%
Sum	693,800	387,700	44%			273,100	147,500	46%
All Baseflow	269,500	128,200	52%	269	276	72,400	35,400	51%
All Storm	424,300	259,400	39%	107	120	45,400	31,200	31%
Sum	693,800	387,700	44%			117,900	66,600	44%
Total 2013-2014	693,800	387,700	44%	227	196	157,200	76,000	52%
Road De-Icing Salt						116,200		

From this table, it is clear that there is a wide range of masses that can be calculated over the period from 2013-2014. In separating the Salt Application and Non-Salt Application periods, weight is still skewed towards the Salt Application period. While the median chloride concentrations are much more representative of the dataset, using more data points over a longer timeframe, the large volume observed at the CSW still increases the influent mass to 273,100 kg. It is possible that the concentrations in the CSW during the 2014 Salt Application season were truly high throughout the season, but it is more likely that there was more variation, and therefore that this estimate is too high. In looking at the baseflow and storm separated calculations, this method takes away emphasis from the different patterns seen between Salt Application and Non-Salt Application events. Because medians are so low, this calculation gives a low estimate of the influent mass (117,900 kg) and this may not be a fair way to determine mass considering that Salt Application and Non-Salt Application period patterns are much more different than storm and baseflow patterns. The last calculation uses the median of all the data together, and the mass estimated is 157,200 kg influent and 76,000 kg effluent. This may be the most accurate estimate of mass, since it counts volumes and concentrations from all seasons and flow types equally. If so, in comparison to road de-icing salt chloride application concentrations for the full two year period, there is still more mass entering the CSW than what is estimated from impervious surfaces (116,200 kg). On the low estimate of chloride mass at the inlet (117,900 kg), calculated from the separated baseflow and storm calculation, there seems to be almost no additional chloride. From the high estimate (273,121 kg) calculated from the separated Salt Application and Non-Salt Application periods, there is a large amount of chloride over that 117,900 kg of road de-icing salt chloride. Without further testing and analysis, especially of storm events during the

Salt Application period, the exact estimate of mass moving into the Villanova CSW cannot be definitively determined.

5.3 Chloride Concentrations and Mass Balance in Mill Creek

In order to get an idea of how the CSW might affect downstream chloride concentrations as well as how mass may be transported after the CSW, a small window of data from Mill Creek was analyzed in order to give insight on the CSW's influence on the surrounding watershed. The sampling locations are marked below on Figure 5.4 and flow and chloride concentration data is used from the periods between 7/2/13 and 3/30/14. This gives a convenient glance into both Non-Salt Application and Salt Application sampling periods.

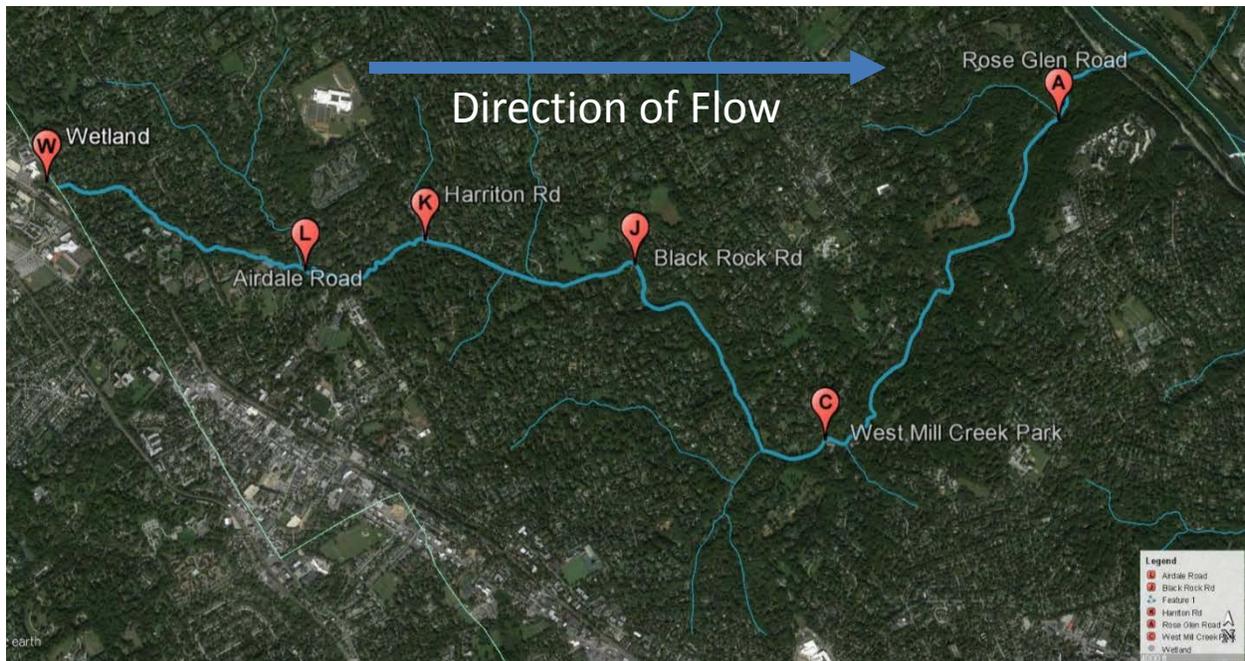


Figure 5.4: Map of Mill Creek and Five Sampling Sites from CSW to the Inlet at the Schuylkill River; L at Airdale Rd, K at Harriton Rd, J at Black Rock Rd, C at West Mill Creek Park, and A at Rose Glen Rd; the Villanova CSW is denoted with a capital W and the word “Wetland”

The Villanova CSW is the headwaters of Mill Creek, which eventually runs into the Schuylkill River. The creek is approximately 6.38 miles long and reaches between sampling locations are these lengths as follows: Villanova CSW to L, 1.13 miles; L to K, 0.62 miles; K to J, 0.91 miles; J to C, 1.33 miles; C to A, 1.91 miles; A to Schuylkill River, 0.48 miles. Each sampling location was chosen because there was a small tributary connecting to the creek just before that location, and for convenience of sampling. Each sampling location is named after the road or location it is connected to (Figure 5.4).

Data was used between the 7/2/13 and 3/30/14 and sampled approximately once a month, although one month, August 2013, was not sampled. Three of the sampling events occurred during storm conditions, 11/1/13, 2/22/14, and 3/30/14. The remaining events occurred during baseflow conditions and consisted of 7/2/13, 9/27/13, 11/22/13, 12/19/13, 1/25/14, and 3/22/14. The full data is organized in Table A18 in the Appendix. Both discharge and chloride concentration were taken at each location on each sampling day. Discharge was recorded in m^3/s and chloride concentration was taken in mg/L . Because the samples taken along Mill Creek were taken independently of the CSW samples, the sampling events do not necessarily occur on the same days. Therefore, chloride concentration could not always be compared directly to the Mill Creek chloride concentrations. Discharge was constantly monitored at the CSW, and therefore discharge was directly compared to Mill Creek data for every sampling event. When CSW and Mill Creek sampling days matched approximately (both CSW and Mill Creek sampling events occurred within the same baseflow or storm period) chloride concentration and also mass were directly compared to the Mill Creek data (Figures 5.9 through 5.12).

Because baseflow and storms have different trends and because they were analyzed separately for the CSW calculations, they are also separated here for the Mill Creek data calculations. Because each sampling location has a tributary connecting to the Mill Creek just upstream of the sampling location, data will be analyzed to determine 1) the trends in discharge over Mill Creek to see if there is any trend in flowrates traveling downstream (it is expected that discharge will increase traveling downstream as tributaries add more flow to Mill Creek), 2) how chloride concentrations change traveling downstream (it is expected that if there is an increase in discharge that chloride concentration may decrease with dilution mechanisms) 3) to track the mass transport of chloride as it travels downstream (this will show any exports or sinks of chloride mass through Mill Creek).

5.3.1 Mill Creek Baseflow Mass Transport Comparison

Figure 5.5 shows the discharge over time along Mill Creek at each location, including the CSW inlet and outlet for comparison. The CSW is the headwaters of Mill Creek, therefore the graph represents flow from the start of the creek until the sampling location just before the Schuylkill River.

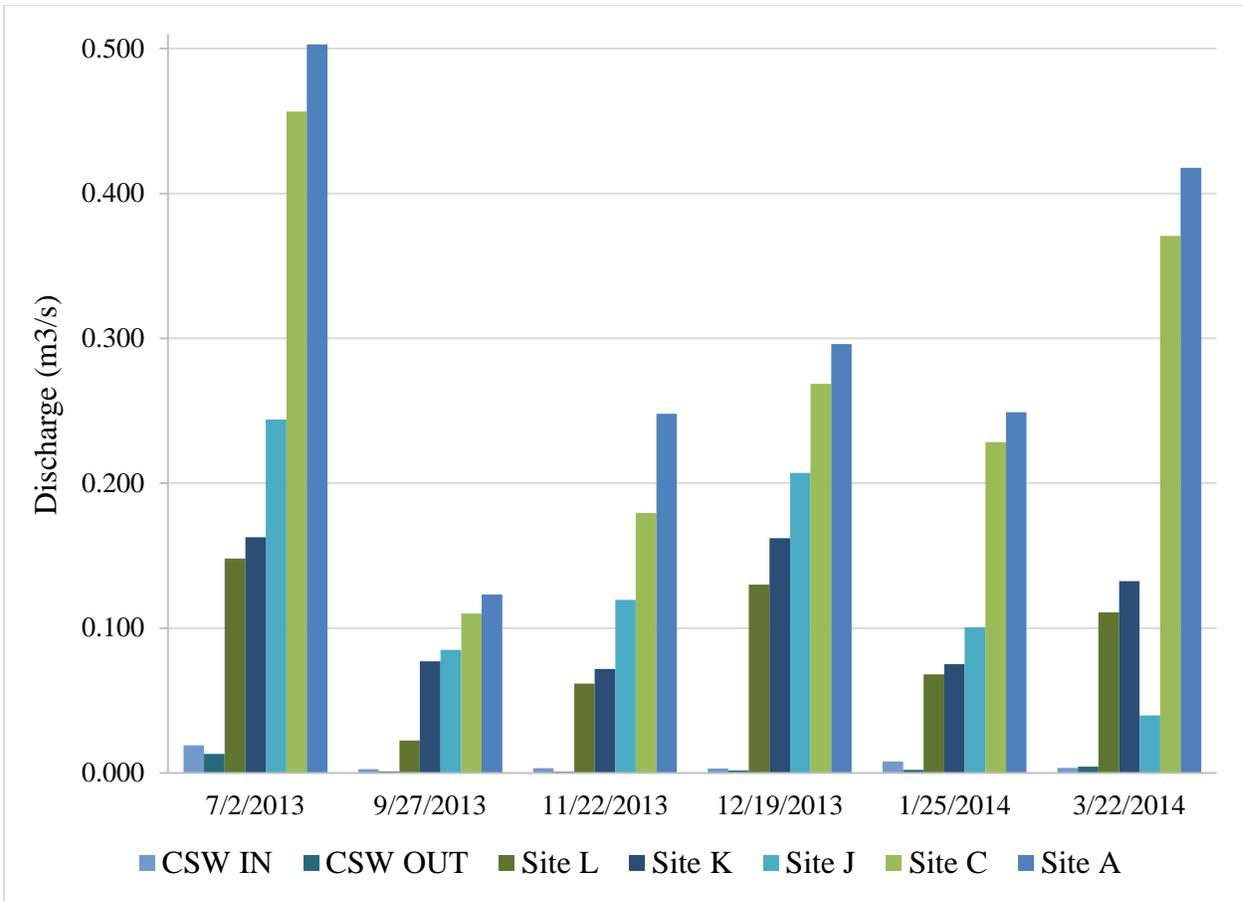


Figure 5.5: Discharge over Time for each Sampling Site along Mill Creek as well as Inlet and Outlet of the CSW; going downstream from left to right (Inlet through A)

As expected, the discharge over Mill Creek increases traveling downstream. The discharge rate as it flows through the Villanova CSW generally decreases from inlet to outlet due to volume retention within the wetland. Baseflow discharge on average over the study period is 21% less at the outlet than at the inlet and the baseflow average discharge at the inlet is $0.0052 \text{ m}^3/\text{s}$ and $0.0035 \text{ m}^3/\text{s}$ at the outlet. Downstream of the CSW, discharge increases at each sampling location, and the trend for each sampling date is the same, showing a consistent pattern. The range of discharge at sampling locations along Mill Creek range from $0.022 \text{ m}^3/\text{s}$ to $0.503 \text{ m}^3/\text{s}$, substantially greater than the flows seen at the Villanova CSW. This is expected; because the CSW is the headwaters of Mill Creek, it contributes the initial flow from which

Mill Creek begins, but tributaries and surface runoff contribute to higher flows incrementally downstream through the creek.

As this discharge increases over Mill Creek, dilution of constituents would be an expected result with the larger volumes of water if there were a constant mass of that constituent. There may be a different pattern if the mass is not constant, however. Figure 5.6 shows the chloride concentration over time for each location. Again, because CSW sampling did not coincide with Mill Creek sampling, the CSW chloride concentration data could not be included in this graph.

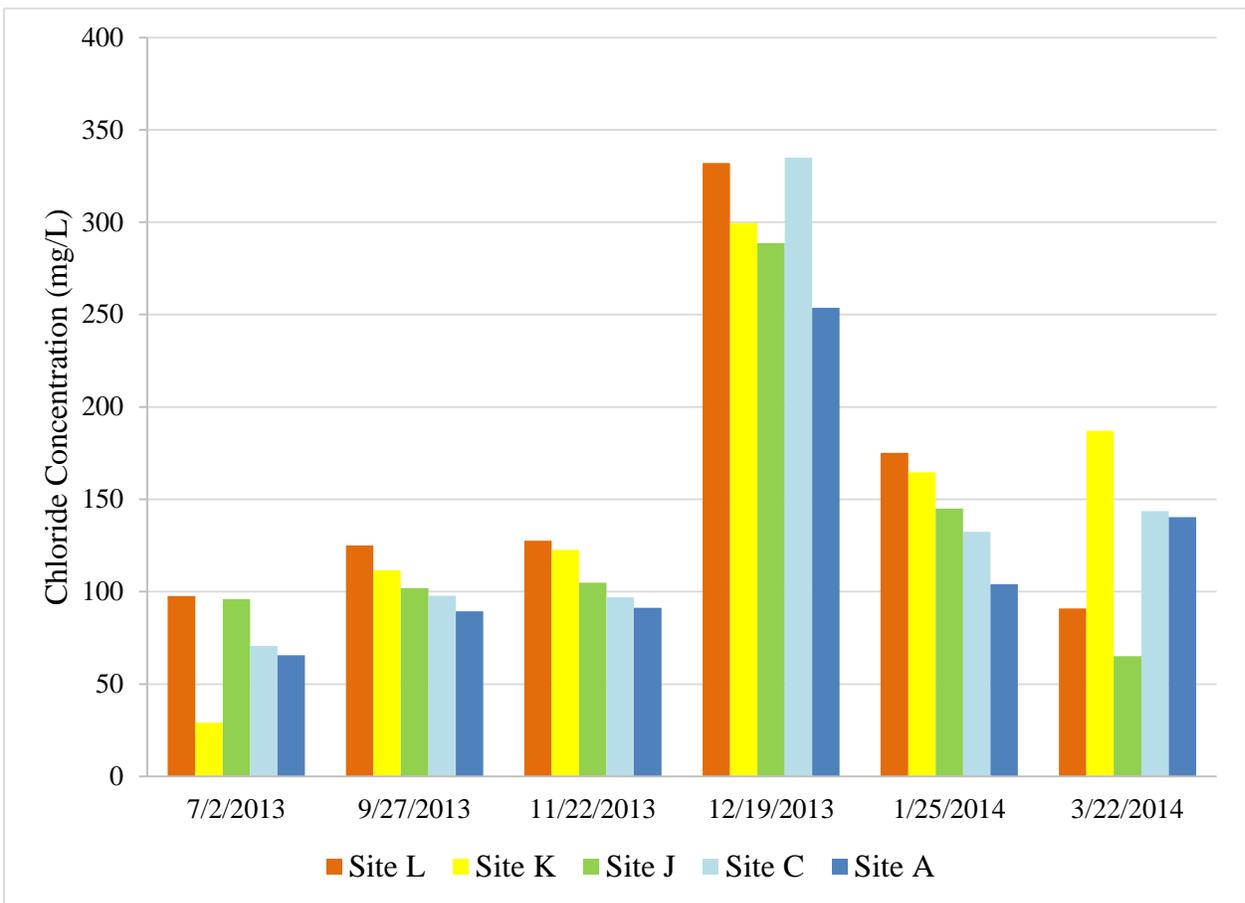


Figure 5.6: Chloride Concentration over Time for each Sampling Site along Mill Creek; going downstream from left to right (L to A)

The general trend for chloride concentration through Mill Creek moving downstream is that concentration decreases through the creek. On 9/27/13, 11/22/13, and 1/25/14 concentration decreases through the creek in a gradual, slow decline in a consistent pattern. On 7/2/13, 12/19/13, and 3/22/14 there is a more erratic pattern, where some of the sampling locations have higher concentrations than both those upstream and downstream. This could be due to irregular chloride loading at those locations for the 12/19/13 and 3/22/14 events, when road de-icing salt would still be washing out of the watershed. Chloride concentrations are fairly low compared to what is seen at the CSW, ranging from 29 mg/L to 335 mg/L. The highest concentrations occur on 12/19/13, the beginning of the Salt Application period, and this is the only sampling date of this dataset where Mill Creek concentrations exceed EPA chronic criteria (230 mg/L).

In order to make a brief comparison to concentrations observed in the CSW, baseflow data at the Mill Creek and the CSW were plotted on the same graph. Sampling event days did not occur at the same time, so baseflow data was used for each month when baseflow occurred for both sites. Figure 5.7 illustrates this simple comparison.

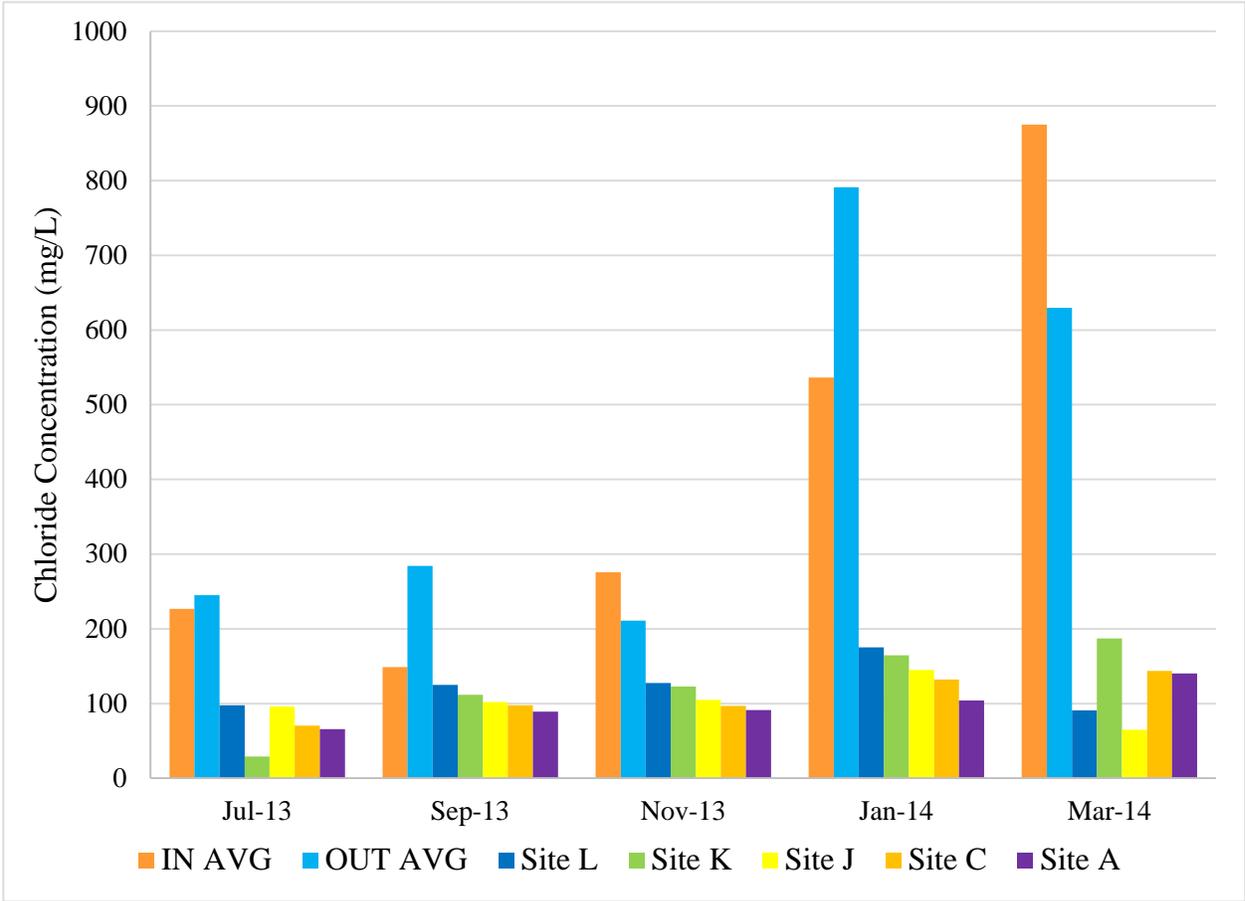


Figure 5.8: Chloride Concentration over Time for each Sampling Site along Mill Creek, including the Inlet and the Outlet at the CSW; sampling dates did not occur on the same day, so baseflow is considered as an average for the month

In order to better understand these patterns, mass transport through Mill Creek was analyzed. Again, because sampling events for the CSW and the Mill Creek did not always coincide, the Mill Creek data was first analyzed alone. Figure 5.9 is a graph of the mass of chloride over time for each of the sampling locations.

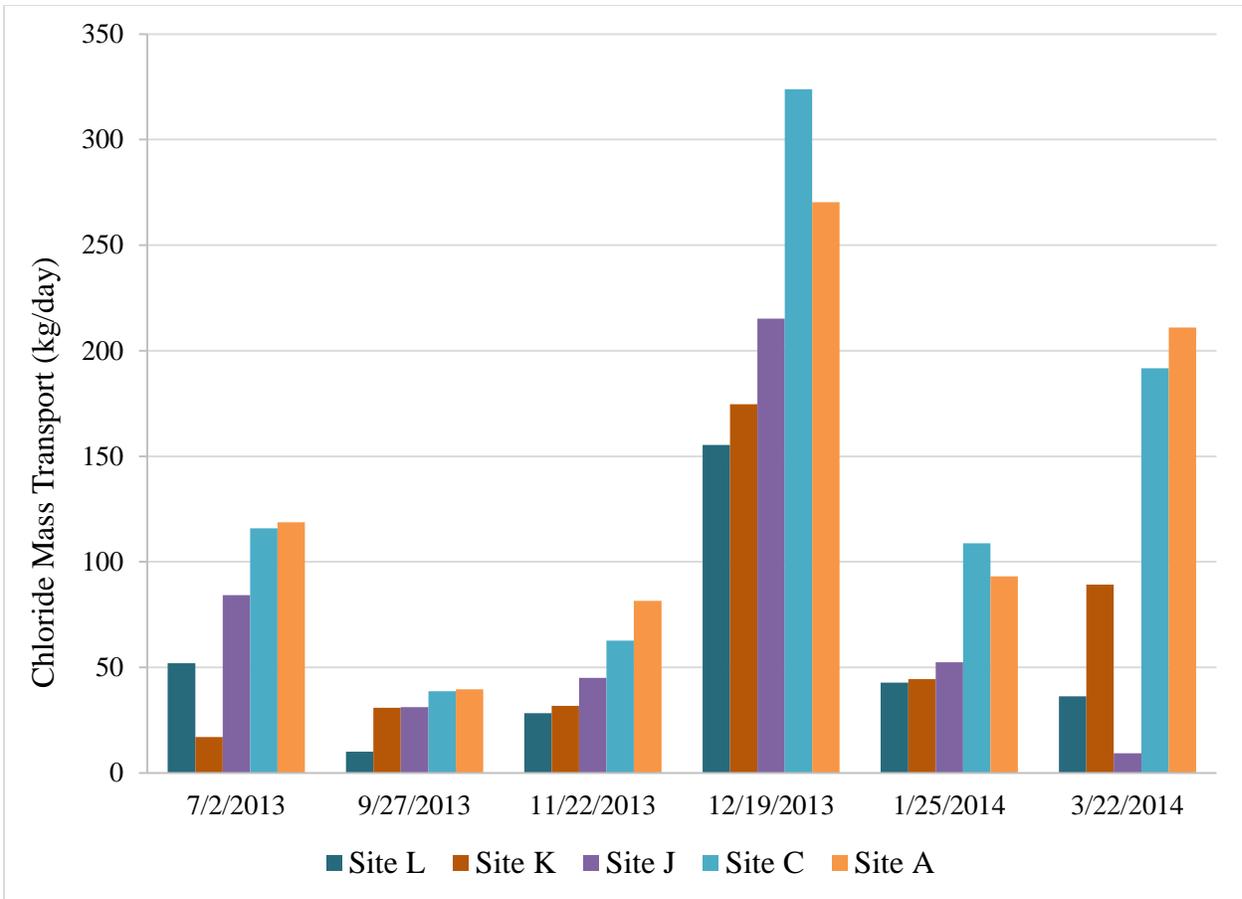


Figure 5.9: Chloride Mass Transport Rate over Time for each Sampling Site along Mill Creek, units of kilograms per day

Mass was illustrated for the Mill Creek samples by finding the mass transport rate, in units of kilograms per day. This was calculated by multiplying the discharge in m^3/s by the chloride concentration in mg/L and then accounting for units to obtain the mass of chloride over time in kg/day . The overall trend seen for chloride mass through Mill Creek is that mass transport rate increases moving downstream, although patterns are fairly erratic for some sampling days. This is probably due to either experimental variation or uneven chloride movement along Mill Creek. For example, certain tributaries may carry more chloride loading into Mill Creek than others, or certain locations may receive additional inputs from non-point source runoff that is inconsistent along the length of the creek, while other points may serve as

a sink of chloride in some conditions. The range of chloride mass transport rates is between 9.3 and 324 kg/day. Figure 5.9 shows that there is additional mass accumulating along Mill Creek after it leaves the CSW. If the only chloride input was from the CSW then mass transport would either stay the same along Mill Creek if there was no added mass, or it would decrease due to mass loss as it flowed through the creek. Because there is no data for the other inputs to Mill Creek, the potential loss of mass along the creek cannot be measured, only the net addition of mass as flow accumulates through each sampling location. Mass transport is the highest for the 12/19/13 event and the 3/22/14 event, which occur during the Salt Application period. This would be expected because there may be additional chloride from road de-icing salts entering Mill Creek from tributaries or groundwater during this period.

Mass transport of chloride through Mill Creek was compared with the mass of chloride flowing through the Villanova CSW. Two CSW baseflow events coincided with Mill Creek sampling events, and these were used to track mass transport from the Inlet to the Outlet, and then through each of the Mill Creek sampling locations (L through A).

The first baseflow event was technically two separate baseflow periods divided by a short storm event of 0.22 inches. The first baseflow occurred between 1/17/14 and 1/27/14 with a duration of 227 hours and the second occurred between 1/30/14 and 2/3/14 with a duration of 86 hours. The combined baseflow period is from 1/17/14 until 2/3/14 with a duration of 314 hours. The Mill Creek was sampled on 1/25/14 and the Villanova CSW was sampled on 1/30/14, with the storm event occurring on 1/27/14, between sampling events. Because the storm was so small, it was ignored in estimating the mass transport rate from the CSW through Mill Creek during this time, and the baseflow events were combined into one. At the Villanova CSW the average flow at the inlet was 0.0072 m³/s and the average flow at the outlet was

0.0026 m³/s with a total inlet volume of 8,490 m³ and outlet volume of 2,640 m³. Figure 5.10 combines the discharge and the concentration graphs for the CSW and Mill Creek samples.

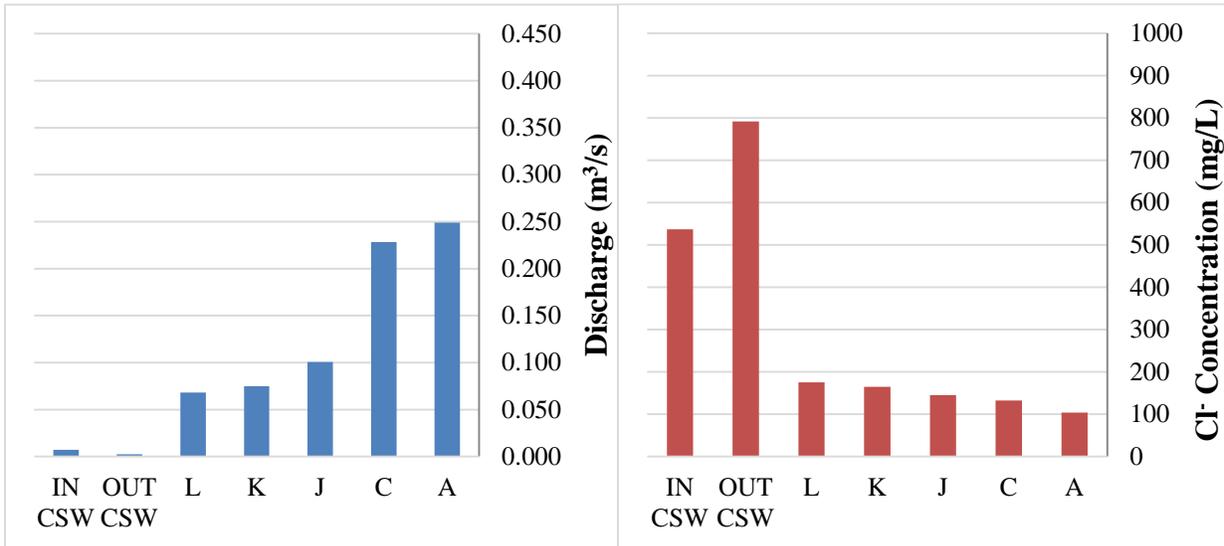


Figure 5.10: Discharge and Chloride Concentration through the CSW and Mill Creek during a January 2014 Baseflow Event: On the left: Discharge at the CSW Inlet, CSW Outlet, and Mill Creek Sampling Locations (L-A) in units of m³/s; On the right: Chloride Concentration at the CSW Inlet, CSW Outlet, and Mill Creek Sampling Locations (L-A) in units of mg/L

The discharge from the inlet to the outlet of the CSW decreases, showing retention of flow within the CSW. Flowrates in Mill Creek are orders of magnitude greater than those in the CSW, starting at 0.068 m³/s and increase going downstream with a maximum of 0.25 m³/s. Chloride concentrations, however, are highest in the CSW. The concentration increases from the inlet to the outlet, from 536 mg/L to 791 mg/L. Concentrations that follow through Mill Creek are much lower, ranging from 175 mg/L to 104 mg/L and slowly decreasing moving downstream.

Using each of these data sets, discharge was multiplied by the chloride concentration in order to determine the mass transport rate, in kg chloride/day. Figure 5.11 shows the mass

transport rate at the CSW inlet and outlet as well as the Mill Creek sampling locations (L-A) during a January 2014 baseflow event.

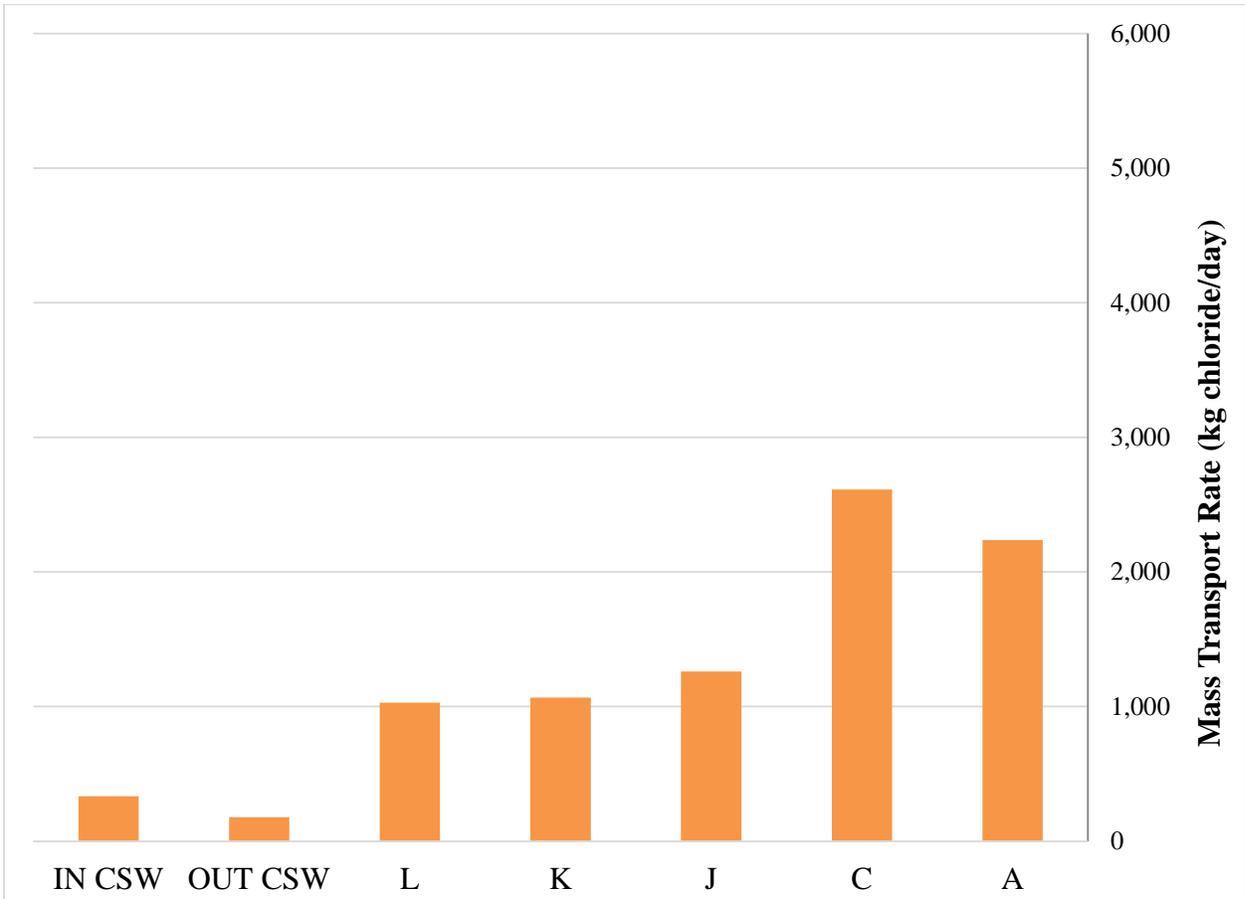


Figure 5.11: Chloride Mass Transport for the CSW Inlet and Outlet as well as each Sampling Site along Mill Creek (L-A) during a January Baseflow Event; in units of kg chloride/day; CSW locations were sampled on 1/30/14 and the Mill Creek locations were sampled on 1/25/14

Mass transport rate decreases from the CSW inlet to the outlet, from 334 kg chloride/day to 178 kg chloride/day, showing a sink of chloride mass in the CSW. Mass transport rates are higher in Mill Creek, ranging from 1,030 kg chloride/day to 2,610 kg chloride/day and the general trend is that mass transport rates increase moving downstream. This would imply that for this specific baseflow event, substantial masses of chloride are being added to Mill Creek after the Villanova CSW.

The second baseflow event occurred between 3/22/14 and 3/29/14, with a duration of 154.67 hours. At the Villanova CSW the average flow at the Inlet was 0.0035 m³/s and the average flow at the Outlet was 0.0043 m³/s with a total Inlet volume of 1,975 m³ and Outlet volume of 2,576 m³. The Mill Creek samples were taken on 3/22/14 and the Villanova CSW was sampled on 3/24/14. Because this was a baseflow event, it was assumed that the concentrations leaving the CSW during that period would be fairly consistent over the entire baseflow period, therefore were usable in order to make a comparison to Mill Creek for the 3/22/14 sampling date.

Figure 5.12 combines the discharge and the concentration graphs for the CSW and Mill Creek samples.

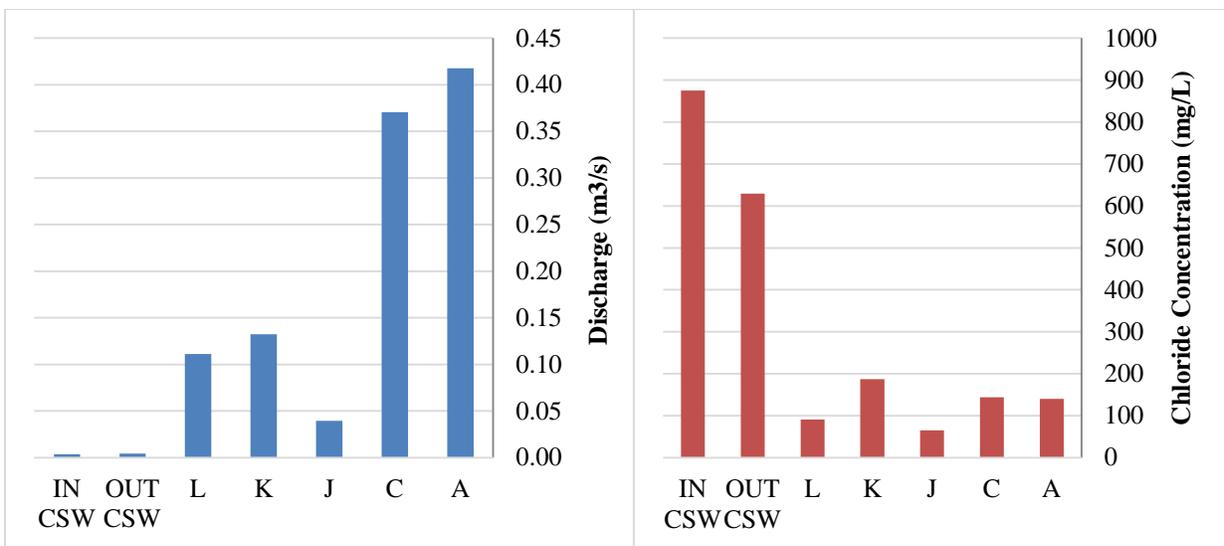


Figure 5.12: Discharge and Chloride Concentration through the CSW and Mill Creek during a March 2014 Baseflow Event: On the left: Discharge at the CSW Inlet, CSW Outlet, and Mill Creek Sampling Locations (L-A) in units of m³/s; On the right: Chloride Concentration at the CSW Inlet, CSW Outlet, and Mill Creek Sampling Locations (L-A) in units of mg/L

The CSW discharges (Inlet = $0.0035 \text{ m}^3/\text{s}$ and Outlet = $0.0043 \text{ m}^3/\text{s}$) are similar and small compared to those along Mill Creek (L = $0.111 \text{ m}^3/\text{s}$, K = $0.132 \text{ m}^3/\text{s}$, J = $0.04 \text{ m}^3/\text{s}$, C = $0.371 \text{ m}^3/\text{s}$, A = $0.418 \text{ m}^3/\text{s}$), and discharge increases along Mill Creek as expected. One interesting point of data is the discharge at location J, which is $0.04 \text{ m}^3/\text{s}$, which is low and does not fit the general pattern of most other sampling days. This may occur as an error rather than an observed phenomenon. Chloride concentration follows an opposite trend than discharge, with concentrations high at the CSW (Inlet = 875 mg/L and Outlet = 630 mg/L) and low along Mill Creek (L = 91 mg/L , K = 187 mg/L , J = 65 mg/L , C = 144 mg/L , A = 140 mg/L). On this day, outlet concentrations in the CSW were lower than the inlet, a different pattern than in the January baseflow event above. Concentrations in Mill Creek on this day do not follow the slow gradual decreasing trend as seen on other sampling days, but rather has a more irregular pattern. Figure 5.13 presents the mass transport rate through the Villanova CSW and then through Mill Creek, which was calculated by multiplying the discharge by the chloride concentration and then accounting for units to obtain kg/day.

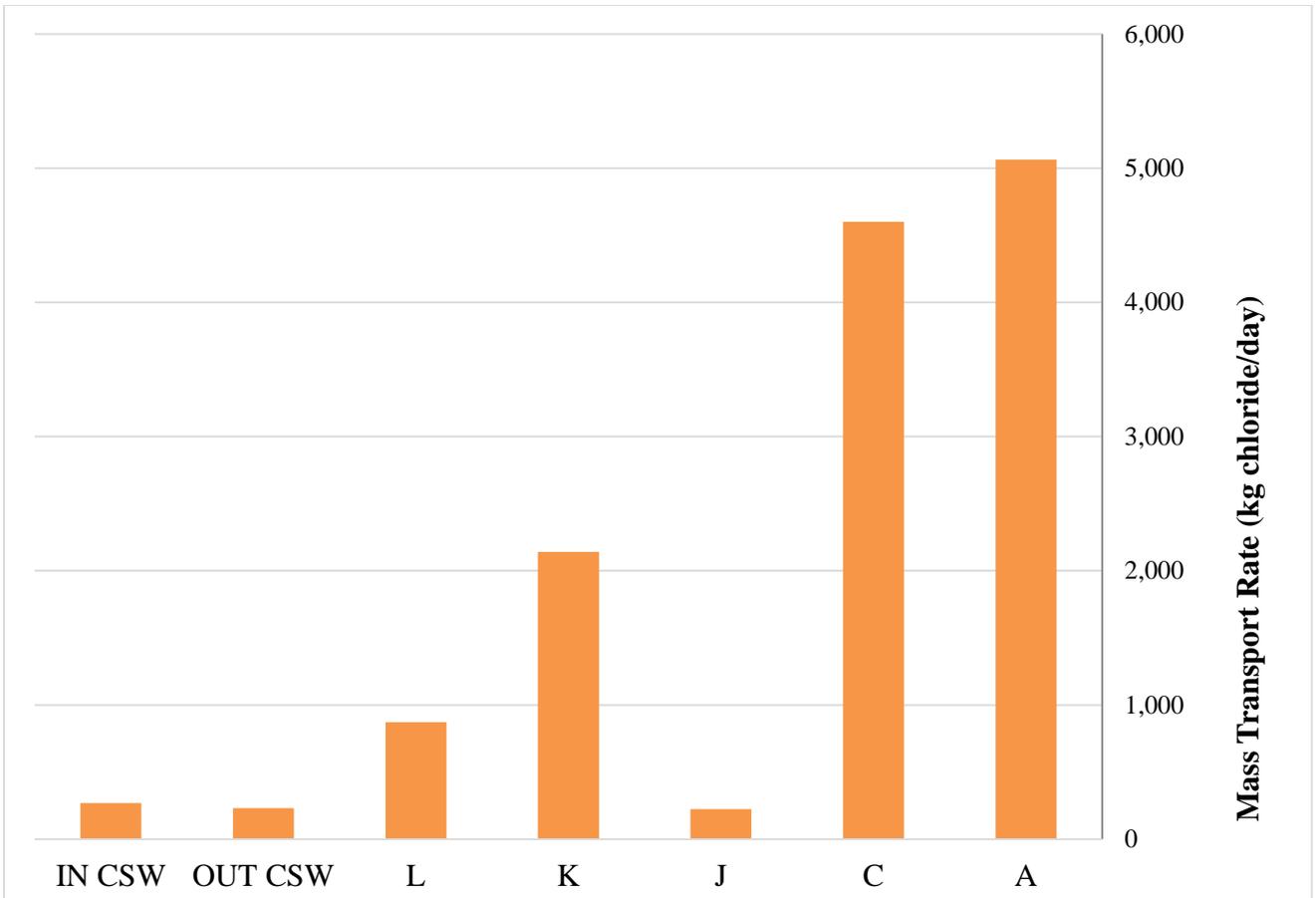


Figure 5.13: Chloride Mass Transport for the CSW Inlet and Outlet as well as each Sampling Site along Mill Creek (L-A) during a March Baseflow Event; in units of kg chloride/day; CSW locations were sampled on 3/22/14 and the Mill Creek locations were sampled on 3/24/14

Mass transport rate decreases only slightly from the CSW inlet to the outlet, from 268 kg chloride/day to 231 kg chloride/day, not significant enough to show a sink or release of chloride mass through the CSW. Mass transport rates are higher in Mill Creek, ranging from 872 kg chloride/day to 5,060 kg chloride/day and the general trend is that mass transport rates increases moving downstream, although the mass transport at location J may be an error due to the low discharge rate. This would again follow the same pattern as the January baseflow event, showing that substantial masses of chloride are being added to Mill Creek after the Villanova CSW, meaning that i) the Villanova CSW is not the only source of chloride mass to Mill Creek

and that ii) it is likely that the tributaries, runoff, or groundwater sources of flow may be adding that mass of chloride at further points along the creek.

5.3.2 Mill Creek Storm Mass Transport Comparison

In addition to baseflow sampling events, several dates which occurred during storm events were observed. Because there was no date when a Villanova CSW storm sampling event coincided with a Mill Creek sampling event, it was not possible to directly compare mass transport rates between the CSW and Mill Creek, however, the Mill Creek data was analyzed separately from the CSW data, with available CSW data shown for comparison when available. Figure 5.14 presents discharge data for the three storms in the study period.

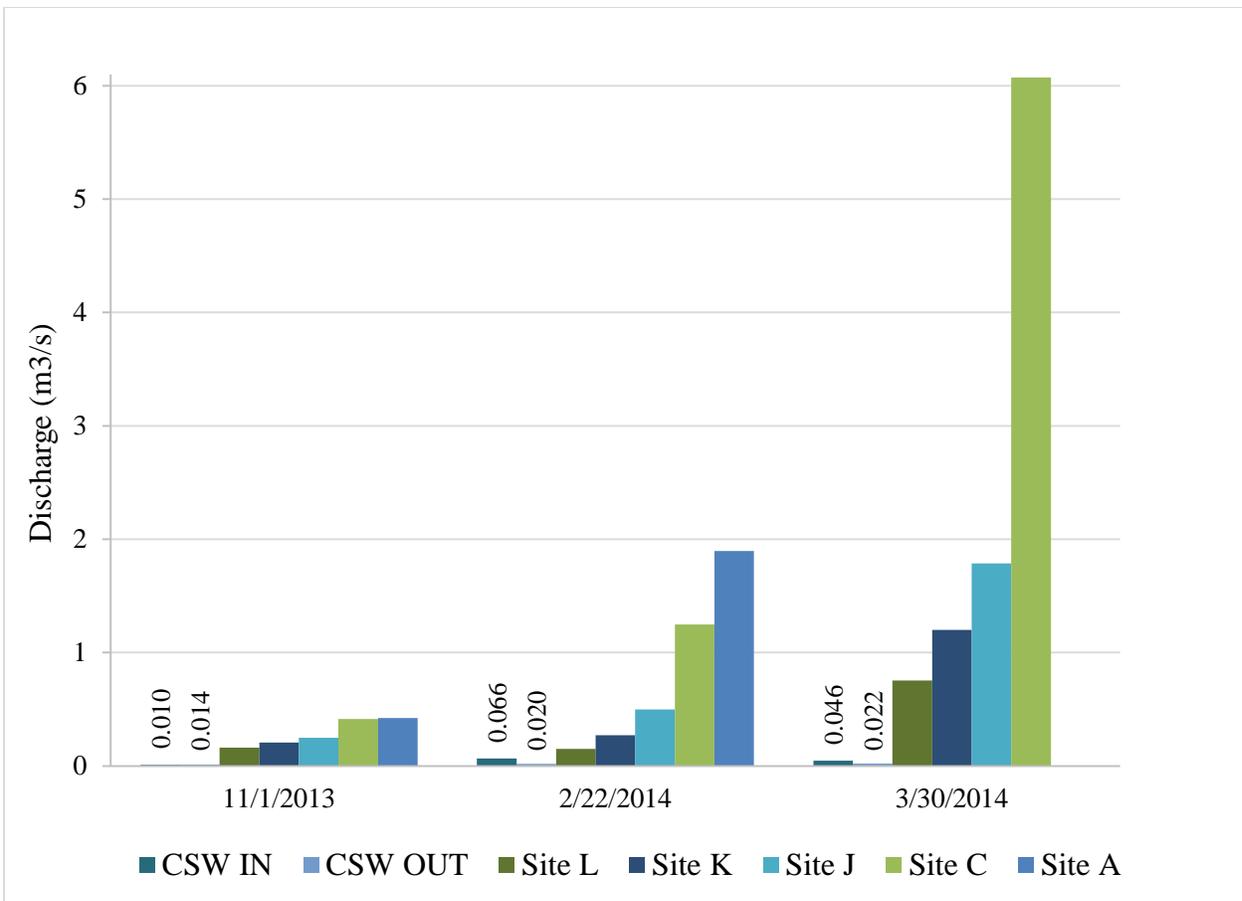


Figure 5.14: Discharge over Time for each Sampling Site along Mill Creek as well as Inlet and Outlet of the CSW during Storm Events; going downstream from left to right (Inlet through A)

The storm events that were sampled at Mill Creek locations occurred on 11/1/13 (event length = 12.17 hours, rainfall = 0.4 inches), 2/22/13 (event length = 75.08 hours, rainfall = 0.59 inches), and 3/30/13 (event length = 116.58 hours, rainfall = 3.01 inches). Discharge is graphed for all of the Mill Creek sites and the Villanova CSW discharge was also available so that is graphed as well. The CSW discharge rates are relatively low compared to Mill Creek rates so that they are not always visible on the graph and for this reason, the discharge rates lie above those data points. Discharge for the CSW ranged from 0.010 m³/s to 0.066 m³/s. For the 11/1/13 storm, inflow and outflow in the CSW were similar, but on 2/22/14 and 3/3/14, the outflow was substantially lower than the inflow. Discharges along Mill Creek were orders of magnitude

higher, ranging from 0.152 m³/s to 6.07 m³/s. During these storm events, discharge increased over the length of Mill Creek, however, much more steeply than was observed over baseflow events. This is expected, because storms carry flow not just from tributaries and groundwater, but also from substantial flow from stormwater runoff. Discharge rates in Mill Creek correlate with the rainfall amounts, also as expected. 11/1/13 had the lowest discharge with only 0.4” of rainfall, while on 3/30/14 it rained 3.01” and discharge was the highest. This is also expected, because higher amounts of rainfall would result in higher volumes of stormwater runoff that would increase flows along Mill Creek.

In comparing the chloride concentrations for these dates, there was no available chloride data for the storm dates in the study period, except for the 2/22/14 storm. The Villanova CSW was sampled on 2/24/14, within the event length of this storm event. Therefore the CSW chloride concentrations for this date only were graphed in order to make an individual comparison for that date. Figure 5.15 depicts the chloride data for all three storm events over the study period, including the CSW data from 2/22/14.

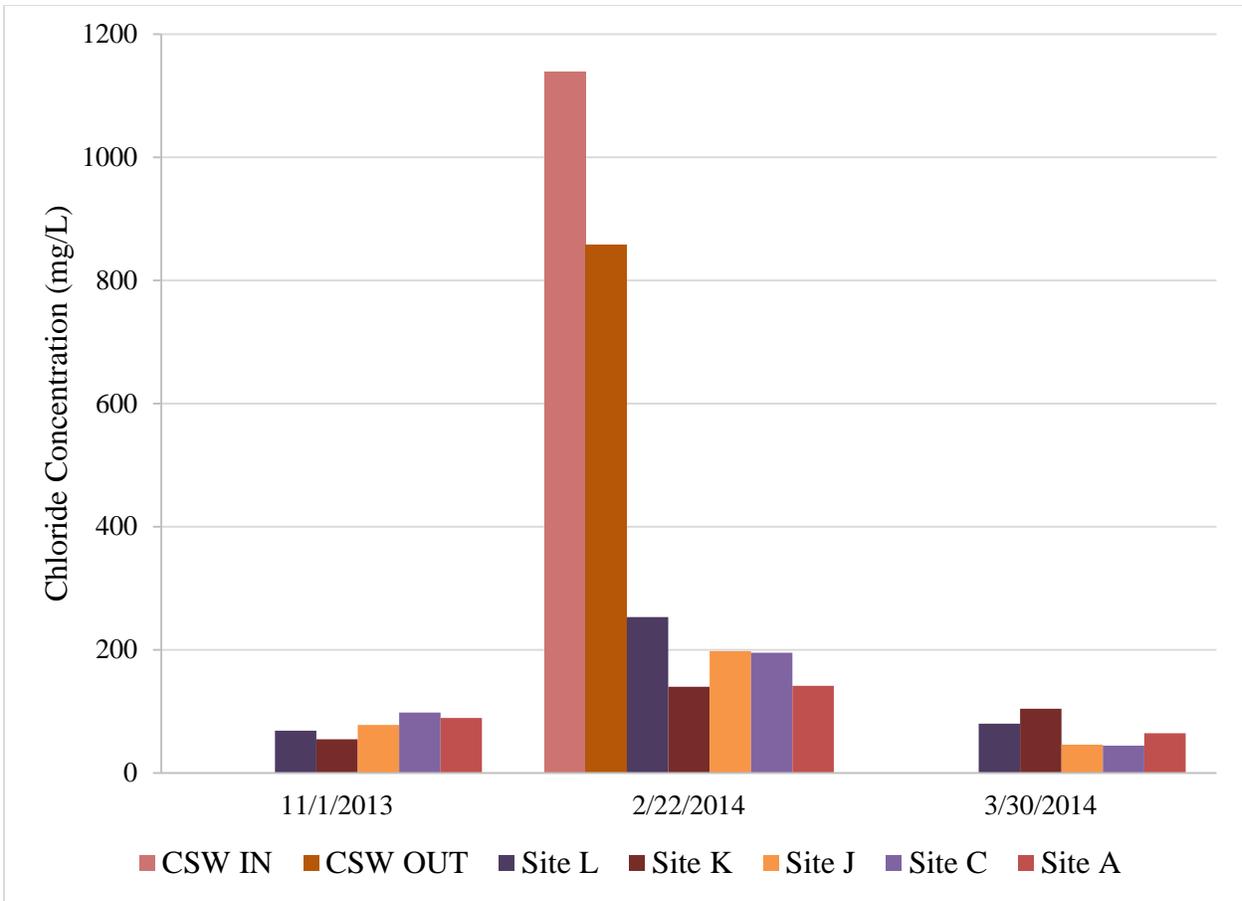


Figure 5.15: Chloride Concentration over Time for each Sampling Site along Mill Creek, including the Inlet and the Outlet at the CSW for the 2/22/14 storm event only; no CSW data was available for 11/1/13 or 3/30/14; units in mg/L

Chloride concentrations at the Villanova CSW are much higher than what is seen in Mill Creek for the 2/22/14 storm event. The CSW inlet concentration on 2/22/14 was 1,139 mg/L and the outlet concentration was lower, 859 mg/L. The Mill Creek chloride concentrations for all storm dates ranged from 44.2 mg/L to 253 mg/L and each storm date did not follow any particular pattern, unlike what was observed for baseflow events. Concentrations fluctuate on each storm date and do not uniformly increase or decrease along the flow path. This is most likely due to the fact that such high volumes of stormwater entering through tributaries and runoff would have varying amounts of chloride and therefore effect each sampling location

differently. With baseflow, there is no stormwater runoff input that would unevenly distribute chloride over Mill Creek. The mass balance calculation will give a better idea of how chloride moves through Mill Creek during a storm event. Figure 5.16 shows the mass transport rates of chloride through Mill Creek. The Villanova CSW mass transport rates for the 2/22/14 storm are also included for individual comparison to that date.

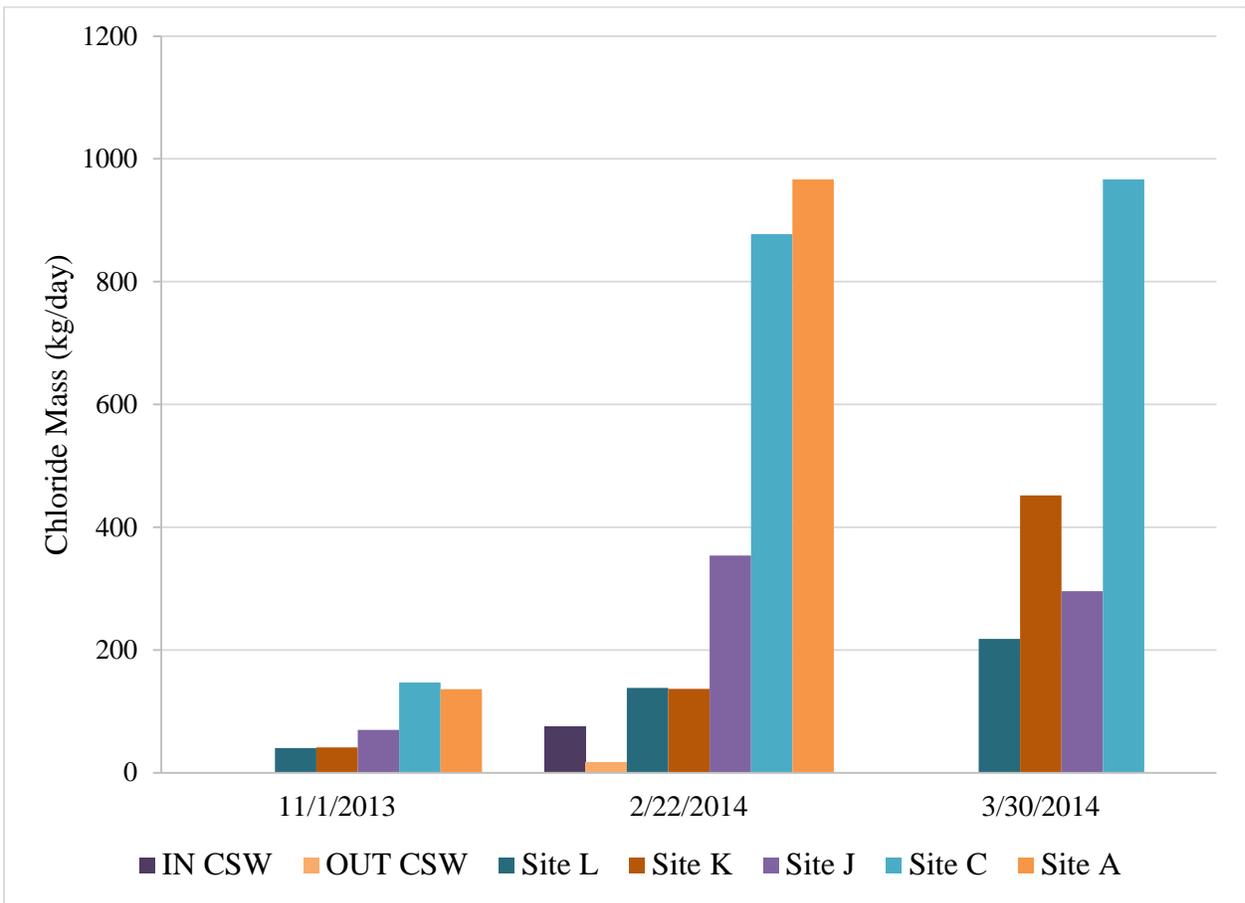


Figure 5.16: Chloride Mass Transport Rate over Time for each Sampling Site along Mill Creek as well as the CSW inlet and outlet for the 2/22/14 Storm Event; units of kilograms per day

Mass transport rates through Mill Creek vary by orders of magnitude from storm to storm and even within the same storm event. On 11/1/13, a 0.4” storm event, chloride mass transport was low, ranging from 40.4 kg chloride/day to 147 kg chloride/day, and the mass transport

increased smoothly moving downstream. Because 11/1/13 lies in the Non-Salt Application period, it makes sense that a smaller mass of chloride is being transported through the Mill Creek on this day than on the other sampling days which occur during the Salt Application period. The 2/2/14 storm was a 0.59” event and the CSW data was available to compare on this day. The CSW inlet has a mass transport rate of 75.3 kg chloride/day while the outlet had a mass transport rate of 17.0 kg chloride/day, suggesting that there is considerable retention of chloride in the CSW for that sampling day. Mill Creek mass transport rates are higher than both inlet and outlet ranging from 137 kg chloride/day to 966 kg chloride/day and there is a general increase in chloride mass moving downstream, with a steep increase in mass transport at the end of the creek. On 3/30/14, a 3.01” storm, there was a more uneven pattern, although generally mass transport rates increased moving downstream as well, ranging from 218 kg chloride/day to 967 kg chloride/day. These storm events are evidence that, just as the baseflow data suggested, there is a considerable amount of chloride mass entering the Mill Creek after the Villanova CSW.

CHAPTER VI: CONCLUSIONS

On Chloride Concentration and EPA Criteria:

High spikes in chloride concentrations were observed during the Salt Application period, between December and May, during both storm and baseflow sampling events, and much lower concentrations overall were observed during the Non-Salt Application period. This phenomena is linked to the presence of thousands of kilograms of road de-icing salts (39,800 kg in 2013, 76,000 kg in 2014, and 34,000 in 2015) on the drainage area of the Villanova CSW during the winter months, which wash out during storm events in the Salt Application period. The median

concentrations during the Salt Application period were 569 mg/L for the inlet and 530 mg/L for the outlet, while the median concentrations during the Non-Salt Application period were 160 mg/L for the inlet and 126 mg/L for the outlet. Maximum concentrations during the Salt Application period generally reached levels in the 1,000-2,000 mg/L range, with the highest concentration observed at the CSW outlet during a baseflow event being 3,343 mg/L in January of 2015. The Non-Salt Application period maximum was only 515 mg/L. This is a significant difference, and shows that the majority of high concentrations occur during the Salt Application period, and a general trend of higher concentrations during that period.

Ranges of chloride concentration throughout the entire CSW (from the inlet, through meanders 1, 2, and 3, and to the outlet) were oftentimes extremely variable for a single storm or baseflow event during the Salt Application period, when concentrations were the highest. Ranges could be anywhere from 500 mg/L to 1,500 mg/L, with the greatest range occurring on the day with the 3,343 mg/L maximum concentration, when the range was about 2,800 mg/L. Ranges in concentration varied in the Non-Salt Application period as well, but not to the same extent because concentrations were generally so much lower. This phenomena occurred during both baseflow and storm sampling events, so it can be inferred that concentrations vary greatly during the Salt Application season during all types of flow with no observable patterns.

Storm event concentrations had a specific repeatable pattern through all four years. Concentrations were the highest early on in the Salt Application period, but concentrations fluctuated from high to low values sharply during that period, which can likely be attributed to differing intensities of storm events, fluctuating flowrates and volumes, and unevenness of salt application over time and space. Dilution effects and the large ranges of observed concentrations throughout the CSW itself from inlet to outlet may also have contributed to these varying

concentrations. For storm events, these high concentrations observed in the Salt Application period (IN median = 709 mg/L, OUT median = 486 mg/L) dropped sharply into the Non-Salt Application period, where concentrations were the lowest of the sampling period (IN median = 68 mg/L, OUT median = 63 mg/L).

This same pattern does not occur for baseflow sampling event concentrations. For baseflow events, concentrations were also the highest during the Salt Application period (IN median = 536 mg/L, OUT median = 588 mg/L) but generally concentrations did not drop sharply off into the Non-Salt Application period (IN median = 202 mg/L, OUT median = 213 mg/L) as they did for storm events. Concentrations remained elevated through the summer and slowly decreased over time. The Non-Salt Application baseflow concentrations rarely reached the low levels that storm events achieved and the inlet remained elevated as well as the outlet.

Baseflows for all seasons overall (IN median = 264 mg/L, OUT median = 280 mg/L) had higher chloride concentrations than did storm events (IN median = 90 mg/L, OUT median = 105 mg/L), as was also observed by Wadzuk (2010), and only two baseflow sampling events had concentrations below 100 mg/L. Both storms and baseflow exhibited high concentrations above 1,000 mg/L, but only storms approached non-detect levels of chloride (< 2 mg/L).

Because inlet baseflow concentrations were observed to be as high as the outlet in the Non-Salt Application period, this implies that over the summer months there is additional chloride entering the CSW from a source that is not from impervious surface runoff. This might mean that chloride is stored within the CSW's drainage area during the Salt Application period and then released over long periods of time downstream to the CSW (as suggested by Demers and Sage 1990, Brown and Scorca 1995, Gardner and Royer 2010, Sadowski 2002, Kaushal et al. 2005, Corsi et al. 2014). A hypothesis for these elevated chloride concentrations is that

groundwater flow enters the CSW and this carries loading of chloride through the summer from the campus' upstream contaminated groundwater. The travel time necessary for this groundwater flow to reach the CSW may be the explanation for the delay in observation of heightened chloride lasting through summer months. Two infiltration trenches and two pervious pavement sites on Villanova's campus infiltrate water from impervious surfaces into the groundwater, and these systems may be contributing to heightened summer baseflow chloride concentrations if groundwater does indeed enter the CSW.

Because baseflow values remain elevated, this is a problem in terms of the EPA water quality criteria. Only 33% of baseflow events were below both chronic (230 mg/L) and acute (860 mg/L) EPA criteria and 12% exceeded the acute criterion. Due to dilution, storms do much better, below both criteria 77% of the time and exceeding the acute criterion only 10% of the time. Baseflow conditions account for a majority of the year, and if interflow events, the time between a defined storm and a defined baseflow when flows are still elevated from the storm event, are counted as baseflow events, baseflow accounts for 89% of the year and storms account for 11%. On this assumption, it can be roughly estimated that the Villanova CSW meets both criteria only 38% of the year, exceeds the chronic criterion 62% of the year, and exceeds the acute criterion 12% of the year. Again, this serves as only an estimate of the CSW's performance, since this study was unable to assess the precise EPA criteria definitions, and can be used as a benchmark estimate.

On Chloride/TDS/Conductivity Correlations:

Chloride/TDS/conductivity correlations were created between each parameter for both the Villanova CSW and the Villanova BTI over the entire 4 year study period. All of the correlations were linear and had a high degree of accuracy. The chloride vs conductivity and

chloride vs TDS correlations were more scattered and less reliable than the TDS versus conductivity correlation, but this was expected because TDS and conductivity ($TDS = k * conductivity$) are more directly related than chloride and conductivity or chloride and TDS. TDS versus conductivity correlations were similar for the BTI and CSW overall. In order to make appropriate comparisons, the BTI was separated into surface and subsurface samples, while the CSW data was separated for a low curve and a high curve. The low range correlation at the CSW was taken for samples with a TDS less than 1,000 mg/L and the k constant obtained was 0.64 (mg/L)/(μ S/cm) with an R^2 of 0.9021. The high range correlation included samples with a TDS above 1,000 mg/L and the k constant was 0.54 (mg/L)/(μ S/cm) with an R^2 of 0.9896. The BTI surface sample correlation had a k constant of 0.56 (mg/L)/(μ S/cm) with an R^2 of 0.9908 and the subsurface sample correlation had a k constant of 0.61 (mg/L)/(μ S/cm) with an R^2 of 0.7969. The low R^2 for the subsurface BTI correlation is most likely due to a low range of data and more scatter.

The k constants were all within the range of 0.54-0.64, similar to each other and within the expected range between 0.55 – 0.7 (American Public Health Assoc. 1999). The BTI and CSW correlations were more similar than expected, especially in the case of subsurface samples. Perhaps this similarity is due to comparable soils and road de-icing salt applications for both sites, as the ionic composition of stormwater entering and passing through both the BTI and the CSW are similar as seen in these correlations. The comparison of CSW correlations to the BTI correlations invites further study into the movement of road de-icing salts through soils and into groundwater at both the BTI and the CSW.

On Mass Transport of Chloride within the Villanova CSW:

In order to better understand the fate and transport of chloride in the Villanova CSW, chloride concentration and volume data for 2013 and 2014 were analyzed and used to perform a mass balance of chloride in the CSW from the inlet to the outlet. In 2013, there was 262,800 m³ volume at the inlet and 130,400 m³ at the outlet. In 2014, there was twice as much flow, 431,000 m³ at the inlet and 257,300 m³ at the outlet. This was due to an unusually large amount of volume observed in the Salt Application storms in 2014 (224,900 m³ influent, 123,200 m³ effluent). In 2014 the Philadelphia area experienced 67.6 inches of snow, about three times the average, and this overabundance of precipitation serves as the probable explanation of these large volumes. Overall, it was clear that a large amount of volume is retained within the CSW, 50% in 2013 overall and 40% in 2014 overall.

In estimating the mass moving through the CSW, the biggest challenge was in dealing with a limited chloride concentration data set in conjunction with a large volume dataset. Chloride concentration was only sampled about 1-3 times a month over the study period, and less so during winter months, and therefore it was difficult to determine accurate estimates of a median concentration over each period, especially over the Salt Application period when concentrations fluctuated so much and exhibited such high concentrations. Simple estimations of each year suggest there might be slightly more retention of chloride mass than there is volume retention overall. This is important because it would imply that 1) with volume retentions of ~40-50%, at least 40-50% of the chloride mass overall is being retained through volume reduction, making groundwater infiltration and/or plant uptake likely mechanisms and 2) if there is more chloride retention than volume reduction, there are other mechanisms retaining chloride within the CSW. Mass and volume retention comparisons are as follows: 2013 Salt Application season

– 71% chloride mass retained, 61% volume retained; 2013 Non-Salt Application season – 46% chloride mass retained, 37% volume retained; 2014 Salt Application season – 55% chloride mass retained, 43% volume retained; 2014 Non-Salt Application season – 36% chloride mass retained, 33% volume retained.

Because of the large volume in the Salt Application period of 2014 (224,900 m³ entering and 123,200 m³ leaving) and high chloride concentrations during that period (IN median = 768 mg/L, OUT median = 530 mg/L), the mass calculated for this season in particular was unusually high (172,800 kg influent, 65,300 kg effluent) compared to the range for all other seasons (~2,000-50,000 kg). Masses were estimated over the entire two year period to see if more accuracy could be achieved by increasing the number of data points and expanding the timeline. Estimations were made by separating Salt Application and Non-Salt Application seasons, baseflow and storm events, and using the full two year period all together. Estimated chloride mass was much lower with the two years together (Salt Application separated estimate: IN = 273,100 kg, baseflow/storm separated estimate: IN = 117,900 kg, full two year period together estimate: IN = 157,200 kg) than when they were calculated separately (separate seasonal analysis - sum of 2013 and 2014: IN = 319,500 kg). It is hypothesized that the full two year period estimate is the most accurate because no weight is given to any season or flow type, and therefore there is less chance that one specific season is dominating the results. In comparison to road de-icing salt estimates, these mass estimates inflowing to the CSW are close to the 116,200 kg estimated to have been applied to the Villanova campus CSW drainage area in 2013 and 2014 combined (39,800 kg in 2013 and 76,400 in 2014 individually). Because most estimates are significantly higher than this number, it is likely that there is additional input of chloride to the

CSW besides what enters as runoff from impervious surfaces. It is possible that there is groundwater flow carrying chloride mass from upstream that interacts with the CSW.

On Mass Transport of Chloride through Mill Creek:

Chloride concentration and discharge data for five sites along Mill Creek were analyzed as part of the chloride mass balance in order to determine how chloride mass was transported downstream of the Villanova CSW between July 2013 and March 2014. The CSW is the headwaters of the creek and discharge ($0.001\text{-}0.01\text{ m}^3/\text{s}$ during baseflow and $0.1\text{-}0.3\text{ m}^3/\text{s}$ during storms) was low in comparison to Mill Creek discharge ($0.02\text{-}0.5\text{ m}^3/\text{s}$ during baseflow and $0.1\text{-}6.0\text{ m}^3/\text{s}$ during storms), which showed an overall increasing trend with distance from the CSW. An increase in discharge with distance downstream is expected since tributaries, runoff, and groundwater add flow along the creek. Chloride concentrations were the highest in the Villanova CSW and decreased moving downstream Mill Creek (range $30\text{-}300\text{ mg/L}$ during storms and baseflows). As shown, chloride concentrations can be in the $1,000\text{-}2,000\text{ mg/L}$ range in the winter. Decreasing concentrations along Mill Creek were expected due to dilution; as more volume enters Mill Creek, the more the chloride concentration would decrease. However, the large drop in concentration between the CSW and concentrations seen in Mill Creek was not expected. In some cases chloride concentration dropped from about $1,000\text{ mg/L}$ at the CSW outlet to 200 mg/L at the first Mill Creek location downstream. The difference (1-2 orders of magnitude) in flowrates at the CSW and in Mill Creek contributed greatly to the low concentrations seen in Mill Creek. Furthermore, in the available dataset, on only one sampling day in the Salt Application period did Mill Creek sampling locations exceed 230 mg/L .

In analyzing specific dates when Mill Creek and CSW sampling events occurred on the same day, an increase of chloride mass along Mill Creek was observed. During two baseflow

events and one storm event, mass increased moving downstream, which suggests that a considerable amount of mass is added to Mill Creek after the Villanova CSW. This would mean that the Villanova CSW is not the only source of chloride mass to the Mill Creek, and that it is only a small percentage of the chloride mass moving through Mill Creek.

Field Scale Implications:

Chloride has been shown to have negative effects on the surrounding environment, and current designs of CSWs, while they have numerous other benefits in terms of volume reduction, as well as heavy metal, suspended solids, and nutrient removal, may not have any benefits in removal of chloride, which may enter stormwater runoff with the use of de-icing salts applied in winter months. In light of this evidence, this study aimed to determine the effects, if any, the Villanova CSW may have on the surrounding watershed in terms of chloride.

Analysis of the past four years of data show patterns of elevated chloride concentrations following the annual road de-icing salt usage on the campus' impervious surfaces, and a large amount of chloride retention within the CSW. This retention of chloride may be resulting in the contamination of groundwater with chloride in conjunction with substantial volume reduction through infiltration in the CSW. Heightened baseflow concentrations through the summer months point towards possible groundwater interaction that may release slow-moving chloride from upstream drainage areas into the CSW late into the summer months. It is possible that other infiltrating SCMs on campus may be contributing to this chloride loading.

In terms of concentration, effluent volume released from the CSW oftentimes exceeds 230 mg/L and annually exceeds 860 mg/L. However, although the levels reached in the CSW effluent are high, concentrations in Mill Creek rarely come near 230 mg/L, and only one Mill Creek baseflow sampling event exceeded 230 mg/L during the study period. An observed mass increase along Mill Creek signals that there is additional mass entering the creek after the Villanova CSW, and the effect that the CSW has on Mill Creek in terms of chloride mass may be small compared to other impervious areas surrounding the creek.

In order to better understand the movement of chloride in the Villanova CSW, it is recommended that further research focus on movement of chlorides through the profile of the CSW and on upstream groundwater chloride concentrations. Studying chloride concentration as it moves vertically through soil and possibly to the groundwater table will give better evidence towards whether or not there is substantial flow of chloride to the groundwater table, and determining what the upstream inputs to the CSW may be will help fill in the missing pieces to determine if there is truly groundwater interaction at the CSW.

Because the Villanova CSW is the headwaters of a high priority stream, Mill Creek, determining the effects of chloride on the downstream waters is one part in understanding the effect that the Villanova campus has on the surrounding environment, even though the CSW and its drainage area are only one small region that contributes runoff and chloride to Mill Creek. While it is a small system, the contributions that the CSW makes to chloride loading in the watershed is still important in terms of looking to the future of stormwater control measures and green infrastructure. Because the CSW collects tens of thousands of kilograms of chloride applied to the CSW drainage area each year in stormwater runoff, with a large portion flowing through surface waters, and the possibility that a large portion of chloride loading enters groundwater, there is significant effect on the surrounding environment. However, pre-CSW conditions may have been no better. Improved designs and unique solutions need to be engineered in order to mitigate the effects of chloride on the environment in the future. Because there are currently no widely-used, practical, and cost-effective methods of removing chloride from contaminated waters, reduction of chloride loading to impervious surfaces in winter months would be the most effective way to reduce chloride loading in the Villanova CSW.

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APPENDIX

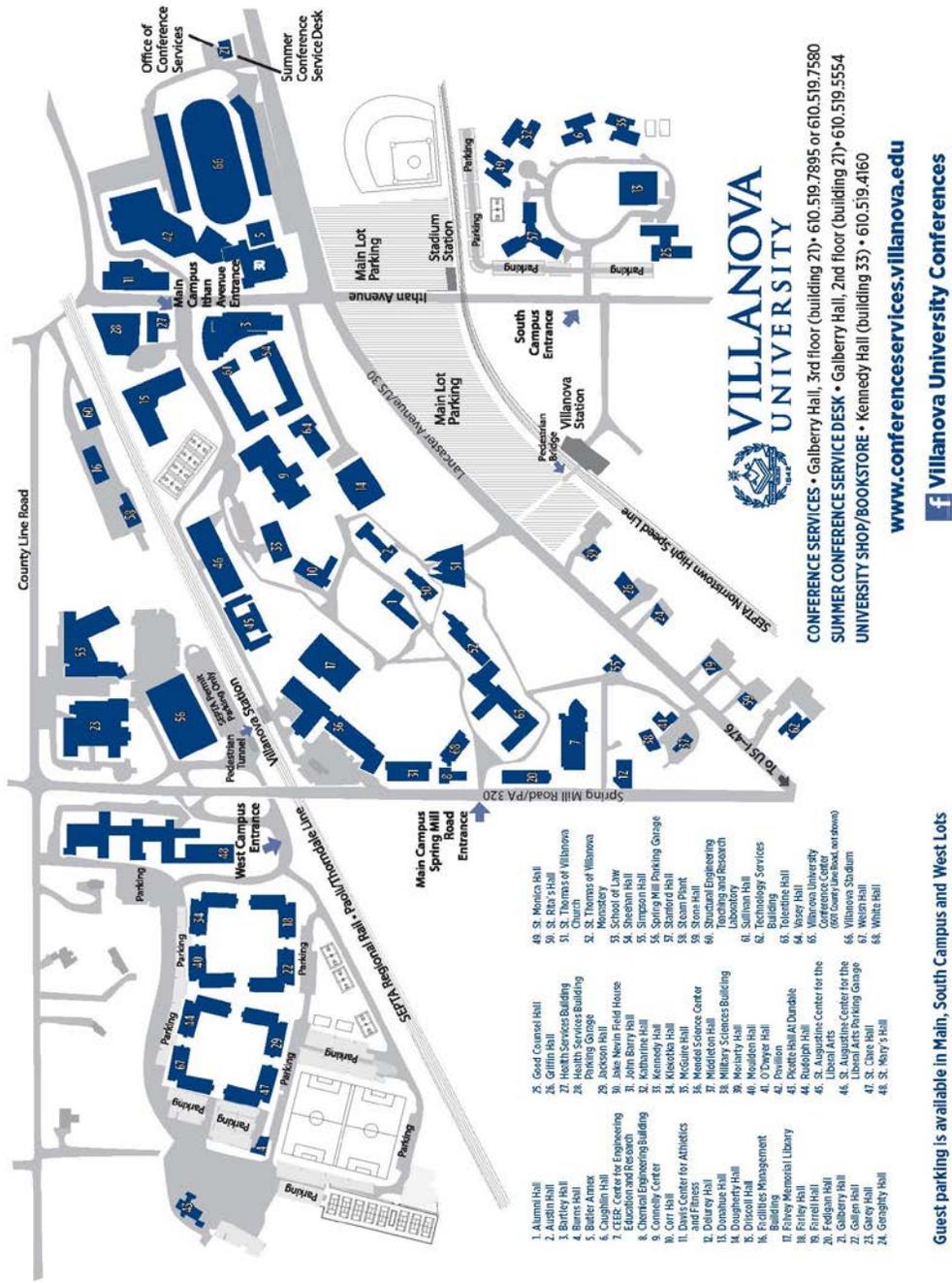


Figure A1: Villanova University Campus Map; Villanova CSW Superimposed

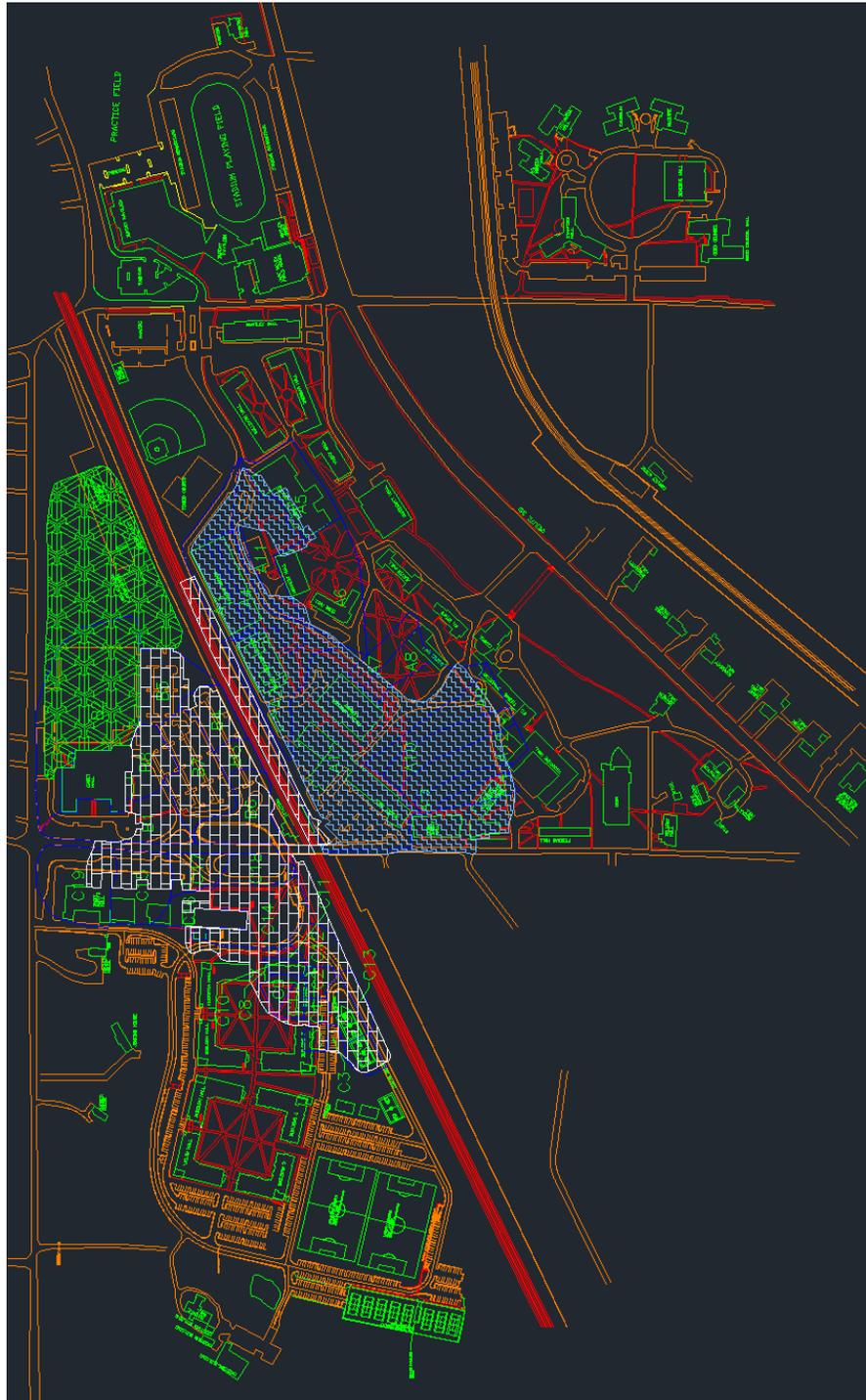


Figure A2: Villanova Campus AutoCAD Drawing of Drainage Areas to the CSW within a full drawing of Villanova campus drainage areas; Credit James Pittman 2011; Main (small blue pattern), West (light blue brick pattern), and Wetland (etched green pattern) drainage areas are shown; Villanova CSW superimposed

Table A1: Salt Usage at Villanova University for the Years 2013-2015; divided into purchases for each year

Date	Supplier	Type	kg purchased	Composition	Cl- (kg)
04/08/15	Chem Equip Labs	Bulk Deicing Salt WILM	20,865	NaCl	12,519
03/16/15	Chem Equip Labs	Deicing Salt	41,730	NaCl	25,038
03/06/15	Chem Equip Labs	Frost Bite Ice Melt	20,003	NaCl	12,002
01/23/15	Chem Equip Labs	Deicing Salt	39,009	NaCl	23,405
01/14/15	Chem Equip Labs	Deicing Salt	40,823	NaCl	24,494
01/12/15	Chem Equip Labs	Deicing Salt	39,916	NaCl	23,950
SUM 2015			202,346		121,408
03/07/14	Peters Chemical Co	Calcium Chloride	19,958	CaCl ₂	12,773
02/28/14	OceanPort, LLC	Chilean Rock	43,454	NaCl	26,072
02/14/14	OceanPort, LLC	Deicing Salt	45,731	NaCl	27,439
02/11/14	OceanPort, LLC	Deicing Salt	66,987	NaCl	40,192
01/24/14	OceanPort, LLC	Chilean Rock	66,107	NaCl	39,664
01/14/14	OceanPort, LLC	Deicing Salt	64,002	NaCl	38,401
12/23/13	Peters Chemical Co	Calcium Chloride	19,958	CaCl ₂	12,773
12/19/13	OceanPort, LLC	Deicing Salt	15,000	NaCl	9,000
12/18/13	OceanPort, LLC	Chilean Rock	46,285	NaCl	27,771
12/17/13	OceanPort, LLC	Chilean Rock	21,246	NaCl	12,748
12/13/13	OceanPort, LLC	Chilean Rock	43,391	NaCl	26,034
SUM 2014			452,118		272,867
02/18/13	Cargill	Deicer Salt	21,664	NaCl	12,998
02/15/13	Cargill	Deicer Salt	21,074	NaCl	12,644
02/15/13	Peters Chemical Co	Calcium Chloride	4,354	CaCl ₂	2,787
02/06/13	Cargill	Deicer Salt	61,670	NaCl	37,002
02/05/13	Peters Chemical Co	CMA	5,000	CaMg ₂ (CH ₃ COO) ₆	-
02/05/13	Peters Chemical Co	Calcium Chloride	20,321	CaCl ₂	13,005
02/01/13	Peters Chemical Co	CMA	5,000	CaMg ₂ (CH ₃ COO) ₆	-
01/28/13	Peters Chemical Co	Calcium Chloride	20,321	CaCl ₂	13,005
01/25/13	Cargill	Deicer Salt	41,277	NaCl	24,766
01/07/13	Cargill	Deicer Salt	43,109	NaCl	25,866
SUM 2013			243,791		142,074

Table A2: CSW 2012 Baseflow Chloride Concentrations for Salt Application and Non-Salt Application Seasons; Average, Median, and Standard Deviation included

DATE	IN 1 Cl ⁻ (mg/L)	IN 2 Cl ⁻ (mg/L)	IN AVG Cl ⁻ (mg/L)	OUT 1 Cl ⁻ (mg/L)	OUT 2 Cl ⁻ (mg/L)	OUT AVG Cl ⁻ (mg/L)
12/13/2011	330	362	346	323	332	328
2/23/2012	565	697	631	687	558	622
3/28/2012	218	211	214	232	232	232
4/12/2012	1513	1885	1699	1901	1773	1837
5/21/2012	122	111	116	238	226	232
Salt Application Period Median			346			328
Salt Application Period Average			601			650
Salt Application Period Stdev			644			683
6/20/2012	270	269	269	298	332	315
7/11/2012	163	157	160	232	224	228
8/21/2012	158	186	172	98	98	98
9/11/2012	259	262	260	80	80	80
10/15/2012	198	199	199	225	247	236
Non-Salt Application Period Median			212			191
Non-Salt Application Period Average			199			228
Non-Salt Application Period Stdev			50			100

Table A3: CSW 2012 Storm Chloride Concentrations for Salt Application and Non-Salt Application Seasons; Average, Median, and Standard Deviation included

DATE	IN 1 Cl⁻ (mg/L)	IN 2 Cl⁻ (mg/L)	IN AVG Cl⁻ (mg/L)	OUT 1 Cl⁻ (mg/L)	OUT 2 Cl⁻ (mg/L)	OUT AVG Cl⁻ (mg/L)
2/29/2012	171	165	168	184	177	181
4/23/2012	70	69	69	28	31	30
5/10/2013	14	16	15	8	4	6
Salt Application Period Median			69			72
Salt Application Period Average			84			30
Salt Application Period Stdev			78			95
6/10/2013	24	17	20	71	67	69
7/23/2013	4	5	5	5	5	5
9/21/2013	2	3	3	3	3	3
Non-Salt Application Period Median			5			26
Non-Salt Application Period Average			9			5
Non-Salt Application Period Stdev			10			38

Table A4: CSW 2013 Baseflow Chloride Concentrations for Salt Application and Non-Salt Application Seasons; Average, Median, and Standard Deviation included

DATE	IN 1 Cl ⁻ (mg/L)	IN 2 Cl ⁻ (mg/L)	IN AVG Cl ⁻ (mg/L)	OUT 1 Cl ⁻ (mg/L)	OUT 2 Cl ⁻ (mg/L)	OUT AVG Cl ⁻ (mg/L)
1/24/2013	695	484	589	1045	854	949
2/19/2013	618	629	623	1226	1204	1215
4/8/2013	444	408	426	470	522	496
5/15/2013	370	361	366	356	267	312
Salt Application Period Median			508			723
Salt Application Period Average			501			743
Salt Application Period Stdev			125			413
6/6/2013	270	270	270	178	173	175
7/17/2013	183	270	227	250	241	245
8/21/2013	115	112	113	500	462	481
9/11/2013	177	120	149	302	266	284
10/28/2013	261	260	261	214	212	213
11/14/2013	276	276	276	227	195	211
Non-Salt Application Period Median			244			229
Non-Salt Application Period Average			216			268
Non-Salt Application Period Stdev			69			111

Table A5: CSW 2013 Storm Chloride Concentrations for Salt Application and Non-Salt Application Seasons; Average, Median, and Standard Deviation included

DATE	IN 1 Cl ⁻ (mg/L)	IN 2 Cl ⁻ (mg/L)	IN AVG Cl ⁻ (mg/L)	OUT 1 Cl ⁻ (mg/L)	OUT 2 Cl ⁻ (mg/L)	OUT AVG Cl ⁻ (mg/L)
1/31/2013	650		650	143	154	148
2/11/2013	1354	1339	1347	1518	1538	1528
3/12/2013	176	176	176	81	85	83
3/25/2013		955	955	670	663	667
4/29/2013	114	101	107	95	104	100
5/8/2013	61	73	67	74	88	81
Salt Application Period Median			413			124
Salt Application Period Average			550			434
Salt Application Period Stdev			525			582
6/10/2013	108	106	107	41	38	39
7/23/2013	73	71	72	36	39	38
8/21/2013		51	51	48	49	48
9/21/2013	244	238	241	42	40	41
10/7/2013	120	210	165	88	88	88
Non-Salt Application Period Median			107			41
Non-Salt Application Period Average			127			51
Non-Salt Application Period Stdev			77			21

Table A6: CSW 2014 Baseflow Chloride Concentrations for Salt Application and Non-Salt Application Seasons; Average, Median, and Standard Deviation included

DATE	IN 1 Cl ⁻ (mg/L)	IN 2 Cl ⁻ (mg/L)	IN AVG Cl ⁻ (mg/L)	OUT 1 Cl ⁻ (mg/L)	OUT 2 Cl ⁻ (mg/L)	OUT AVG Cl ⁻ (mg/L)
1/30/2014	347	726	536	890	692	791
3/24/2014	504	1246	875	627	632	630
5/13/2014	452	522	487	479	668	574
Salt Application Period Median			536			630
Salt Application Period Average			633			665
Salt Application Period Stdev			211			113
7/8/2014	298	303	301	270	281	276
7/21/2014	189	215	202	269	277	273
8/6/2014	201	214	208	190	179	185
8/27/2014	139	220	180	123	126	124
9/17/2014	258	277	268	126	126	126
11/4/2014	191	190	190	59	60	59
Non-Salt Application Period Median			205			155
Non-Salt Application Period Average			225			174
Non-Salt Application Period Stdev			48			87

Table A7: CSW 2014 Storm Chloride Concentrations for Salt Application and Non-Salt Application Seasons; Average, Median, and Standard Deviation included

DATE	IN 1 Cl ⁻ (mg/L)	IN 2 Cl ⁻ (mg/L)	IN AVG Cl ⁻ (mg/L)	OUT 1 Cl ⁻ (mg/L)	OUT 2 Cl ⁻ (mg/L)	OUT AVG Cl ⁻ (mg/L)
12/10/2013	1970	1674	1822	734	894	814
1/14/2014	692	844	768	583	478	530
2/24/2014	1145	1134	1139	959	760	859
4/9/2014	388	387	388	246	221	234
4/30/2014			60			152
Salt Application Period Median			768			530
Salt Application Period Average			835			518
Salt Application Period Stdev			684			324
6/26/2014			93			196
7/14/2014			71			40
8/21/2014			52			162
9/26/2014			23			125
10/22/2014			49			58
11/17/2014			56			115
Non-Salt Application Period Median			54			120
Non-Salt Application Period Average			57			116
Non-Salt Application Period Stdev			23			60

Table A8: CSW 2015 Baseflow Chloride Concentrations for Salt Application and Non-Salt Application Seasons; Average, Median, and Standard Deviation included

DATE	IN 1 Cl ⁻ (mg/L)	IN 2 Cl ⁻ (mg/L)	IN AVG Cl ⁻ (mg/L)	OUT 1 Cl ⁻ (mg/L)	OUT 2 Cl ⁻ (mg/L)	OUT AVG Cl ⁻ (mg/L)
1/29/2015	728	1048	888	3361	3325	3343
2/26/2015	1354	1120	1237	1877	1795	1836
3/18/2015	574	564	569	598	578	588
5/6/2015	244	306	275	333	334	334
5/21/2015	150	200	175	285	283	284
Salt Application Period Median			569			588
Salt Application Period Average			629			1277
Salt Application Period Stdev			439			1316
7/6/2015	101	147	124	256	247	252
7/23/2015	526	500	513	524	506	515
8/6/2015	356	370	363	364	340	352
8/13/2015	161	172	166	148	148	148
8/27/2015	175	190	182	188	190	189
9/2/2015	259		259	310		310
9/17/2015	162	168	165	177	181	179
10/7/2015	207	190	198	174	182	178
Non-Salt Application Period Median			190			221
Non-Salt Application Period Average			246			265
Non-Salt Application Period Stdev			131			124

Table A9: CSW 2015 Storm Chloride Concentrations for Salt Application and Non-Salt Application Seasons; Average, Median, and Standard Deviation included

DATE	IN 1 Cl ⁻ (mg/L)	IN 2 Cl ⁻ (mg/L)	IN AVG Cl ⁻ (mg/L)	OUT 1 Cl ⁻ (mg/L)	OUT 2 Cl ⁻ (mg/L)	OUT AVG Cl ⁻ (mg/L)
1/18/2015			910			483
2/2/2015			973			1138
3/11/2015	496	513	505	498	480	489
Salt Application Period Median			910			489
Salt Application Period Average			796			703
Salt Application Period Stdev			254			377
6/1/2015			68			60
6/9/2015	147	160	153			111
7/15/2015			16			190
8/20/2015			39			63
9/10/2015			95			105
10/28/2015			62			48
11/10/2015			87			104
11/19/2015			23			16
Non-Salt Application Period Median			65			84
Non-Salt Application Period Average			68			87
Non-Salt Application Period Stdev			45			53

Table A10: 2013 Salt Application Season Baseflow Events and Total Volumes; Data from December 2012 through June 2013

BF Start	BF End	Duration (hrs)	Total Inflow (m3/s)	Outflow (m3/s)	Inlet Volume (m3)	Outlet Volume (m3)
1/2/2013	1/6/2013	106.08	0.0081	0.0005	3,079	176
2/3/2013	2/8/2013	120.42	0.0079	No Data	3,414	No Data
2/14/2013	2/14/2013	1.17	0.0079	No Data	35	No Data
2/17/2013	2/19/2013	47.58	0.0106	No Data	1,817	No Data
2/22/2013	2/23/2013	8.83	0.0011	0.0045	35	145
2/24/2013	2/26/2013	54.42	0.0029	0.0026	566	519
3/2/2013	3/6/2013	103.00	0.0030	0.0038	1,110	1,396
3/11/2013	3/12/2013	12.42	0.0019	0.0021	87	96
3/15/2013	3/17/2013	42.33	0.0071	0.0059	1,085	901
3/22/2013	3/25/2013	77.25	0.0053	0.0036	1,484	1,012
3/29/2013	4/10/2013	298.58	0.0021	0.0018	2,304	1,899
4/15/2013	4/19/2013	94.25	0.0040	0.0026	1,349	891
4/23/2013	4/29/2013	144.33	0.0023	0.0019	1,211	996
5/3/2013	5/7/2013	112.83	0.0016	0.0018	640	750
5/15/2013	5/18/2013	81.67	0.0016	0.0022	475	655
5/22/2013	5/23/2013	25.33	0.0024	0.0032	218	291
5/27/2013	5/28/2013	19.25	0.0020	0.0028	138	196
5/31/2013	6/2/2013	51.67	0.0024	0.0017	449	311
Total (Days):		53.97	Total Volumes (m3):		19,497	10,234

Table A11: 2013 Non-Salt Application Season Baseflow Events and Total Volumes; Data from June 2013 through November 2013

BF Start	BF End	Duration (hrs)	Total Inflow (m³/s)	Outflow (m³/s)	Inlet Volume (m³)	Outlet Volume (m³)
6/6/2013	6/6/2013	4.33	0.0021	0.0017	33	27
6/17/2013	6/18/2013	31.75	0.0046	0.0024	533	271
6/21/2013	6/25/2013	98.75	0.0046	0.0071	1,651	2,513
7/4/2013	7/8/2013	98.00	0.0040	0.0021	1,429	754
7/16/2013	7/22/2013	160.08	0.0028	0.0024	1,596	1,360
7/26/2013	7/28/2013	60.92	0.0030	0.0020	669	439
8/1/2013	8/1/2013	4.17	0.0025	0.0012	38	19
8/4/2013	8/7/2013	80.42	0.0034	0.0015	976	426
8/11/2013	8/13/2013	51.17	0.0028	0.0016	514	297
8/16/2013	8/28/2013	288.08	0.0024	0.0017	2,529	1,747
8/31/2013	9/2/2013	38.25	0.0047	0.0011	643	155
9/5/2013	9/12/2013	173.25	0.0033	0.0013	2,085	793
9/16/2013	9/16/2013	2.50	0.0109	0.0015	101	14
9/25/2013	10/7/2013	288.42	0.0026	0.0011	2,653	1,098
10/14/2013	10/17/2013	71.33	0.0040	0.0014	1,016	362
10/22/2013	11/1/2013	222.50	0.0030	0.0013	2,384	1,012
11/4/2013	11/16/2013	282.83	0.0032	0.0010	3,261	1,005
11/21/2013	11/26/2013	127.42	0.0033	0.0009	1,506	399
11/30/2013	12/6/2013	127.92	0.0026	0.0016	1,203	716
Total (Days):		92.17	Total Volumes (m³):		24,820	13,407

Table A12: 2014 Salt Application Season Baseflow Events and Total Volumes; Data from December 2013 through May 2014

BF Start	BF End	Duration (hrs)	Total Inflow (m3/s)	Outflow (m3/s)	Inlet Volume (m3)	Outlet Volume (m3)
12/12/2013	12/15/2013	59.33	0.0154	0.0085	3,294	1,826
12/18/2013	12/19/2013	15.92	0.0031	0.0018	178	104
12/26/2013	12/29/2013	60.75	0.0025	0.0016	557	343
1/1/2014	1/5/2014	97.67	0.0094	0.0034	3,294	1,202
1/9/2014	1/10/2014	21.17	0.0028	0.0101	212	770
1/17/2014	1/27/2014	227.42	0.0079	0.0021	6,429	1,682
1/30/2014	2/3/2014	86.17	0.0066	0.0031	2,060	957
2/8/2014	2/13/2014	109.75	0.0103	0.0031	4,081	1,210
2/17/2014	2/18/2014	18.50	0.0073	0.0067	486	445
2/24/2014	3/2/2014	144.42	0.0059	0.0078	3,079	4,037
3/7/2014	3/12/2014	120.75	0.0085	0.0090	3,693	3,894
3/15/2014	3/19/2014	89.75	0.0045	0.0064	1,448	2,083
3/22/2014	3/29/2014	154.67	0.0035	0.0043	1,975	2,376
4/3/2014	4/3/2014	13.67	0.0127	0.0088	631	435
4/6/2014	4/7/2014	11.83	0.0162	0.0081	696	347
4/11/2014	4/15/2014	93.67	0.0180	0.0042	6,088	1,428
4/18/2014	4/25/2014	163.67	0.0208	0.0090	12,277	5,323
4/29/2014	4/29/2014	10.67	0.0295	0.0086	1,142	333
5/4/2014	5/10/2014	151.25	0.0207	0.0141	11,254	7,660
5/13/2014	5/16/2014	53.83	0.0075	0.0106	1,454	2,064
5/19/2014	5/22/2014	71.33	0.0119	0.0168	3,049	4,313
5/26/2014	5/27/2014	21.17	0.0069	0.0133	527	1,014
5/31/2014	6/3/2014	71.92	0.0034	0.0048	894	1,240
Total (Days):		77.89	Total Volumes (m3):		68,800	45,086

Table A13: 2014 Non-Salt Application Season Baseflow Events and Total Volumes; Data from June 2014 through November 2014

BF Start	BF End	Duration (hrs)	Total Inflow (m³/s)	Outflow (m³/s)	Inlet Volume (m³)	Outlet Volume (m³)
6/8/2014	6/9/2014	13.33	0.0025	0.0031	122	150
6/16/2014	6/19/2014	57.50	0.0019	0.0038	386	778
6/22/2014	6/25/2014	71.67	0.0011	0.0051	293	1,327
6/28/2014	7/2/2014	90.75	0.0078	0.0036	2,556	1,191
7/6/2014	7/13/2014	187.83	0.0048	0.0027	3,254	1,807
7/19/2014	7/23/2014	112.92	0.0041	0.0014	1,686	565
7/31/2014	8/1/2014	34.50	0.0037	0.0012	455	150
8/6/2014	8/12/2014	145.67	0.0031	0.0013	1,640	665
8/17/2014	8/22/2014	101.92	0.0058	0.0036	2,113	1,330
8/26/2014	8/31/2014	117.58	0.0062	0.0013	2,612	530
9/6/2014	9/13/2014	179.58	0.0055	0.0012	3,574	805
9/16/2014	9/24/2014	194.75	0.0036	0.0011	2,535	796
9/28/2014	10/3/2014	128.17	0.0041	0.0010	1,875	471
10/7/2014	10/7/2014	11.83	0.0032	0.0004	136	17
10/10/2014	10/11/2014	3.58	0.0087	0.0008	114	11
10/14/2014	10/15/2014	22.75	0.0118	0.0061	973	500
10/19/2014	10/21/2014	67.17	0.0057	0.0006	1,379	144
10/26/2014	11/1/2014	137.58	0.0059	0.0006	2,920	304
11/4/2014	11/6/2014	35.00	0.0048	0.0005	600	69
11/9/2014	11/13/2014	95.42	0.0064	0.0005	2,192	178
11/20/2014	11/24/2014	80.17	0.0039	0.0009	1,140	263
Total (Days):		74.84	Total Volumes (m³):		31,294	11,640

Table A14: 2013 Salt Application Season Storm Events and Total Volumes; Data from December 2013 through May 2013

Storm Start	Storm End	Duration (hrs)	Rainfall (in)	Inflow (m ³ /s)	Outflow (m ³ /s)	Inlet Volume (m ³)	Outlet Volume (m ³)
12/7/2012	12/7/2012	9.08	0.12	0.0080	0.0026	264	87
12/7/2012	12/8/2012	19.08	0.33	0.0062	0.0033	431	228
12/9/2012	12/10/2012	30.00	0.38	0.0064	0.0030	688	327
12/11/2012	12/11/2012	10.08	0.13	0.0041	0.0031	151	112
12/16/2012	12/17/2012	16.67	0.15	0.0042	0.0022	253	135
12/17/2012	12/18/2012	11.00	0.15	0.0047	0.0025	188	100
12/18/2012	12/18/2012	6.33	0.11	0.0038	0.0031	89	71
12/20/2012	12/21/2012	13.08	2.60	0.1205	0.0036	5,711	173
12/25/2012	12/26/2012	20.17	0.32	0.0102	0.0042	746	308
12/26/2012	12/26/2012	7.67	1.08	0.0719	0.0031	2,007	85
12/27/2012	12/27/2012	9.42	0.26	0.0201	0.0025	687	85
1/11/2013	1/12/2013	15.92	0.48	0.0176	0.0033	1,015	191
1/14/2013	1/15/2013	8.17	0.41	0.0288	0.0034	856	102
1/15/2013	1/16/2013	19.83	1.15	0.0404	0.0039	2,897	278
1/28/2013	1/29/2013	32.33	0.28	0.0065	0.0066	760	772
1/30/2013	1/31/2013	16.33	2.04	0.0718	0.0057	4,246	338
2/8/2013	2/9/2013	18.50	0.37	0.0170	0.0000	1,139	0
2/10/2013	2/10/2013	9.17	0.14	0.0086	0.0000	288	0
2/11/2013	2/11/2013	11.00	0.48	0.0199	0.0000	793	0
2/14/2013	2/14/2013	7.08	0.22	0.0114	0.0000	295	0
2/15/2013	2/16/2013	9.50	0.11	0.0100	0.0000	344	0
2/19/2013	2/19/2013	11.92	0.25	0.0155	0.0000	669	0
2/23/2013	2/24/2013	26.67	0.16	0.0029	0.0066	279	635
2/26/2013	3/1/2013	76.17	0.52	0.0074	0.0131	2,028	3,597
3/16/2013	3/7/2013	17.75	0.12	0.0071	0.0263	466	1,688
3/8/2013	3/9/2013	14.50	0.13	0.0050	0.0280	265	1,472
3/12/2013	3/13/2013	34.42	1.22	0.0305	0.0225	4,142	2,796
3/17/2013	3/17/2013	9.75	0.23	0.0063	0.0031	231	111
3/18/2013	3/20/2013	39.50	0.76	0.0258	0.0204	3,939	2,905
3/25/2013	3/27/2013	37.42	0.74	0.0112	0.0109	1,581	1,472
4/10/2013	4/11/2013	18.58	0.49	0.0140	0.0160	1,018	1,074
4/12/2013	4/12/2013	14.08	0.60	0.0278	0.0208	1,515	1,059
4/12/2013	4/13/2013	20.17	0.50	0.0164	0.0158	1,277	1,154
4/19/2013	4/20/2013	20.33	0.80	0.0257	0.0239	2,088	1,756
4/29/2013	4/30/2013	35.00	0.57	0.0147	0.0128	1,956	1,613
5/7/2013	5/8/2013	22.50	0.66	0.0195	0.0169	1,685	1,377
5/8/2013	5/9/2013	21.92	0.34	0.0125	0.0135	993	1,072

Storm Start	Storm End	Duration (hrs)	Rainfall (in)	Inflow (m³/s)	Outflow (m³/s)	Inlet Volume (m³)	Outlet Volume (m³)
5/10/2013	5/11/2013	24.50	1.25	0.0406	0.0227	4,385	2,009
5/11/2013	5/12/2013	15.75	0.16	0.0102	0.0097	676	555
5/18/2013	5/20/2013	48.33	0.40	0.0079	0.0083	1,416	1,451
5/23/2013	5/24/2013	20.00	0.78	0.0220	0.0254	1,698	1,834
5/24/2013	5/25/2013	17.17	0.18	0.0104	0.0107	687	662
5/28/2013	5/29/2013	28.25	0.38	0.0183	0.0127	1,976	1,291
Total (Days):		36.46	22.55	Total Volumes (m³):		58,817	34,978

Table A14: continued

Table A15: 2013 Non-Salt Application Season Storm Events and Total Volumes; Data from June 2013 through November 2013

Storm Start	Storm End	Duration (hrs)	Rainfall (in)	Inflow (m ³ /s)	Outflow (m ³ /s)	Inlet Volume (m ³)	Outlet Volume (m ³)
6/2/2013	6/3/2013	14.92	0.86	0.0316	0.0210	1,851	1,137
6/3/2013	6/4/2013	19.83	0.14	0.0089	0.0123	651	882
6/6/2013	6/9/2013	67.33	4.43	0.0564	0.0248	15,178	6,012
6/10/2013	6/12/2013	61.67	2.71	0.0377	0.0219	8,955	4,861
6/13/2013	6/13/2013	11.58	0.52	0.0271	0.0251	1,229	1,054
6/13/2013	6/14/2013	26.33	0.58	0.0151	0.0120	1,490	1,137
6/18/2013	6/21/2013	79.33	1.21	0.0140	0.0104	4,255	2,986
6/25/2013	6/26/2013	17.42	0.34	0.0083	0.0117	539	737
6/26/2013	6/27/2013	21.00	0.69	0.0282	0.0142	2,585	1,080
6/27/2013	6/28/2013	21.00	0.50	0.0233	0.0129	2,080	980
6/28/2013	6/30/2013	46.00	0.19	0.0077	0.0125	1,388	2,074
6/30/2013	6/30/2013	10.33	0.27	0.0203	0.0148	884	554
6/30/2013	7/2/2013	44.17	1.01	0.0192	0.0132	3,538	2,106
7/9/2013	7/10/2013	24.42	0.33	0.0071	0.0078	643	686
7/12/2013	7/13/2013	25.92	1.13	0.0294	0.0239	3,055	2,237
7/22/2013	7/24/2013	32.50	1.41	0.0194	0.0121	2,504	1,422
7/28/2013	7/29/2013	23.58	0.88	0.0164	0.0185	1,489	1,579
8/1/2013	8/2/2013	33.00	1.30	0.0259	0.0186	3,378	2,217
8/7/2013	8/8/2013	20.75	0.39	0.0105	0.0131	836	986
8/13/2013	8/14/2013	34.00	3.34	0.0447	0.0194	6,098	2,375
8/28/2013	8/29/2013	18.08	1.37	0.0257	0.0187	1,836	1,221
9/2/2013	9/2/2013	7.42	0.28	0.0153	0.0123	451	332
9/12/2013	9/13/2013	16.50	0.61	0.0160	0.0189	1,038	1,126
9/16/2013	9/16/2013	8.42	0.12	0.0063	0.0074	200	225
9/21/2013	9/22/2013	15.92	1.44	0.0418	0.0259	2,722	1,495
10/7/2013	10/7/2013	15.83	0.77	0.0183	0.0188	1,144	1,080
10/10/2013	10/11/2013	21.00	0.58	0.0202	0.0163	1,650	1,238
10/11/2013	10/12/2013	36.17	2.00	0.0371	0.0249	5,295	3,251
10/17/2013	10/18/2013	10.08	0.12	0.0096	0.0054	366	199
10/19/2013	10/20/2013	7.33	0.26	0.0104	0.0130	295	347
11/1/2013	11/1/2013	12.17	0.40	0.0104	0.0138	479	610
11/18/2013	11/18/2013	10.42	0.15	0.0067	0.0063	261	237
11/26/2013	11/28/2013	54.08	3.59	0.0400	0.0226	8,718	4,400
Total (Days):		36.19	33.92	Total Volumes (m³):		87,079	52,861

Table A16: 2014 Salt Application Season Storm Events and Total Volumes; Data from December 2013 through May 2014

Storm Start	Storm End	Duration (hrs)	Rainfall (inches)	Inflow (m ³ /s)	Outflow (m ³ /s)	Inlet Volume (m ³)	Outlet Volume (m ³)
12/6/2013	12/7/2013	37.83	1.31	0.0294	0.0244	4,338	3,325
12/9/2013	12/11/2013	50.58	0.48	0.0167	0.0167	3,119	3,035
12/15/2013	12/16/2013	23.92	0.63	0.0216	0.0165	1,984	1,424
12/19/2013	12/19/2013	11.00	0.36	0.0062	0.0026	255	102
12/22/2013	12/23/2013	18.83	0.16	0.0145	0.0120	1,039	816
12/23/2013	12/24/2013	38.83	0.73	0.0244	0.0180	3,621	2,520
12/29/2013	12/30/2013	34.50	1.18	0.0329	0.0183	4,556	2,277
1/5/2014	1/9/2014	89.83	1.42	0.0215	0.0186	7,301	6,018
1/10/2014	1/14/2014	90.75	1.52	0.0249	0.0201	8,560	6,589
1/14/2014	1/16/2014	65.17	0.40	0.0089	0.0090	2,141	2,125
1/27/2014	1/27/2014	12.75	0.22	0.0109	0.0068	507	315
2/3/2014	2/5/2014	52.17	0.35	0.0268	0.0180	5,143	3,395
2/5/2014	2/7/2014	43.92	0.90	0.0280	0.0257	4,958	4,070
2/13/2014	2/14/2014	21.33	0.65	0.0360	0.0203	2,909	1,565
2/14/2014	2/17/2014	79.92	0.75	0.0237	0.0106	6,992	3,051
2/18/2014	2/19/2014	21.25	0.52	0.0121	0.0105	980	809
2/19/2014	2/21/2014	52.58	0.31	0.0462	0.0184	8,815	3,482
2/21/2014	2/24/2014	75.08	0.59	0.0661	0.0198	18,037	5,350
3/4/2014	3/5/2014	15.25	0.16	0.0038	0.0072	214	398
3/12/2014	3/15/2014	77.50	0.50	0.0122	0.0110	3,578	3,073
3/19/2014	3/22/2014	80.08	0.73	0.0163	0.0114	4,948	3,301
3/29/2014	4/3/2014	116.58	3.01	0.0463	0.0217	20,568	9,117
4/3/2014	4/6/2014	76.25	0.29	0.0254	0.0102	7,118	2,793
4/7/2014	4/20/2014	79.50	0.38	0.0236	0.0141	6,873	4,051
4/15/2014	4/18/2014	91.42	2.37	0.0457	0.0178	15,600	5,852
4/25/2014	4/29/2014	78.08	0.64	0.0332	0.0119	9,496	3,330
4/29/2014	5/4/2014	114.33	5.13	0.0744	0.0316	32,742	13,036
5/10/2014	5/13/2014	82.75	0.25	0.0195	0.0178	5,855	5,315
5/16/2014	5/19/2014	82.25	4.27	0.0565	0.0322	17,919	9,548
5/22/2014	5/23/2014	27.08	0.19	0.0195	0.0264	1,919	2,578
5/23/2014	5/26/2014	73.25	0.34	0.0233	0.0197	6,200	5,191
5/27/2014	5/28/2014	17.83	0.40	0.0216	0.0274	1,479	1,769
5/28/2014	5/31/2014	61.58	0.89	0.0223	0.0159	5,113	3,537
Total (Days):		78.92	32.03	Total Volumes (m³):		224,877	123,154

Table A17: 2014 Non-Salt Application Season Storm Events and Total Volumes; Data from June 2014 through November 2014

Storm Start	Storm End	Duration (hrs)	Rainfall (inches)	Inflow (m ³ /s)	Outflow (m ³ /s)	Inlet Volume (m ³)	Outlet Volume (m ³)
6/3/2014	6/4/2014	12.42	0.17	0.0097	0.0210	441	946
6/4/2014	6/5/2014	23.67	0.14	0.0067	0.0113	583	965
6/9/2014	6/9/2014	14.00	0.17	0.0115	0.0203	589	1,027
6/9/2014	6/11/2014	55.83	0.77	0.0139	0.0171	2,876	3,451
6/11/2014	6/12/2014	12.83	0.13	0.0133	0.0138	640	641
6/12/2014	6/13/2014	26.83	0.41	0.0195	0.0270	1,935	2,615
6/13/2014	6/16/2014	72.42	0.14	0.0070	0.0134	1,832	3,489
6/19/2014	6/19/2014	12.25	0.15	0.0145	0.0179	661	793
6/19/2014	6/20/2014	28.83	0.23	0.0098	0.0149	1,044	1,547
6/25/2014	6/25/2014	6.83	0.14	0.0191	0.0243	482	606
6/25/2014	6/26/2014	24.92	0.75	0.0276	0.0239	2,698	2,147
7/2/2014	7/4/2014	49.08	1.14	0.0158	0.0259	2,899	4,583
7/13/2014	7/14/2014	18.08	0.15	0.0115	0.0121	767	788
7/14/2014	7/15/2015	21.83	0.98	0.0340	0.0150	2,849	1,186
7/15/2014	7/16/2014	15.75	0.32	0.0165	0.0113	982	644
7/23/2014	7/24/2014	15.42	0.43	0.0236	0.0170	1,393	948
7/26/2014	7/26/2014	11.08	0.20	0.0180	0.0112	750	450
7/27/2014	7/28/2014	18.25	1.38	0.0527	0.0228	3,737	1,504
8/1/2014	8/2/2014	10.00	0.31	0.0176	0.0216	662	783
8/2/2014	8/2/2014	17.83	0.49	0.0213	0.0184	1,514	1,184
8/2/2014	8/3/2014	16.00	0.21	0.0105	0.0082	623	474
8/12/2014	8/13/2014	33.83	1.04	0.0248	0.0196	3,272	2,394
8/14/2014	8/15/2014	17.33	0.23	0.0121	0.0119	777	746
8/22/2014	8/22/2014	16.92	0.58	0.0233	0.0174	1,511	1,066
8/23/2014	8/24/2014	31.00	0.51	0.0149	0.0136	1,749	1,527
8/31/2014	9/1/2014	20.25	1.02	0.0327	0.0136	2,564	994
9/2/2014	9/3/2014	11.08	0.18	0.0139	0.0094	572	376
9/13/2014	9/13/2014	11.08	0.42	0.0195	0.0211	834	848
9/24/2014	9/26/2014	25.08	0.65	0.0215	0.0174	2,079	1,580
10/3/2014	10/4/2014	18.83	0.52	0.0196	0.0210	1,403	1,430
10/7/2014	10/8/2014	15.67	0.30	0.0156	0.0150	936	851
10/11/2014	10/12/2014	20.67	0.43	0.0174	0.0156	1,393	1,162
10/15/2014	10/16/2014	30.67	1.02	0.0287	0.0222	3,366	2,455
10/21/2014	10/23/2014	46.33	0.75	0.0182	0.0133	3,152	2,228
Total (Days):		32.62	16.46	Total Volumes (m³):		53,565	48,431

Table A18: Mill Creek Discharge and Chloride Concentration Data at Each Location

Date	Subwatershed	Notes	Discharge m ³ /s	Cl ⁻ (mg/L)
7/2/13	A	Mainstem (@Rose Glen Road)	0.503	65.6
7/2/13	C	Mainstem (@West Mill Creek Park)	0.457	70.5
7/2/13	J	Mainstem (@Black Rock Road)	0.244	95.8
7/2/13	K	Mainstem (@ Harritan Road)	0.163	29.1
7/2/13	L	Mainstem (@Airdale Road)	0.148	97.6
9/27/13	A	Mainstem (@Rose Glen Road)	0.123	89.3
9/27/13	C	Mainstem (@West Mill Creek Park)	0.110	97.8
9/27/13	J	Mainstem (@Black Rock Road)	0.085	102
9/27/13	K	Mainstem (@ Harritan Road)	0.077	112
9/27/13	L	Mainstem (@Airdale Road)	0.022	125
11/22/13	A	Mainstem (@Rose Glen Road)	0.248	91.3
11/22/13	C	Mainstem (@West Mill Creek Park)	0.180	97.0
11/22/13	J	Mainstem (@Black Rock Road)	0.120	105
11/22/13	K	Mainstem (@ Harritan Road)	0.072	123
11/22/13	L	Mainstem (@Airdale Road)	0.062	128
12/19/13	A	Mainstem (@Rose Glen Road)	0.296	254
12/19/13	C	Mainstem (@West Mill Creek Park)	0.269	335
12/19/13	J	Mainstem (@Black Rock Road)	0.207	289
12/19/13	K	Mainstem (@ Harritan Road)	0.162	299
12/19/13	L	Mainstem (@Airdale Road)	0.130	332
1/25/14	A	Mainstem (@Rose Glen Road)	0.249	104
1/25/14	C	Mainstem (@West Mill Creek Park)	0.228	132
1/25/14	J	Mainstem (@Black Rock Road)	0.101	145
1/25/14	K	Mainstem (@ Harritan Road)	0.075	165
1/25/14	L	Mainstem (@Airdale Road)	0.068	175
2/22/14	A (STORM)	Mainstem (@Rose Glen Road)	1.896	142
2/22/14	C (STORM)	Mainstem (@West Mill Creek Park)	1.248	195
2/22/14	J (STORM)	Mainstem (@Black Rock Road)	0.497	198
2/22/14	K (STORM)	Mainstem (@ Harritan Road)	0.271	140
2/22/14	L (STORM)	Mainstem (@Airdale Road)	0.152	253
3/22/14	A	Mainstem (@Rose Glen Road)	0.418	140
3/22/14	C	Mainstem (@West Mill Creek Park)	0.371	144
3/22/14	J	Mainstem (@Black Rock Road)	0.040	65.0
3/22/14	K	Mainstem (@ Harritan Road)	0.132	187
3/22/14	L	Mainstem (@Airdale Road)	0.111	90.9