Dissolved Road Salt Transport in Urban and Rural Watersheds in Massachusetts

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DISSOLVED ROAD SALT TRANSPORT IN URBAN AND RURAL WATERSHEDS IN MASSACHUSETTS

a thesis

by

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ABSTRACT

Dissolved Road Salt Transport in Urban and Rural Watersheds in Massachusetts

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Chloride-based deicers (NaCl, $CaCl_2$, $MgCl_2$), also referred to as road salt, are the most common substances used in maintaining safe roadway surfaces during the winter months. Upon application, road salt reacts with the accumulated snow or ice to form brine equilibrium solutions along the liquidus line in the salt-water system. Dissolved salts dissociate, leading to increased concentrations of the respective ions in nearby soils, surface water, and groundwater. Of the ions present in road salt, chloride has the advantage of tracking all chloride deicers at the same time and since chloride ions are conservative tracers in soils it stays unaffected by ionic exchange interferences. This study explores the mechanisms of chloride return flows by investigating chloride dissolved loads, chloride concentrations in stream waters, seasonal patterns, and changes over the course of four years in two separate watersheds in Massachusetts with differing degrees of urbanization.

The chloride tracking technique used in this study is based on calibrated chloride concentrations obtained from specific conductance signals recorded every 15 minutes by automatic recording systems at two locations, one in rural central Massachusetts and the other in urban eastern Massachusetts. These systems are maintained by the USGS, which also provide the simultaneously recorded stream

flow datasets. The dissolved chloride load carried by each river is calculated for each single 15-minute interval by multiplying water volume with the corresponding chloride concentration, resulting in a total of over 34,000 data points per annum per site.

Hydrograph separation techniques were used to separate dissolved load transported by each river into two separate flow components, event flow resulting from precipitation events, and baseflow resulting from groundwater discharge. Well defined hydrograph baseflow supported periods yield consistent chloride concentrations independent of the season at either urban or rural study sites. Comparison of direct runoff dissolved chloride loads with the total annual dissolved loads suggests that only a small fraction of the deicers actually removed during the overland runoff events and that a minimum of 60% of the total load discharged each year in both urban and rural systems is transported by groundwater. From groundwater recharge by brines rural watersheds are currently retaining as much as 95% of the total chloride applied to roadways each year while urban and suburban watersheds may only retain 75% of the total chloride applied to roadways each year. The increased retention of chloride in rural areas is likely due to the decreased amount of chloride transported during winter seasons as event flow compared to urban watersheds.

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LIST OF FREQUENTLY USED TERMS

CFS: Cubic Feet Per Second

High-Frequency: 15-minute Interval Readings

in: Inches

lnmi: Lane Mile

kg: Kilograms

kg/hour: Kilograms Per Hour

kg/sqmi: Kilograms Per Square Mile

mg/l: Milligrams Per Liter

S: Siemens

sqmi: Square Mile

μS/cm: Micro Siemens Per Centimeter

1. INTRODUCTION

Chloride-based deicing chemicals, referred to as road salt, are applied to assure safe driving conditions on roadway surfaces during winter storms. According to the Massachusetts Highway Department (2009), "when a deicing solution such as salt is applied to a surface, a brine solution is created… the brine loosens the ice or snow from the pavement" which allows easier snow removal and safer travel on roadways during winter snow and ice storms. Brine (or saline) solutions have a lower freezing point and a higher density compared to snow and ice remaining in the liquid form on roadway surfaces even when temperatures drop below 0°C. This prevents buildup of snow and ice on road surfaces. It is the property of freezing point depression caused by increased salinity of water that makes road salt a desired street deicer during winter storms. Road salt is used liberally in cold weather climates during the winter months and contributes to safer vehicular travel on roadways during and after winter storms and has been found to reduce the cost of winter accidents by 88% (Marquette University, 1992). Deicing agents used in the United States primarily consist of sodium chloride (NaCl), however small amounts of calcium chloride ($CaCl_2$) and magnesium chloride ($MgCl_2$) are also used in small quantities when temperatures are below the effective temperature of NaCl (-10°C) (Yehia and Taun, 1998). The total amount of road salt used on United States highways to assist in clearing roadways of snow and ice during winter storms has increased over 12,000% from 1940 to 2005 (Figure 1). The US currently uses in excess of 15,000,000 tons of road salt per year, depending on the severity of the winter season (The Salt Institute, 2005).

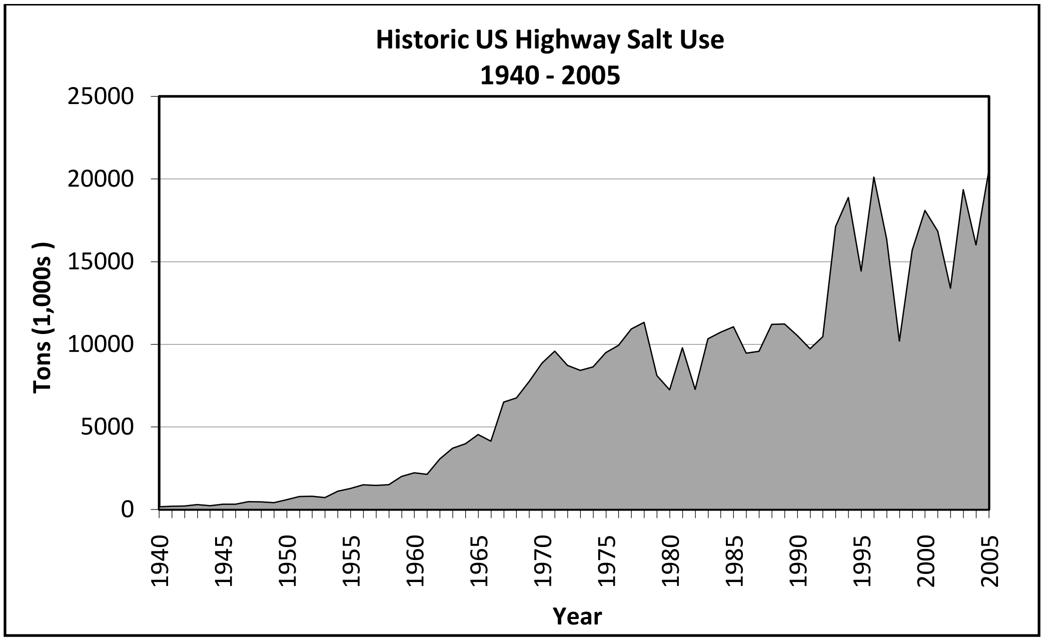

Figure 1: United States deicing chemical use in thousands of tons per year from 1940 to 2005 (The Salt Institute, 2005). Highways are defined as any public roadway maintained by federal, state or town run organizations.

The benefits of using deicing agents on roadways are accompanied by the need for removal of these chemicals from the environment mainly as dissolved salts through steamflow, a process that is not well understood. Chloride-based deicers dissolve readily in water, and the application and open storage of deicing chemicals have been linked to the increased salinization of groundwater and surface water near areas where deicing chemicals are stored or applied

(Ostendorf, et al., 2001; Thunqvist, 2003; Williams, et al., 2000; Mason, et al., 1999). The lower freezing point and increased density of brine solutions allows for infiltration of the saline solution to groundwater sources and direct runoff to streams and rivers during the winter season, when frost and freezing temperatures usually inhibit water infiltration and direct runoff. The observed increased dissolved chloride concentration in surface waters has been associated with a decrease in aquatic plant populations and a shift in plant population toward non-native species, as well as a decrease in macroinvertabrates present in surface waters (Williams et al., 2000; Environment Canada, 2001). A study by Environment Canada (2001) found that increased sodium concentrations in soil near roadways where deicers are commonly used are linked to the release of nutrients from soils through cation exchange. Cation exchange is caused by increased amounts of sodium in soils that can lead to the release of the micronutrients calcium, magnesium and potassium normally found at sorption sites within soils (Environment Canada, 2001). Such loss of micronutrients can lead to a decrease in the terrestrial plant population along roadsides in addition to a population shift in terrestrial plant species toward non-native species more tolerant of high sodium content (Environment Canada, 2001). The increased salinization of groundwater and surface water can also adversely affect human health by degrading the quality of drinking water sources, specifically increasing the concentration of sodium and chloride in drinking water supplies (Howard, et al., 1993; US Environmental Protection Agency, 2002).

The salinization of public water supplies is further accelerated by current population increases and urbanization trends in many areas throughout the world, which cause the demand for potable water to exceed the available supply (Vorosmarty et al., 2000). Increased water demand due to urbanization places additional stress on current water sources and brings with it many activities that can lead to the degradation of the quality of available water (Kelly, 2008). In colder climates, the deterioration of water quality is primarily due to increased salinization of drinking water sources due to deicing chemical application, and, to a lesser extent, leachate from private septic systems, water softeners, and wet deposition Nimiroski, et al., (2002) and Kelly et al. (2008) found that even in rural environments, where the use of water softeners is prevalent, along with private septic system discharge to groundwater, deicing chemicals accounted for 91% of the sodium and chloride input to the watershed. The increased salinization of groundwater, if allowed to continue unabated, could render water supplies in the colder climates unfit for human consumption within this century by exceeding a baseline dissolved chloride concentration of 250 mg/l (the secondary maximum contaminant level for potable water) (Kaushal et al., 2005). The salinization of groundwater over time suggested by Kaushal et al. (2005) and others indicates long-term sodium and dissolved chloride retention within watersheds where ever deicing chemicals are applied, which could lead to long-term degradation of surface water and groundwater, even if the use of dissolved chloride based deicers were to decrease or stop in the near future (Kelly et al., 2008).

The retention of sodium and chloride in the subsurface as a result of deicing chemical use was found by Demers et al., (1990), Kelly et al., (2008), Likens et al., (2009), and Rosenberry et al, (1999), among others. All of these studies found that dissolved chloride concentrations (a proxy for road salt) in groundwater and stream discharge during the summer months remained much higher than background dissolved chloride concentrations, many months after any road salt had been applied within the watershed boundaries. In order to account for the increased summer concentration of dissolved chloride, it is apparent that some dissolved chloride must be retained in the subsurface and removed from the watershed over time through groundwater discharge to streams (Kelly, et al., 2008; Likens, et al., 2009; Demers, et al., 1990; Rosenberry, et al., 1999). It is this retention that poses the greatest threat to public water supplies over the next century. The dissolved chloride is removed from the environment via return flow pathways displayed in Figure 2, following a general model developed by Kelly et al. (2008). This model displays two return paths of dissolved chloride after deicing agent use. One is through direct runoff which bypasses the subsurface, and the other is through infiltration and storage in the subsurface dissolved chloride pool followed by eventual discharge to streams via groundwater recharge. This model also indicates that the total load of dissolved chloride removed from a watershed is highly dependent on streamflow. In order to calculate the dissolved chloride load removed from a watershed, one needs to know the dissolved chloride concentration of the streamwater leaving the watershed, as well as the volume of water removed from the watershed.

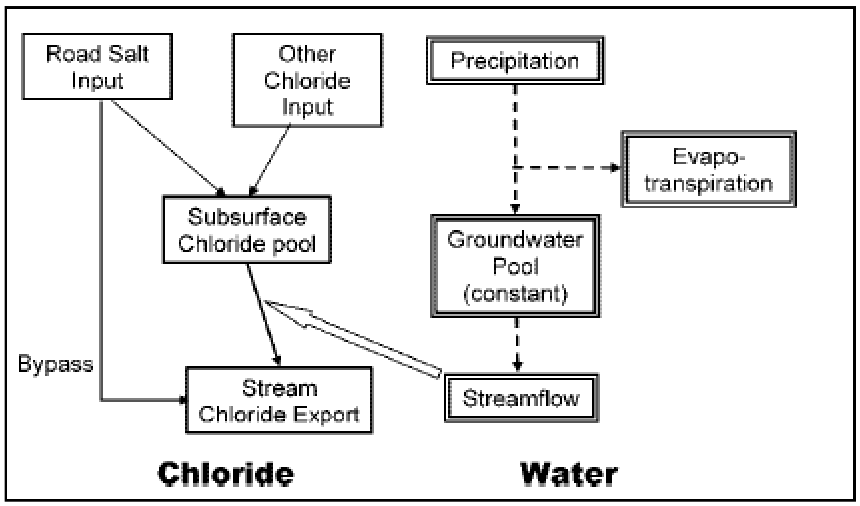

Figure 2: General model for dissolved chloride removal from a watershed. Left hand side represents dissolved chloride pools and fluxes (single lines), and right-hand side represents water pools and fluxes (dashed lines). Block arrow indicates that streamflow is used in the calculation of dissolved chloride export (Adopted from Kelly, et al., 2008).

To accurately quantify amounts of dissolved chloride bypassing the subsurface and entering streams directly (via direct runoff) and amounts of dissolved chloride that enter the existing subsurface dissolved chloride pool, a converted high-frequency dissolved chloride concentration dataset along with a high-frequency stream discharge dataset are needed to prevent the temporal biasing in sample collection seen by Kelly et al. (2008) that could lead to inaccuracies in analysis. In this study we attempt for the first time to partition dissolved chloride transport into direct runoff and baseflow components of transport using high-frequency (15-minute interval) dissolved chloride concentration and streamflow datasets over a four-year period.

2. BACKGROUND

2.1 STUDY SITES

This study uses four-year high-frequency (15-minute interval) datasets consisting of simultaneously collected specific conductance and stream discharge records at USGS monitoring stations in two rivers in Massachusetts. One is located in a highly urbanized area, and the other located in a rural setting. The Saugus River watershed (USGS station ID #01102345) is located within the Greater Boston Area, has a drainage area of 23.31 square miles, with a population density of 2,291 people per square mile, and 55.9% of the area designated as urban (Table 1) (Campo, Flanagan and Robinson, 2003). The Stillwater River watershed (USGS station ID #01095220) is located in rural central Massachusetts with a drainage area of 30.38 square miles that is 75.2% forested with a population density of 166 people per square mile (Table 1) (Campo, Flanagan and Robinson, 2003). Figure 3 is a locus map displaying the location of both the Saugus River drainage area and Stillwater River drainage area within Massachusetts along with the surrounding major roads. Figure 4 displays the drainage areas for the Saugus River and Stillwater River with roads and hydrology present within the drainage area boundaries. These two drainage areas are similar in size and located in areas containing primarily glacial till and unconsolidated stratified drift of varying thickness overlying crystalline bedrock (Campo, Flanagan and Robinson, 2003). The drainage areas were chosen for this study because they have varying land use characteristics, a contrast in road density and population density in their respective drainage areas, and both have real-time datasets with overlapping timeframes available from the USGS archives.

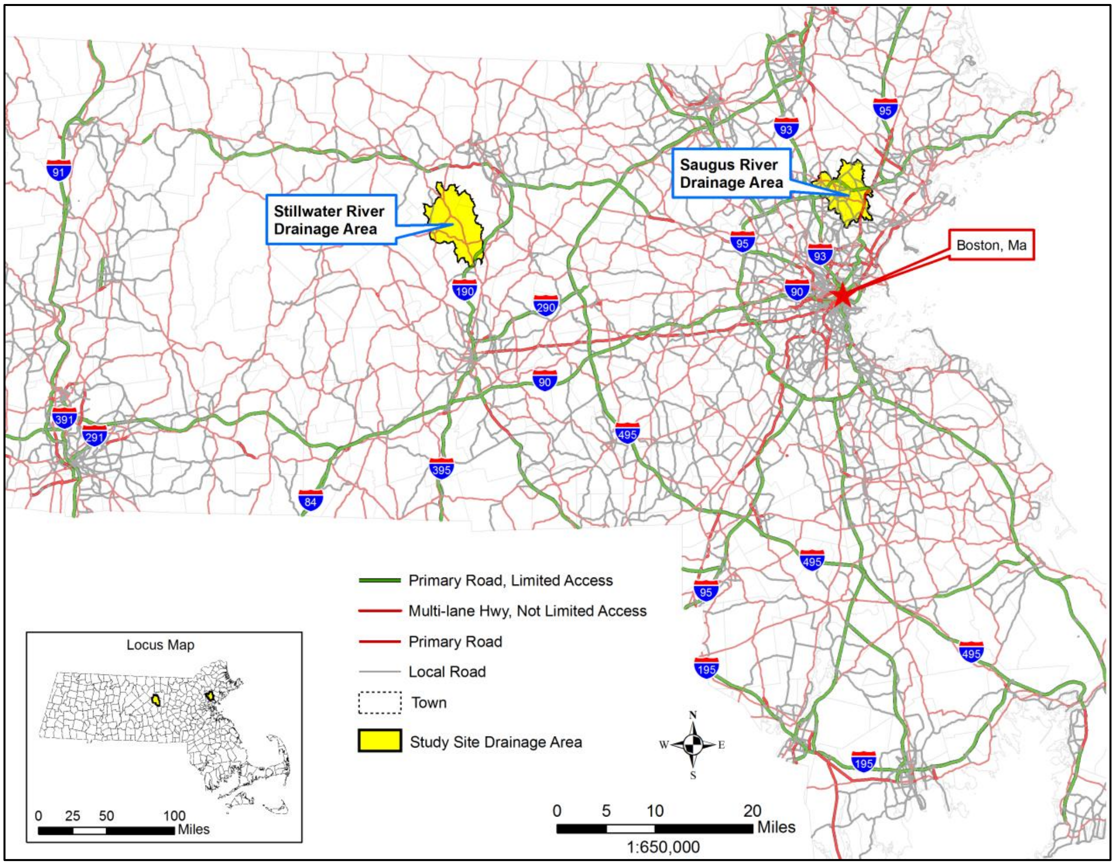

Figure 3: Locus map displaying drainage areas for the Saugus River and Stillwater River and major roadways near each drainage area

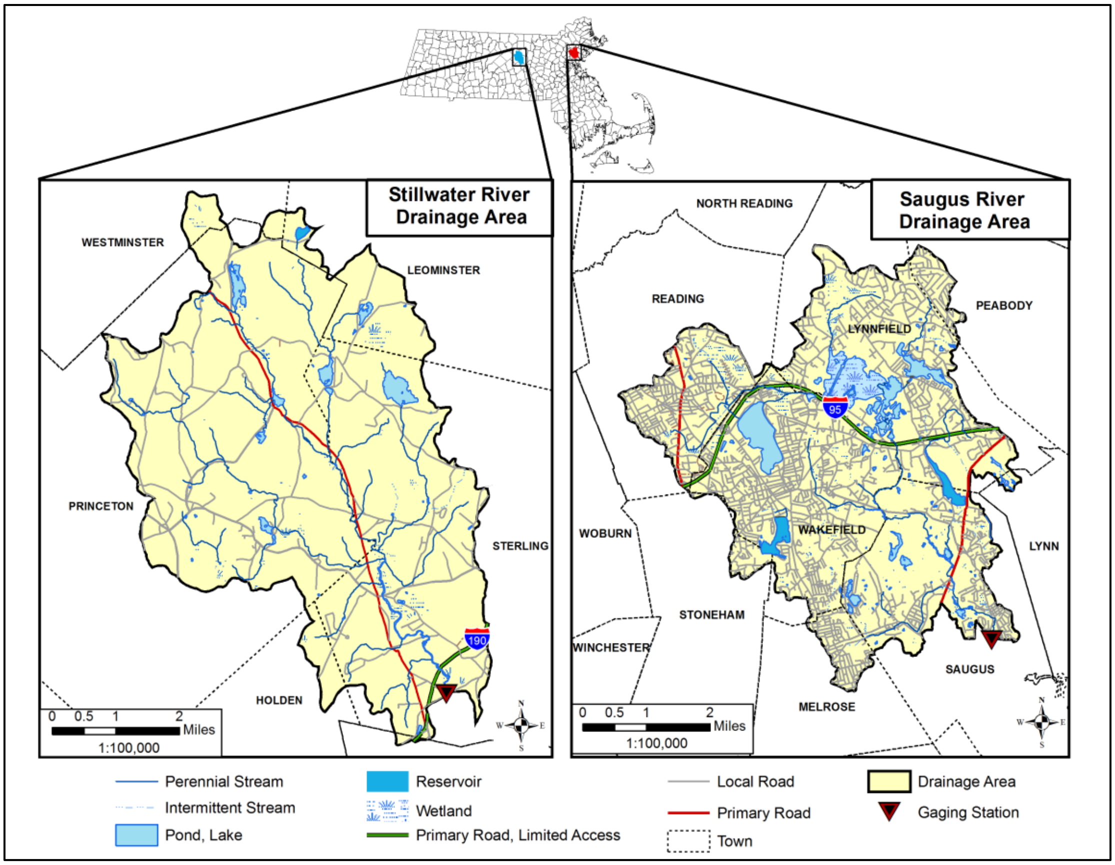

Figure 4: Site map displaying the drainage areas for both the Saugus River and Stillwater River. (Mass GIS, 2007).

Study Site Characteristics						
Station Name	**Drainage Area (square miles)**	**Population Density (people/ square mi)**	**Main Land Use**	**Total Roadway Length (mi)**	**Stream Discharge Mean Annual (CFS)**	**Precipitation Average (in)**
Saugus River	23.31	2291	Urban 55.9%	369	31.2	45.10
Stillwater River	30.38	166	Forested 75.2%	160	54.2	49.34

Table 1: Drainage area characteristics for the Saugus River and Stillwater River drainage basins. All data from USGS NAWQA program New England Coastal Basin Study Area project (Campo, Flanagan and Robinson, 2003); (Mass GIS, 2007).

2.1.1 Regional Drainage Analysis

In order to establish regional relevance of flow records collected at each of the two watersheds selected for this study, the flow records from each site are compared and with flow records collected in three other separate drainage areas in close proximity to each site. Figure 5 displays the drainage areas of other rivers included in this analysis along with the location of each gauging station. Ten-year (1998-2008) daily average streamflow datasets for each river are obtained from the USGS in order to perform the regional consistency correlations.

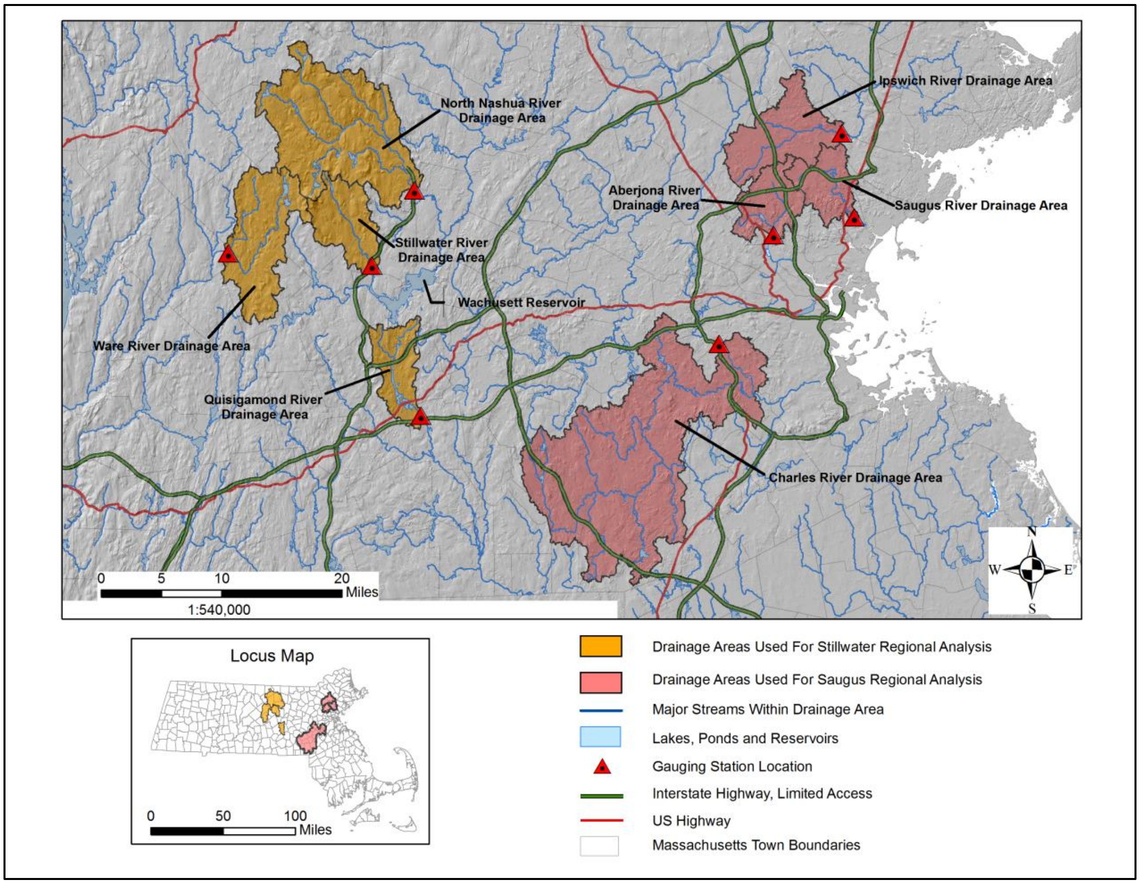

Figure 5: Drainage area extents for rivers chosen for regional consistency analysis. Yellow drainage areas represent drainage areas chosen for regional consistency analysis of the Stillwater River streamflow record. Pink drainage areas represent drainage areas chosen for regional consistency analysis of the Saugus River streamflow record (Mass GIS, 2007).

2.1.1.1 Saugus River

Ten-year daily average stream discharge records for the Saugus River, Charles River, Aberjona River, and Ipswich River (USGS, 2008) are compared to test Saugus River data for regional consistency (see Figure 5 for drainage area extents and gauging station locations). As can be seen in Table 2, the drainage areas range from 23.31mi^2 for the Saugus River to 211 mi^2 for the Charles River and maximum, minimum and average daily flow values increase with increasing drainage area extent.

Saugus River, Charles River, Aberjona River and Ipswich River Drainage Area and Flow Statistics 1998 – 2008				
	Saugus River	**Charles River**	**Aberjona River**	**Ipswich River**
Drainage area (mi^2)	23.31	211	24.7	44.5
Max daily average flow rate (CFS/sq mi)	2.18	0.30	1.67	1.07
Min daily average flow rate (CFS/sq mi)	$8.94\text{x}10^{-4}$	$6.17\ \text{x}10^{-4}$	$1.66\ \text{x}10^{-3}$	$1.67\ \text{x}10^{-5}$
Daily average flow rate (CFS/sq mi)	**0.061**	**0.056**	**0.059**	**0.065**

Table 2: Drainage areas and flow statistics of rivers used to analyze regional consistency of the flow recorded at the Saugus River gauging station. All data provided by USGS (USGS, 2008). All averages displayed are 10 year averages from 1998 – 2008. CFS is cubic feet per second; sq mi is square mile.

The daily average flow rates for each river are normalized to their respective drainage areas. The flow rates are then split into 28 day averages over the 10 year period in order to smooth out large localized daily flow rate fluctuations. Figure 6 displays the normalized 28-day average flow rate in each river over the 10-year period. As can be seen from Figure 6, all four rivers' flow rates increase and decrease with similar magnitude, indicating regional consistency in flow rate per square mile. This correlation in flow rates between the four rivers is further tested by conducting a correlation coefficient analysis on Saugus River 28-day average flow rate and the 28-day combined average flow rate of the Charles River, Aberjona River, and Ipswich River. The results of this correlation coefficient analysis between the Stillwater River 28-day average and the combined average from the other three rivers' 28-day averages is an R value of 0.956, an R^2 value of 0.912, and a P value of <0.001. The results of the correlation analysis indicate that approximately 91% of the changes in regional flow near the Stillwater River can be explained using the flow rate recorded at the Saugus River gauging station, and this correlation is not the result of random chance.

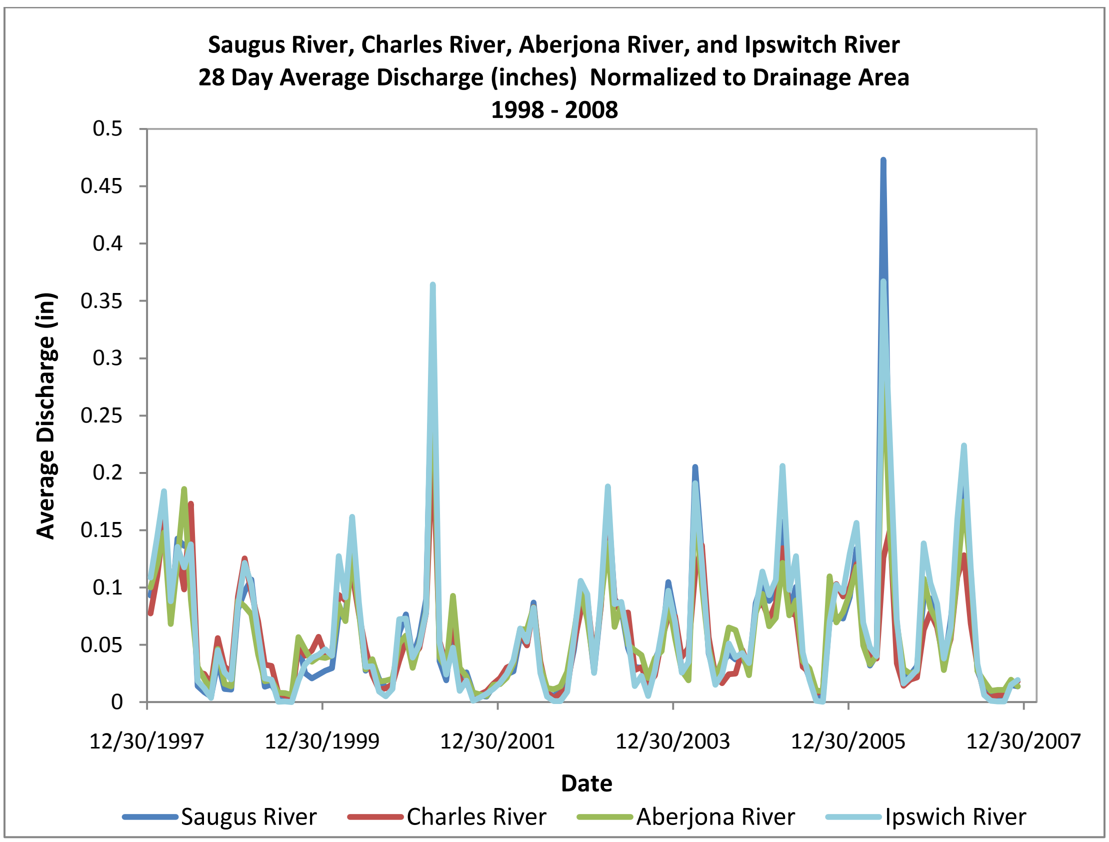

Figure 6: 28 day average flow rates for rivers used to analyze the regional consistency of flow measurements recorded at the Saugus River gauging station. Data provided by the USGS (USGS, 2008).

2.1.1.2 Stillwater River

Ten-year daily average flow records from the Stillwater River, Quinsigmond River, Ware River, and North Nashua River(USGS, 2008) are compared, to test Stillwater River data for regional (see Figure 5 for drainage area extents and gauging station locations). As can be seen in Table 3, the drainage areas range from 25.6 mi^2 for the Quinsigmond River to 110 mi^2 for the North Nashua River and maximum, minimum, and average daily flow values increase with increasing drainage area extent. When comparing the 10-year daily average flow rates for the Stillwater River analysis (Table 3) to daily average flow rates from the Saugus River regional analysis (Table 2) we see that the rivers part of the Stillwater River regional analysis have averages that are approximately 10% higher than averages for rivers part of the Saugus River drainage analysis. This is most likely due to the difference in elevation between the rivers used for each analysis. The rivers part of the Stillwater River regional drainage analysis are at higher elevations which can lead to increased precipitation (the Stillwater River watershed approximately 9% more precipitation per year that the Saugus River watershed (Campo, Flanagan and Robinson, 2003)) which will lead to overall higher average flow rates.

Stillwater River, Quinsigmond River, Ware River and North Nashua River Drainage Area and Flow Statistics 1998 – 2008				
	Stillwater River	**Quinsigmond River**	**Ware River**	**North Nashua River**
Drainage Area (mi^2)	30.38	25.60	55.10	110.00
Max Daily Average Flow Rate (CFS/sq mi)	1.58	0.82	0.72	1.65
Min Daily Average Flow Rate (CFS/sq mi)	1.28E-04	1.45E-05	3.44E-04	7.10E-03
Daily Average Flow Rate (CFS/sq mi)	**0.069**	**0.060**	**0.066**	**0.076**

Table 3: Drainage areas and flow statistics of rivers used to analyze regional consistency of the flow recorded at the Stillwater River gauging station (USGS, 2008). All averages displayed are 10 year averages from 1998 – 2008. CFS is cubic feet per second; sq mi is square mile

Daily average flow data for each river is then normalized to their respective drainage areas. The flow rates are split into 28-day averages over the 10-year period in order to smooth out large localized daily flow rate fluctuations. Figure 7 displays the normalized 28-day average flow rate in each river over the 10-year period. As can be seen from Figure 7, the four rivers' flow rates increase and decrease with similar magnitude, indicating regional consistency in flow rate per square mile. This correlation in flow rates between the 4 rivers is further tested by conducting a correlation coefficient analysis on Stillwater River 28-day average flow rate and the 28-day combined average flow rates of the Quinsigmond River, Ware River, and North Nashua River. The results of this correlation coefficient analysis between the Stillwater River 28 day average and the combined average from the other 3 rivers' 28 day averages is an R value of 0.975, an R^2 value of 0.950, and a P value of <0.001. The results of the correlation analysis indicate that approximately 95% of the changes in regional flow near the Stillwater River can be explained using the flow rate recorded at the Stillwater River gauging station and confirm that this correlation is not the result of random chance. The lower R^2 value obtained during the analysis of the Saugus River regional drainage analysis as compared to the R^2 value obtained during the Stillwater River regional drainage analysis can most likely be explained by the use of dams for flood control on the Charles River (USGS, 2008), which is part of the Saugus River drainage analysis.

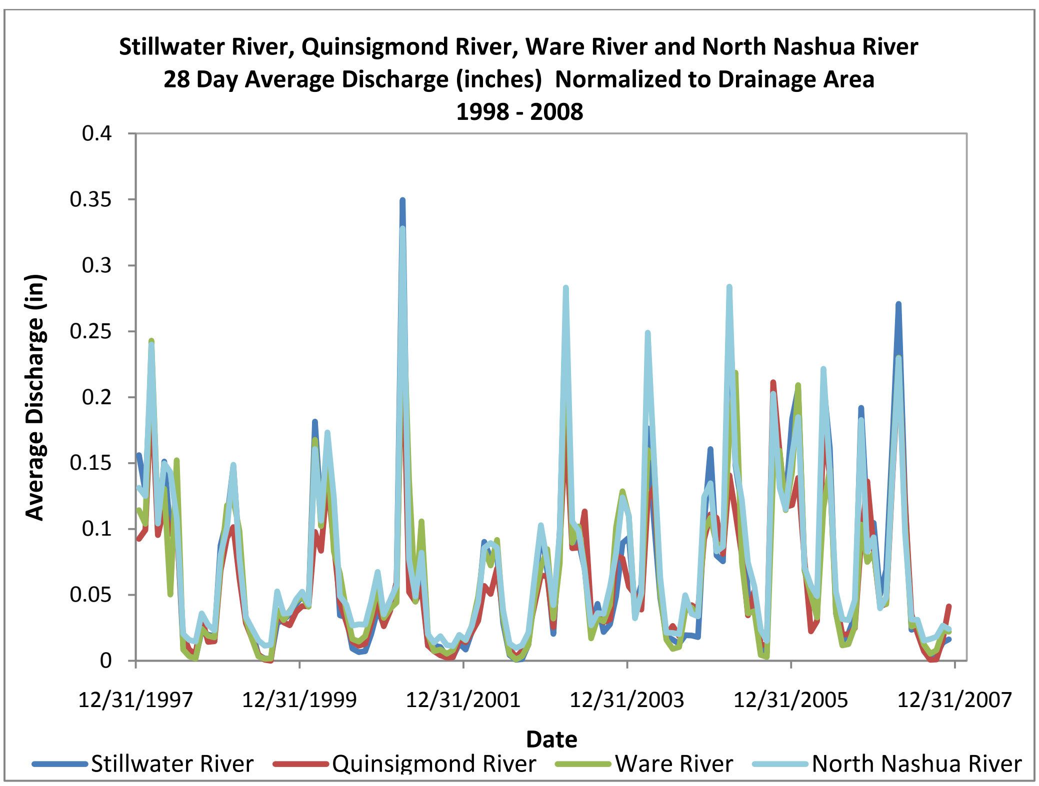

Figure 7: 28 day average flow rates for rivers used to analyze the regional consistency of flow measurements recorded at the Stillwater River gauging station (USGS, 2008).

2.1.1.3 Regional Drainage Analysis Conclusions

The strong correlation displayed by each of the Study River's flow rates with the flow rates recorded in surrounding rivers, after normalizing to drainage area extent, indicates that the flow rates recorded at the Stillwater River and the Saugus River gauging stations are representative of their respective regional trends in flow rate. Therefore, the findings in this study are not restricted to the studied watersheds, but are also indicative of general regional trends. Furthermore, the similarities in discharge characteristics indicate that any water quality differences seen between drainage basins in each region are due to land use changes and not a consequence of varying basin size.

3. PURPOSE AND SCOPE

This study is focused on the mechanisms of road salt return flow transport within urban (Saugus River) and rural (Stillwater River) watersheds in Massachusetts by investigating dissolved chloride loads and chloride concentration patterns over a span of four years. Deicing agents used during the winter season are removed either by direct runoff (event flow) to streams after their application during winter storms, or by percolation to groundwater and eventual discharge to streams via baseflow over a much longer period of time (decades). Using hydrograph traces and dissolved chloride loads calculated from specific conductance records, this study tracks the role of each return-flow mechanisms (event flow and baseflow) in removing roadway deicers from the environment following winter application on roadways. Both mechanisms are quantified and evaluated.

4. METHODOLOGY

4.1 Study Approach

Due to the fact that chloride is a common component of the most abundantly used deicing chemicals (NaCl, $CaCl_2$, $MgCl_2$) and the fact that chloride is the most conservative tracer in the environment of the cations and anions used in deicing chemicals (Kelly, 2008), chloride will be used as a proxy for roadway deicers and is the focus of this study. Currently there are no stream water chemical records with a high enough sampling frequency to accurately track chloride transport in the environment. Therefore, a new chloride tracking technique is developed for this study utilizing high-frequency (15-minute) streamflow and specific conductance records from the Saugus River and Stillwater River. We use specific conductance as a proxy for chloride concentrations (see section 4.1.1) and the volume of water discharged during each 15-minute measurement interval to calculate the dissolved chloride load removed from each system. This high-frequency dissolved chloride load dataset is partitioned into dissolved chloride removed from each system as baseflow and event flow throughout the year using hydrograph separation techniques on hydrograph records from each river. This technique allows us to track dissolved chloride load movement in urban and rural watersheds throughout four years and allows us to determine which return flow transport mechanism removes the most dissolved chloride from urban and rural watersheds. The four-year records (2003 – 2007) allow us to identify any innate yearly, monthly, or seasonal trends found in the transport of dissolved chloride and statistically validates any trends seen in one calendar year by comparing results between the four calendar years used for this study.

4.1.1 Specific Conductance as a Proxy for Chloride Concentration

Conductivity is a measure of a substance's ability to conduct electric current. In natural water, this is proportional to the ionic strength of the solution; therefore, as the concentration of ionic species present in solution increases, the conductivity of the solution also increases. Conductivity is measured using an electrode, which has a known functional electrode surface over which the resistance of the solution is measured (Wu et al., 1987). The conductivity of a solution is the reciprocal of resistivity or the reciprocal of ohm per centimeter with SI unit of Siemens per meter (S/m). Specific conductance is the conductivity of the solution normalized to 25^0 C and in natural water is reported in micro Siemens per centimeter (μS/cm)(Hem, 1985). The relationship between the conductivity of a solution and ion concentration in a solution is found in Equation 1, Kohlrausch's law of independent migration of ions (Kohlrausch, 1876).

$$\Lambda = \sum_{i=1}^{n} \nu_i \lambda_i \qquad [1]$$

Equation 1: Kohlrausch's law of independent migration of ions. Where Λ=molar conductivity of the solution, *n*=the total number of ionic species present in the solution, ν = the number of ions *i* in the solution, and λ= the molar ionic conductivity of ion *i*

The study by Kohlrausch found that the molar conductivity of a solution is equal to the sum of the concentration of each ion present in solution multiplied by that ion's molar conductivity. Kohlraush's law of independent migration reveals that the conductivity of a solution has linear relationship with the concentration of each ion present in dilute solutions (where Henrys Law can be applied), and the conductivity of a solution is equal to sum of the partial molar conductivities of all the ions present. Using this linear relationship between increased dissolved ion concentrations and increased specific conductance, specific conductance can be calibrated to estimate the concentrations of dissolved constituents (including chloride) in streams through empirical calibration(Hem, 1985). Using Table 4, the empirical relationship between specific conductance and chloride at infinite dilution is displayed in Equation 2.

$$Cl^{-} = 0.215 \times SC \qquad [2]$$

Equation 2: Empirical relationship between specific conductance (SC) in µS/cm and chloride (Cl^-) in mg/l.

Molar Conductivities of Ions in Infinitely Dilute Aqueous Solution at 298.15K	
Ion	Molar Conductivity ($S\ cm^2\ mol^{-1}$)
H^+	0.03498
Na^+	0.00501
K^+	0.00735
Mg^{2+}	0.01062
Ca^{2+}	0.0119
OH^-	0.01986
Cl^-	0.00764
SO_4^{2-}	0.016
CO_3^{2-}	0.01386

Table 4: Table of select ion (i in Equation 1) molar conductivities (λ in equation 1) at infinite dilution. Table adopted from Zhang, 2008. S is Siemens, cm is centimeters, mol is mole and K is degrees Kelvin.

Another study, conducted by Granato and Smith (1999) proved that specific conductance can be used to estimate the concentration of deicing chemical constituents in roadway runoff impacted by deicing chemical use using a semi-empirical model. The semi-empirical model was developed to estimate road salt constituents at high concentrations using specific conductance measurements (reaching over 50,000 μS/cm) in roadway runoff, where ion-ion interactions can alter the linear relationship between specific conductance and ion concentration (Granato and Smith, 1999). Continuous specific conductance records, when periodically calibrated to solute concentrations, like chloride, which is a proxy for road salt, in stream water can provide a valuable tool in analyzing water quality trends, avoiding temporal sampling bias.

4.1.2 Hydrograph Records

A perennial stream discharge hydrograph, such as the ones produced by the Saugus River and Stillwater River, fluctuates in response to groundwater table elevation, evapotranspiration, any water withdrawals, and intermittent recharge from precipitation events (Sloto and Buxton, 2005). In general, groundwater discharge to the stream will decrease with decreasing water table elevation. In general, water table elevation is highest in the spring and lowest in the fall, with temporary increases in groundwater discharge in response to water table elevation increases associated with precipitation event recharge (Pettyjohn and Henning, 1979). Streamflow discharge has been found to have multiple components contributing to the overall discharge recorded at any given time. Flow directly associated with precipitation events can be split into two parts, overland flow, and interflow (Barnes, 1939). Overland flow takes place during the rising and falling limb of the hydrograph trace (Figure 8) and is a result of direct runoff from precipitation that enters the river by flowing on the ground surface to the river. Interflow results from flow within the upper vadose zone to the stream channel and occurs primarily during the falling limb of the hydrograph trace (Figure 8). For the purposes of this study, we will be treating overland flow and interflow as one hydrologic element called event flow. We have combined overland flow and interflow into one unit in this study because both hydrograph components discharge water received during a single precipitation event within days of the precipitation event, while water that infiltrates to the water table can take years to discharge to streams, therefore they will be treated as two different modes of water transport. Water that infiltrates to the groundwater table is eventually transported to a stream and discharged as baseflow or groundwater recharge to the stream (Barnes, 1939). After event flow has subsided, flow in a stream is dominated by groundwater discharge to a stream, see Figure 8 for a visual representation. By partitioning the streamflow and estimated chloride concentration records into baseflow and event flow components, we can use the partitioned records to calculate dissolved chloride load in each of these two hydrograph components and track the movement of dissolved chloride in the environment.

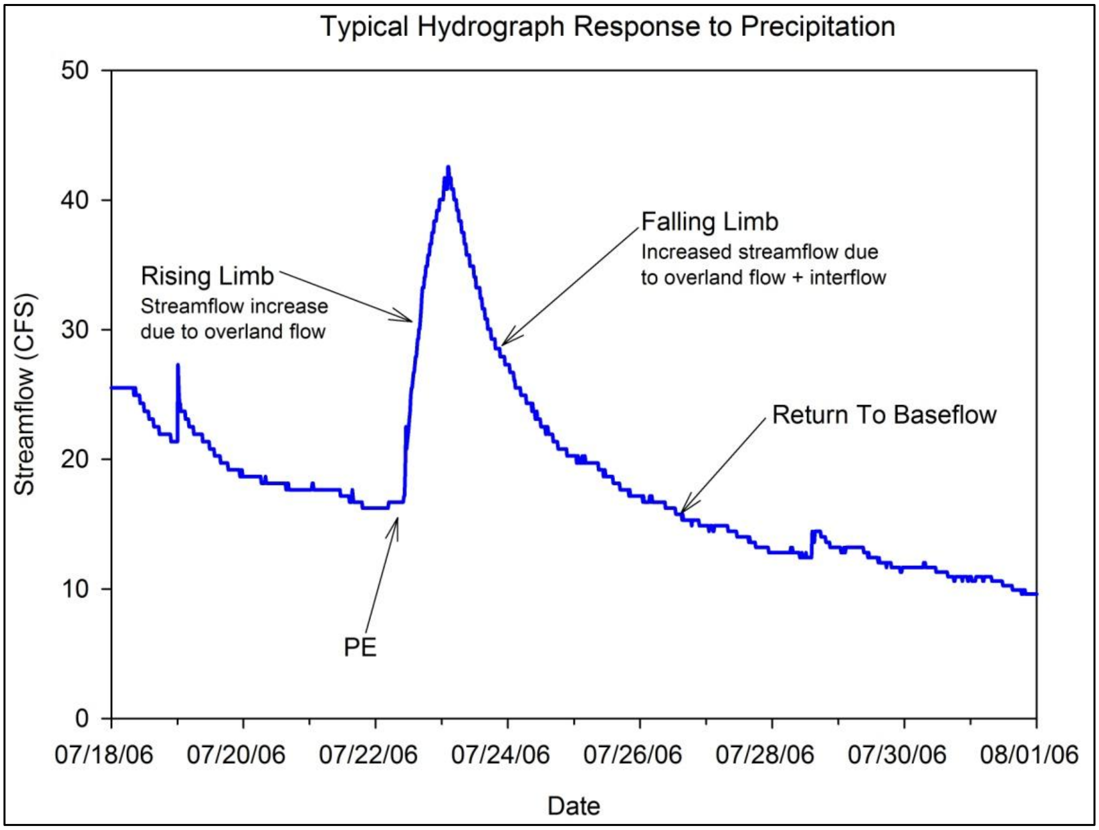

Figure 8: Typical hydrograph trace response to precipitation taken from the Stillwater River. PE stands for approximate beginning of precipitation event.

4.2 Data Sources and Data Quality

Four-year (1/1/2003 – 1/1/2007), high-frequency (15-minute) specific conductance and discharge datasets collected from Saugus River (USGS Station ID # 01102345) and Stillwater River (USGS Station ID# 01095220) were obtained from Linda Comeau at the USGS(Comeau, 2007) for use in this study. The Saugus River and Stillwater River are both part of a fixed site monitoring network of which there are 9 other real-time monitoring stations collecting simultaneous discharge and specific conductance measurements in Massachusetts (USGS, 2008). Each four-year dataset for the Saugus River and

Stillwater River consists of 140,255 records that are collected every 15 minutes. Each of the 140,255 15-minute records consists of: (1) Date/Time stamp, (2) specific conductance value recorded in micro Siemens per centimeter (µS/cm), and (3) streamflow rate calculated using the gauge height and a rating curve developed by the USGS and reported in cubic feet per second (CFS). The datasets for the Saugus River and Stillwater River used in this study were obtained in raw form with no alteration by the USGS before use (Comeau, 2007).

The Saugus River and the Stillwater River are also included in the 8 rivers that are part of the USGS National Water Quality Assessment Program (NAWQA) as part of the New England Coastal Basin study area (Campo, Flanagan and Robinson, 2003). As part of the NAWQA study, multiple water quality parameters were collected monthly at 8 rivers in New England from October 1998 to September 2001. These data include concentrations of chloride and specific conductance measurements made at the time of sampling that are used to calibrate chloride concentration to specific conductance values as discussed in section 4.4.

4.2.1 Review of Data Quality

The four-year specific conductance and stream discharge records measured by the USGS at the Saugus River and Stillwater River gauging stations were manually inspected for missing values as reported by the USGS, and abnormal data points. Missing values as reported by the USGS are considered the result of periodic equipment maintenance, equipment replacement, or telemetry malfunction. Abnormal data points are selected by visually locating data abnormalities during periods of data reported as estimated by the when downloading daily average data from the USGS. Daily data reported as estimated by the USGS indicates that, during that particular day, USGS personnel found data abnormalities and estimated values during that day using surrounding watersheds or removed small sections of data from the daily average (Comeau, 2007).   The raw streamflow and specific conductance datasets from the Saugus River and Stillwater River were visually inspected for periods of data abnormalities only during days where the USGS reported streamflow or specific conductance averages as estimated. This technique was employed to prevent data elimination bias. The periods of data abnormalities included: 1) negative specific conductance measurements; 2) specific conductance measurements that did not respond to increases in streamflow; 3) discharge records not producing a hydrograph response during periods of increased streamflow; 4) specific conductance measurements responding to tidal influence (Saugus River only); 5) apparent instrumental calibration drift. The circled section of Figure 9, plot A displays an example of specific conductance values changing rapidly with no discharge fluctuation, indicating a potentially inaccurate section of specific conductance data. Figure 9, plot B displays an example of specific conductance values that slowly decrease over time until apparent calibration back to the baseline level of specific, indicating apparent calibration drift in the specific conductance sensor. The circled section in Figure 9, plot C displays an example of stream discharge records that are not creating hydrograph responses to precipitation. In this example, the discharge decreases at an unnaturally rapid rate. Figure 9, plot D displays tidal influence in the Saugus River specific conductance record with specific conductance values periodically reaching over 10,000 μS/cm. The circled portion of Figure 9 plot E displays an example of negative specific conductance values. Upon the identification of abnormal discharge rate or specific conductance measurements, similar to the examples displayed in Figure 9, the data point in question along with the corresponding discharge or specific conductance measurement are removed from the datasets in an attempt to rid the datasets collected at the Saugus River and Stillwater River of values not representative of the system.

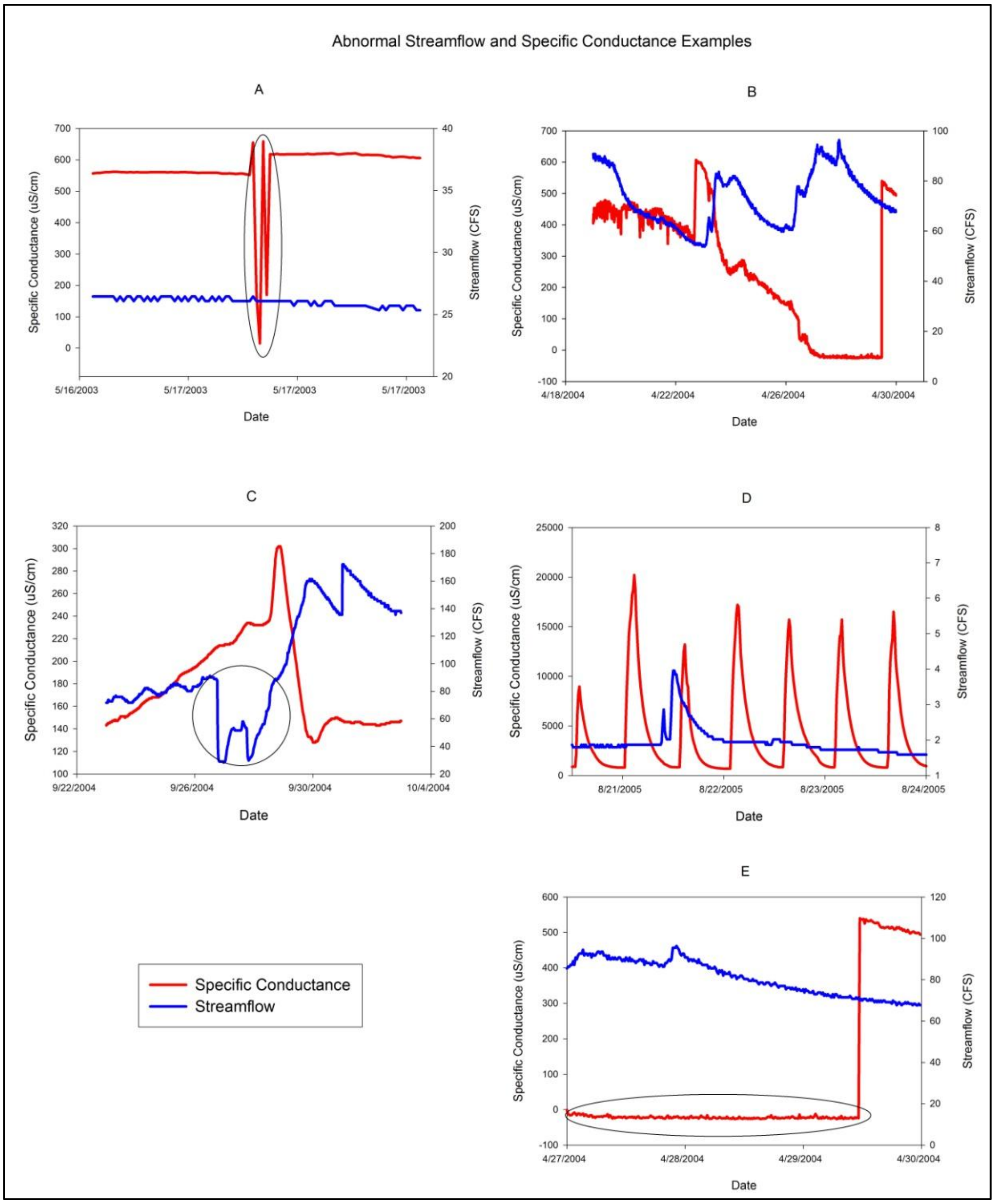

Figure 9: Examples of visually identified abnormal specific conductance and discharge recordings in the Saugus River and Stillwater River. Plot A is an example of specific conductance fluctuating during a period of steady discharge in the Saugus River. Plot B is an example of specific conductance calibration drift in the Saugus River where measurements are not expected or erratic. Plot C is an example of discharge measurements not producing an expected hydrograph for an apparent precipitation event in the Stillwater River. Plot D is an example of tidal influence (Saugus River data only). Plot E is an example of negative specific conductance measurements due to instrumental malfunction in the Stillwater River.

4.2.1.1 Saugus River

The four-year specific conductance and discharge rate datasets collected at the Saugus River gauging station had a total of 140,255 data points, 15,116 of which (approximately 11%) are either missing or declared abnormal and not included in this study. Table 5 displays the number of missing and abnormal data points determined during the manual assessment of the data collected at the Saugus River broken up by year. As can be seen from Table 5, 2004 contained the most missing and abnormal data points, with 2006 having the least number of total missing and abnormal measurements. All missing or abnormal data records found in the Saugus River datasets are not used as part of this study in order to more accurately represent the conditions in the Saugus River

Saugus River Missing/Abnormal Discharge or Specific Conductance Measurements 2003- 2007				
Year	2003	2004	2005	2006
Abnormal measurements	4520	7646	1751	0
Missing measurements	0	1068	0	131
Total number of missing or abnormal measurements	4520	8714	1751	131
Percent missing or abnormal of total collected	12.9	24.8	5.0	0.4

Table 5: Missing or abnormal measurements made in the Saugus River from 2003 – 2007 as identified during the manual data quality analysis. All measurements are acquired from the USGS (USGS, 2008) as 15 minute specific conductance and discharge measurements. Data only inspected for abnormalities during days reported as estimated by the USGS (USGS, 2008).

4.2.1.2 Stillwater River

The four-year specific conductance and discharge records collected at the Stillwater River gauging station had a total of 140,255 data points, 16,646 of which (approximately 12%) are either missing or declared abnormal and not included in this study. Table 6 displays the number of missing and abnormal data points determined during the manual assessment of the data retrieved from the Stillwater River, broken up by year. As can be seen from Table 6, 2004 contained the most missing and abnormal data points, with 2005 having the least number of total missing and abnormal measurements. Discharge rate measurements collected from 5/16/2004 – 11/4/2004 are assumed abnormal due to a malfunctioning discharge sensor, due to the fact that the discharge rate was not producing typical hydrologic responses to precipitation events as first described by Barnes (1939). During this same time period, the specific conductance sensor remained operational. This assumption was confirmed by the fact that daily streamflow averages as reported by the USGS are labeled estimates and are not calculated using the Stillwater River discharge sensor, but the specific conductance was not missing during this same timeframe (USGS, 2008). Due to the fact that approximately 47% of the discharge data collected during 2004 is unusable for this study, the decision was made to fill in the missing discharge values with daily average discharge estimates for the period of missing data in 2004, as reported by the USGS (USGS, 2008). This is done in order to preserve the specific conductance data recorded in the Stillwater River during this time period. The estimated average discharge rates are calculated using discharge data collected at surrounding rivers, during the same time period and can therefore be considered an accurate estimate of the discharge rate in the Stillwater River, see Regional Drainage Analysis (section 2.1.1).

Stillwater River Missing/Abnormal Discharge or Specific Conductance Measurements 2003 – 2007				
Year	2003	2004	2005	2006
Abnormal measurements	0	16512	0	0
Missing measurements	1	0	0	133
Total number of missing or abnormal measurements	1	16512	0	133
Percent missing or abnormal of total collected	0.0	47.0	0.0	0.4

Table 6: Missing or abnormal measurements made in the Stillwater River from 2003 – 2007 as identified during the manual data quality analysis. All measurements are acquired from the USGS (USGS, 2008) as 15 minute specific conductance and discharge measurements. Data only inspected for abnormalities during days reported as estimated by the USGS (USGS, 2008).

4.3 Hydrograph Separation

To track the movement of chloride in baseflow or storm event flow, the four-year hydrograph traces from the Saugus River and Stillwater River needs to first be separated into baseflow and event flow components. Currently, the most common technique for conducting hydrograph separation on multiyear discharge datasets is a USGS computer program, HYSEP (Sloto and Crouse, 1996). HYSEP uses daily average discharge records to automate hydrograph separation. However, the discharge records used in this study are composed of discharge measurements recorded every 15 minutes, making the use of HYSEP impossible without a significant loss of resolution within each dataset (see section 0). A study by Mau and Winter in 1997 also found that differences in baseflow estimations made using manual and automated hydrograph separation techniques were not statitstically significant. Therefore, this study will utilize a manual estimation of baseflow recession constants in each river by identifying periods of streamflow dominated by groundwater discharge to the stream first developed by Barnes (1939) and improved upon by Pettyjohn et al. (1979) and Vogel et al. (1996). These recession constants are used in a digital filter to extract periods of baseflow from the hydrograph records. Baseflow will be estimated between periods of identified baseflow using cubic spline interpolation. Discharge greater than interpolated baseflow between periods of identified baseflow are quantified as event flow.

4.3.1 Identifying Baseflow Recession Constants

Baseflow recession constants in the Saugus River and Stillwater River are identified in order to separate hydrograph traces into a baseflow and event flow component. Each river has consistent recession curves based primarily on the topography, geology and the water table elevation within a given watershed at any given moment in time. Event flow, or flood responses to precipitation events, is superimposed on consistent groundwater discharge recession curves (Pettyjohn and Henning, 1979). The constant recession curves produced by groundwater discharge to the Stillwater River and Saugus River as suggested by Barnes (1939) and Pettyjohn and Henning (1979) are visually identified during periods of constantly decaying discharge, and the slope of the recession curves is calculated by straight line approximation on semi-log plots of stream discharge. Figure 10 and Figure 11 display the four-year hydrograph traces from the Saugus River and Stillwater River respectively, split up into 6 month sections. Each plot contains straight line estimations of baseflow recession constants drawn in green during periods of discharge determined to be dominated by groundwater discharge to the stream and the hydrographs are displayed in semi-log scale with the y axis in log scale in order to make baseflow recession constants linear (Vogel and Kroll, 1996), thus making linear estimations of baseflow recession constants possible. The average decay constants for the Saugus River and Stillwater River are -0.012 CFS/hour $\pm$ 0.005 CFS/hour and -0.008 CFS/hour $\pm$ 0.004 CFS/hour respectively. The high standard deviation in decay constants within each site are the result from error incurred during manual estimation of baseflow recession constants. However it should be noted that a study by Mau and Winter in 1997 found that despite error incurred during manual estimation of baseflow recession constants, the differences in total amount of baseflow identified using manual and automated techniques (such as the ones used in HYSEP) were not statistically significant (Mau and Winter, 1997). For a more detailed discussion of the error incurred using visual estimations of baseflow recession constants see section 4.3.3.1.

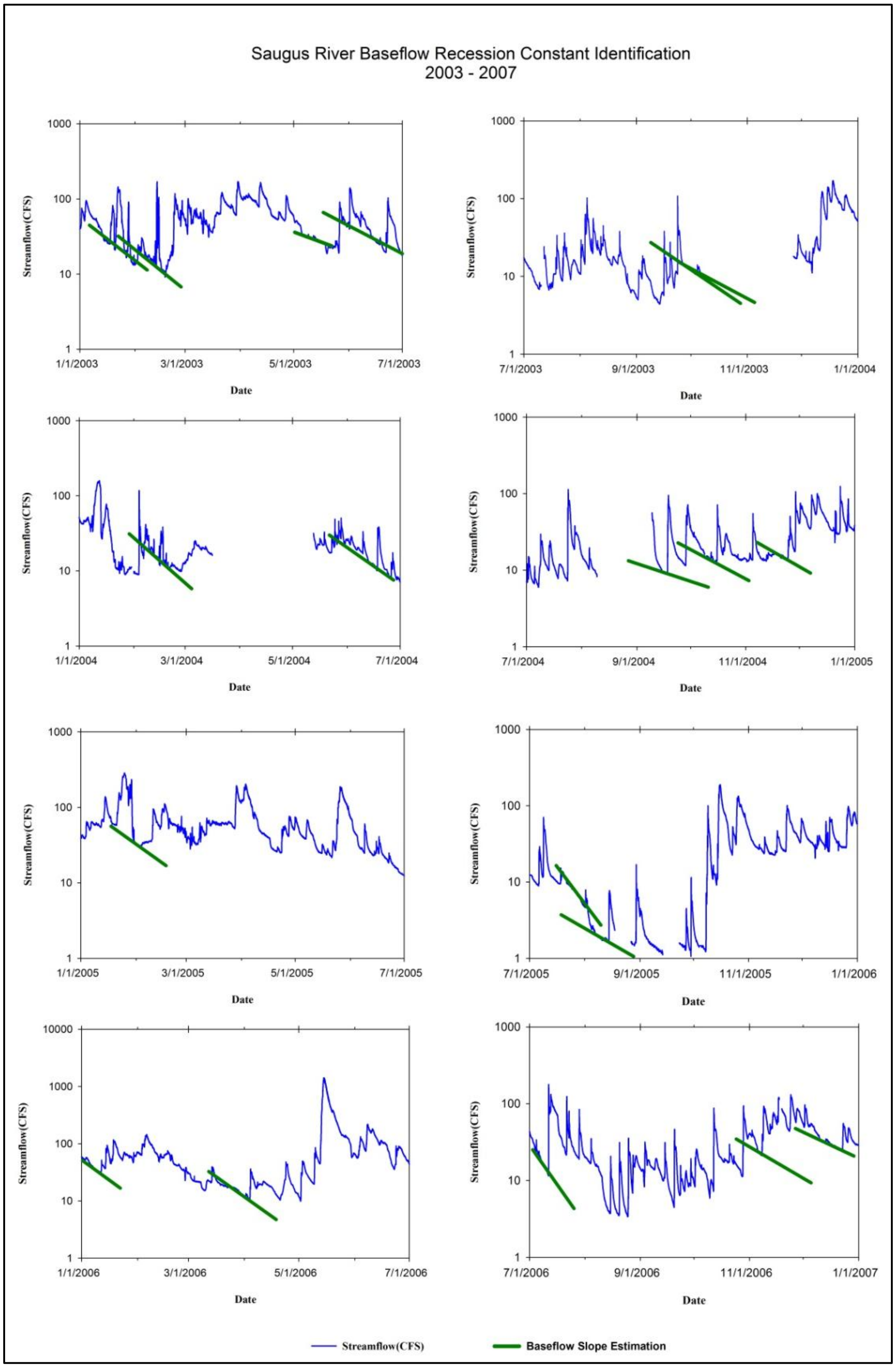

Figure 10: Visual baseflow recession constant estimation for the Saugus River. Hydrographs are split into 6 month periods and displayed in semi-log scale for in order for baseflow recession to plot as a linear decay constant (Vogel and Kroll, 1996).

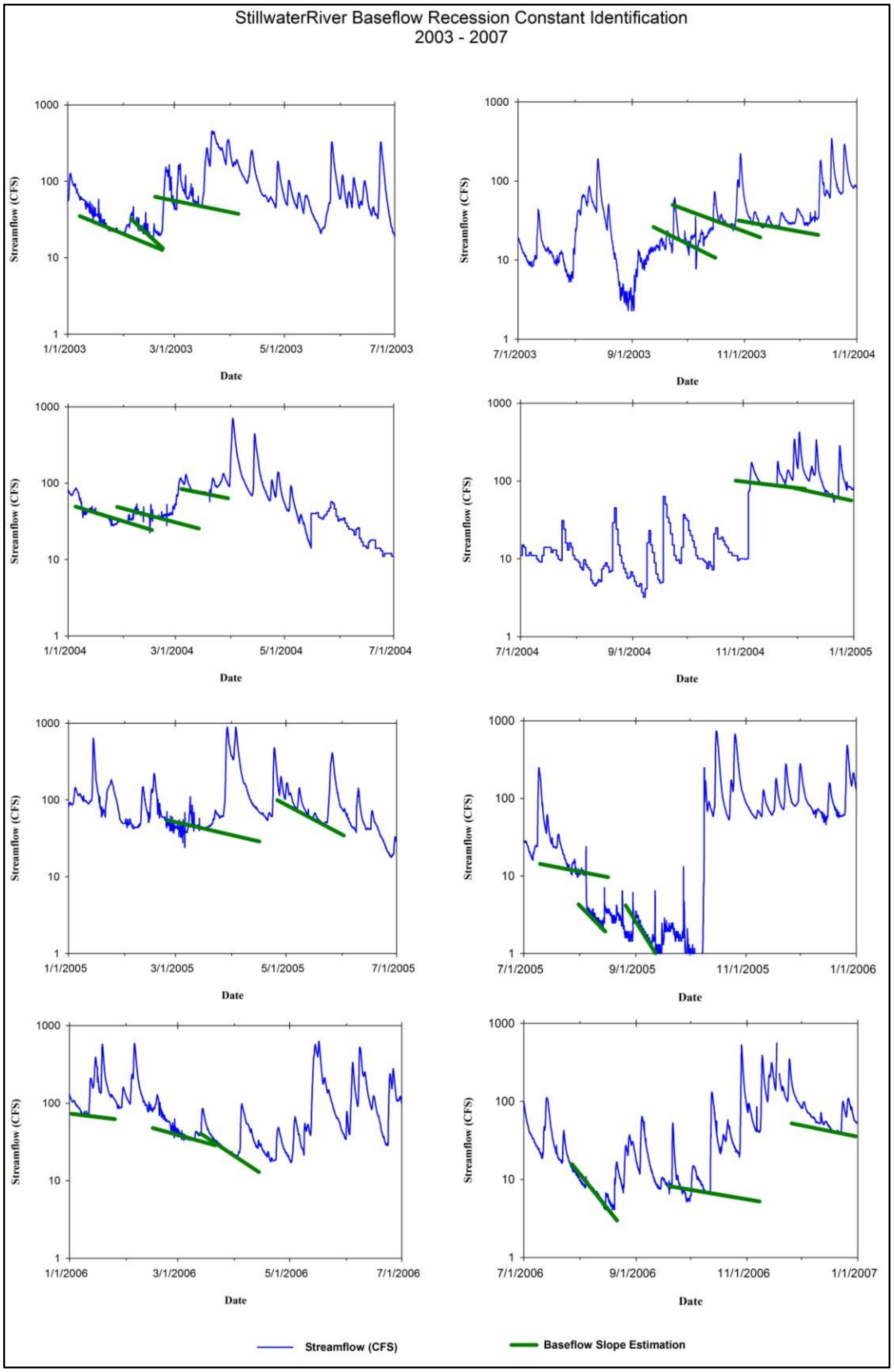

Figure 11: Visual baseflow recession constant estimation for the Stillwater River. Hydrographs are split into 6 month periods and displayed in semi-log scale in order for baseflow recession to plot as a linear decay constant (Vogel and Kroll, 1996).

4.3.2 Separation of Streamflow into Baseflow and Event Flow Components

Using the average baseflow recession constants for the Saugus River and Stillwater River the four-year discharge records from each river are split into a baseflow component and an event flow component. The four-year discharge records are averaged into half hour readings to facilitate the filter process and smoothed using a 21 point weighted moving average filter to remove signal noise in the records. Data gaps in the records as identified in section 3 are filled with linear trendlines between the two points before and after the data gap. Once smoothed, a fixed five-hour window digital filter is run on each dataset filtering out any five-hour periods where the discharge rate is decaying faster than the discharge rate designated as baseflow for each river, or where discharge rate is found to be increasing. This filter parameter equaled -0.047 CFS/4 hours and -0.034 CFS/4 hours for the Saugus River and Stillwater River respectively. After running a fixed window digital filter on the datasets any values found above two standard deviations of the average discharge rate in the new baseflow discharge datasets are removed in order to rid the dataset of storm flow peaks erroneously identified as baseflow. After filter completion, the baseflow filter identified 15% of the data points collected at the Saugus River gauging station as baseflow and 11% of the data points collected in the Stillwater River as baseflow. Each streamflow data point determined to be baseflow has a corresponding specific conductance data point that was collected simultaneously so is also deemed a baseflow specific conductance data point, creating both specific conductance and streamflow datasets for baseflow components of the hydrographs. The gaps in the new baseflow datasets (streamflow and specific conductance) for each river are connected using cubic spline interpolation, creating full four-year baseflow discharge datasets for each river. Figure 12 displays the estimated baseflow stream discharge records from 2003 to 2007 superimposed on the total discharge records for the Saugus River and Stillwater River. The baseflow datasets are then subtracted from the total flow datasets in order to create event flow streamflow and specific conductance datasets over the four-year period of record for the Saugus River and Stillwater River.

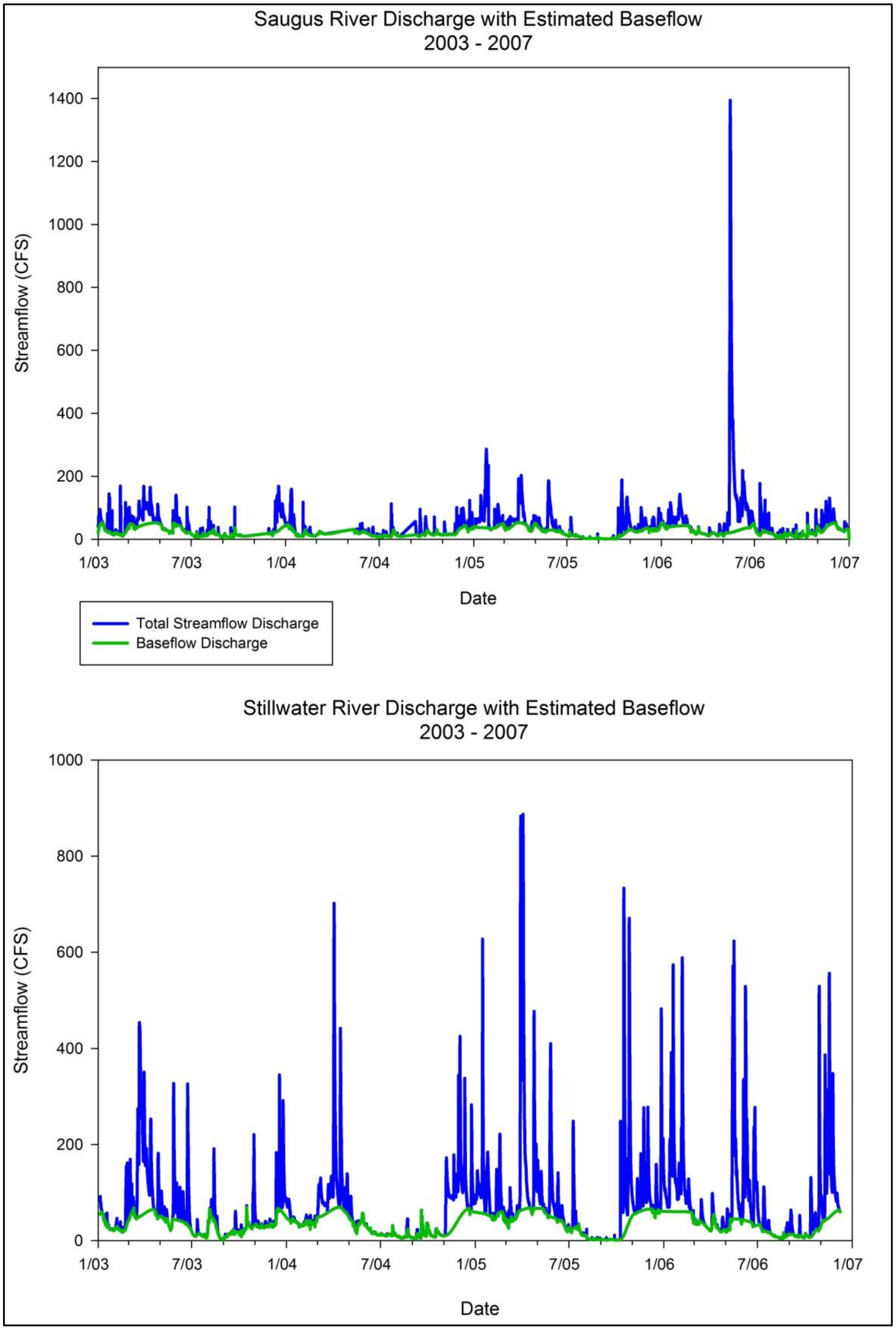

Figure 12: Estimated baseflow discharge and total discharge data from the Saugus River and the Stillwater River. Baseflow discharged estimated using 5-hour fixed window filter and baseflow recession constant designated for each river (Section 4.3.1).

4.3.3 Hydrograph Separation Results

The results of the hydrograph separation can be found in Table 7 and Table 8 for the Saugus River and Stillwater River respectively, all values are normalized to each rivers' drainage area extent. Over the four-year period of record the Saugus River discharged an average of 23.5 inches of water per year, 53.7% of which is designated as coming from groundwater recharge (or baseflow) to the Saugus River. The Stillwater River discharged an average of 31.4 inches of water per year over the four-year period of record with 44.4% designated as groundwater recharge to the Stillwater River. The results of the hydrograph separation during 2004 for the Saugus River resulted in a comparatively low amount of event flow resulting in 72.2% of the total discharge during 2004 to be designated as baseflow when compared to hydrograph separation results from 2003, 2005 and 2006. This number is most likely skewed due to missing periods of discharge data during the spring of 2004 in the Saugus River dataset. The missing streamflow data in the Saugus river dataset could also explain why the Saugus River discharged an average of 7.9 inches of water per year less than the Stillwater River over the four-year period of record.

Saugus River Hydrograph Separation Results				
Year	Total Discharge (in)	Baseflow Discharge (in)	Event Flow Discharge (in)	Baseflow Percent
2003	22.0	12.3	10.0	55.9
2004	14.9	10.7	4.1	72.2
2005	24.6	13.9	11.5	56.7
2006	32.4	13.4	19.4	41.4
Average	**23.5**	**12.6**	**11.2**	**53.7**

Table 7: Hydrograph separation results from Saugus River discharge records normalized to Saugus River watershed drainage area.

Stillwater River Hydrograph Separation Results				
Year	Total Discharge (in)	Baseflow Discharge (in)	Event Flow Discharge (in)	Baseflow Percent
2003	27.4	12.1	15.3	44.3
2004	25.2	12.7	12.5	50.5
2005	38.5	17.3	21.3	44.8
2006	34.6	13.7	20.9	39.5
Average	**31.4**	**14.0**	**17.5**	**44.4**

Table 8: Hydrograph separation results from Stillwater River discharge records normalized to the Stillwater River watershed drainage area.

4.3.3.1 Hydrograph Separation Reliability Assessment

The fact that the hydrographs from the Saugus River and Stillwater River are separated by manually estimating the baseflow recession constant for each river introduces error into the estimation of the baseflow and event flow components of each river's four-year hydrograph. However, currently there are no automated processes that use high-frequency datasets to conduct hydrograph separations. Baseflow recession constant estimation error for each river can be seen in section 4.3.1, with estimation error for both the Saugus River and Stillwater River at near 50% of the average baseflow recession estimate.

However, when baseflow recessions constants are increased by 1 standard deviation of the mean for the Saugus River and Stillwater River, the amount of flow designated as baseflow changes by less than 5% in both rivers. Bent (1999) used the USGS automated hydrograph separation program HYSEP (Sloto and Crouse, 1996) on hydrographs from 11 sub-basins within the Housatonic watershed in western Massachusetts and found that the baseflow component of stream hydrographs ranges from 45.5% to 85.0% of the total discharge recorded at each of the 11 sites. When comparing the results of the hydrograph separation conducted on the Saugus River and Stillwater River hydrographs as part of this study with the results produced by Bent (1999), we see that the results of our analysis (Table 7 and Table 8) fall near the range of baseflow contribution to streamflow found by Bent (1999). The results of the Saugus River 2006 hydrograph separation analysis found that the baseflow contribution to the Saugus River is low when compared to the results reported by Bent (1999), however this is most likely due to large amount of total streamflow in 2006 when compared to 2003, 2004, and 2005. The results of the Stillwater River hydrograph separation analysis found that the baseflow contribution to the Stillwater River is low when compared to the results reported by Bent (1999) in all years except 2005. The slightly lower (less than 6%) baseflow component seen in the Stillwater River compared to the results reported by Bent (1999) could be due to slight regional changes in substrate, elevation, and slope between the Berkshire Mountains in western Massachusetts (where Bent did his study) and central Massachusetts. The fact that the baseflow components found during this hydrograph separation analysis are similar to the results found in the same geographic region and the fact that changing the baseflow recession constants 1 standard deviation of the mean found in each stream does not significantly change the results of the hydrograph separation lends credibility to the results found in this study.

4.4 Specific Conductance and Chloride Concentration Interdependence

As mentioned in section 4.1.1, specific conductance can be used as an estimator of chloride concentration. A previous study estimating chloride concentrations in natural water using specific conductance conducted by Granato and Smith (1999) used a semi-empirical model to determine road salt constituent concentrations in surface water using specific conductance data. The reason for choosing a semi-empirical model is to use a small number of complete water quality analyses to calibrate specific conductance data to road salt constituents including dissolved chloride, sodium, and calcium. However, when a larger dataset, such as the NAWQA dataset (Campo, Flanagan and Robinson, 2003) of surface water quality data exists, an empirical model such as suggested by Hem (1985) for determining chloride concentration using specific conductance may be preferred because it accounts for localized effects other dissolved constituents have on specific conductance in individual rivers, therefore minimizing error.

Specific conductance and dissolved chloride data from all 8 rivers that are part of the New England Costal Basin study area of the NAWQA program is used to conduct linear regression analyses between chloride concentrations, and specific conductance. The regression analysis is done to test for regional consistency in regression results and provide further justification for the use of an empirical model for this study. Table 9 displays the results of linear regression analyses conducted using data from all 8 rivers, including the Saugus River and Stillwater River. Table 9 also displays the range of specific conductance measurements at each river and the number of samples used in the linear regression analysis after all outliers had been removed. As can be seen from Table 9, the R^2 values and slopes for each river are within 95% of the average value for all rivers. The average slope found in this analysis is also within 10% of the theoretical slope between dissolved chloride and specific conductance found in Equation 2. The low regional variation in slope and the fact that the average slope found in Table 9 and was close to the theoretical slope between specific conductance and chloride concentration provides additional justification for the use of linear regression analyses to determine chloride concentration from specific conductance measurements.

	Conductance Range (µS/cm)	Number of Measurements	R^2	Slope	y Intercept	P Value
Stillwater River	56 - 171	37	0.918	0.201	-2.067	<0.001
Merrimack River	83 - 277	38	0.958	0.230	-5.969	<0.001
Wading River	148 - 290	28	0.823	0.225	-3.431	<0.001
Neponset River	176 - 297	27	0.934	0.242	-9.027	<0.001
Ipswich River	166 - 439	41	0.818	0.240	-7.019	<0.001
Saugus River	160 - 830	38	0.975	0.244	-13.009	<0.001
Charles River	219 - 877	62	0.974	0.260	-15.588	<0.001
Aberjona River	150 - 1010	87	0.882	0.245	-20.884	<0.001
Average			**0.910**	**0.236**	**-9.624**	
Standard Deviation			**0.063**	**0.017**	**6.434**	

Table 9: Results of linear regression analyses on specific conductance and chloride concentration data collected from 8 rivers in New England as part of the NAWQA program (Campo, Flanagan and Robinson, 2003).

The specific conductance measurements, coupled with chloride concentration data in the Saugus River and Stillwater River are then used to calibrate the specific conductance recorded in each stream to chloride concentrations measured during each monitoring event. Figure 13 displays specific conductance and chloride concentrations at the Saugus and Stillwater Rivers as well as Bootstrap correlation analyses conducted on the data. The Bootstrap correlation analyses are conducted to test the validity of an apparent outlier among each dataset. The results of both Bootstrap correlation analyses that included the outliers is a bimodal distribution of correlation coefficients, while the results of the Bootstrap correlation analyses for each river conducted with the outliers omitted is normally distributed (see Figure 13 for histograms of Bootstrap analysis results). Due to this fact, and the fact that after conducting an initial regression analysis on the entire datasets the residuals for each outlier is greater than 5 standard deviations away from the respective estimated values, the outliers in each dataset are not used during the final linear regression.

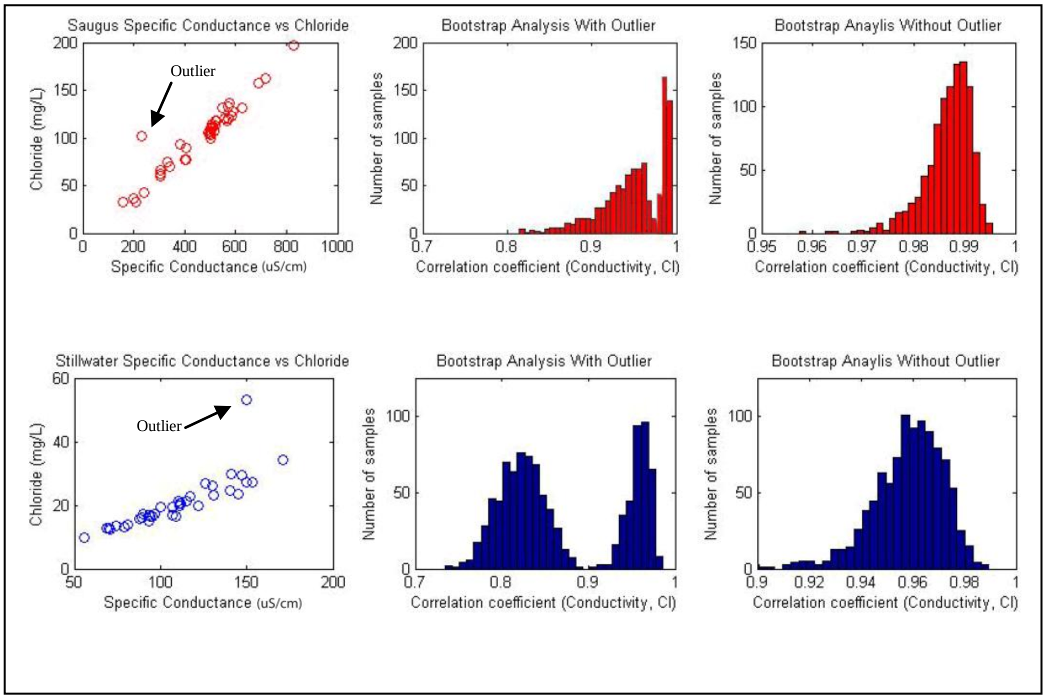

Figure 13: Specific Conductance and chloride concentration data are displayed for the Saugus and Stillwater Rivers. A Bootstrap analysis is conducted on each river with and without a suspected outlier. The Bootstrap analyses consisted of creating 1000 random datasets of specific conductance and chloride concentration data from each river's original datasets by sampling with replacement and conducting a correlation coefficient analysis on each dataset. Specific Conductance and Dissolved chloride data are from the USGS NAWQA program (Campo, Flanagan and Robinson, 2003).

4.4.1 Chloride Concentration Equations for the Saugus River and Stillwater River

The linear calibration equations for the Saugus River and Stillwater River are calculated through linear regression analysis conducted on specific conductance and chloride concentration NAWQA data (Campo, Flanagan and Robinson, 2003) excluding data points found to be outliers in Section 4.4. R^2 values in Figure 14 reported during the regression analyses show a strong covariance between the two variables in each river and over 90 percent of the variation in dissolved chloride concentrations can be explained by changes in specific conductance measurements in each river. Low P values (<0.001) reported during the regression analyses indicate that the linear relationship found between specific conductance and chloride concentration in each river are not the result of random chance. Figure 14 also displays the residual data from the correlation analysis. The average absolute percent error for the Saugus River and Stillwater River calculated chloride concentrations using the equations displayed in Figure 14 are 5.22% and 5.78% respectively.

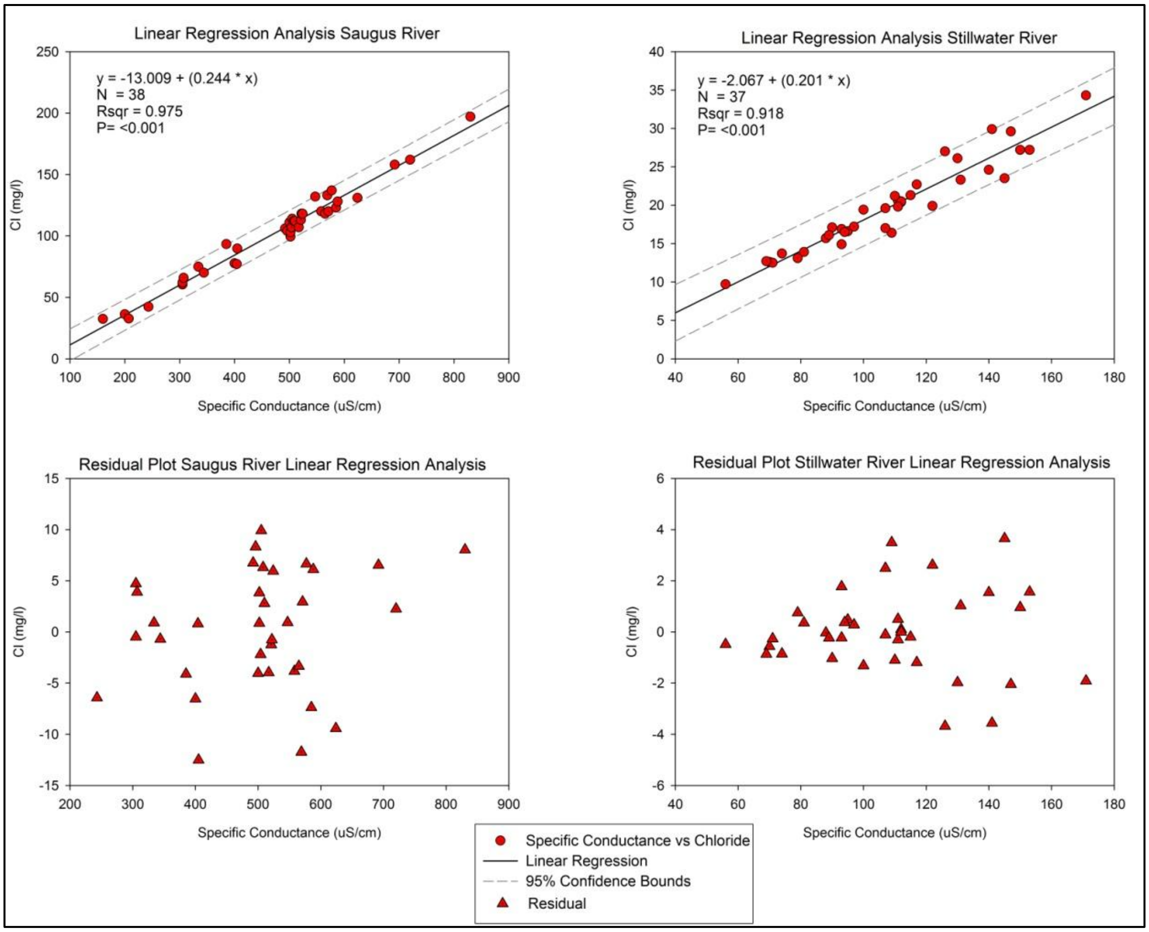

Figure 14: Linear regression analysis conducted using specific conductance measurements and dissolved chloride concentration values from the Saugus River (left) and the Stillwater River (right). Data are collected monthly from October 1998 – September 2001 as part of the USGS NAWQA program (Campo, Flanagan and Robinson, 2003).

The empirical calibration equations for the Saugus River (Equation 3) and the Stillwater River (Equation 4) are used to determine chloride concentrations using specific conductance values at each river's gauging station. It should be noted that specific conductance values in each river can exceed as much as five times the highest specific conductance value used in the regression analyses. In this case, the empirical equation is extrapolated beyond the range defined by the regression datasets. However, a study by Hem (1985) found that the linear relationship between dissolved chloride and specific conductance does not vary significantly in natural waters until a specific conductance of approximately 12,000 - 14,000 μS/cm is reached, at which point the slope of the line increases. The maximum specific conductance value reached in either the Saugus River or the Stillwater River during the four-year records is approximately 5,000 μS/cm, well within the linear range suggested by Hem (1985).

$$Cl^- = 0.244 \times SC - 13.009 \qquad [2]$$

Equation 3: Saugus River empirical equation for estimating chloride concentration from specific conductance measurements. Where Cl^- = chloride concentration in mg/L and SC = specific conductance in μS/cm.

$$Cl^- = 0.201 \times SC - 2.067 \qquad [3]$$

Equation 4: Stillwater River empirical equation for estimating chloride concentration from specific conductance measurements. Where Cl^- = chloride concentration in mg/L and SC = specific conductance in μS/cm.

4.5 Dissolved Chloride Loads

The linear relationship between specific conductance and chloride concentrations allowed for the estimation of chloride concentration in the Saugus River and Stillwater River at each 15-minute specific conductance value. Equation 5 uses the chloride concentration estimated every 15 minutes in each river, coupled with the discharge measured every 15 minutes to calculate the load of dissolved chloride moving through each system in kg of dissolved chloride per hour. This total load of dissolved chloride is then further broken up into flow components of baseflow and event flow using periods of discharge and chloride concentration designated as either event flow or baseflow. This allows us to track the movement of dissolved chloride in these different transport components within the Saugus and Stillwater watersheds.

$$Cl\ load_{\left(\frac{kg}{Hour}\right)} = \left(Cl^{-}_{\left(\frac{mg}{L}\right)} \times \frac{kg}{1{,}000{,}000mg}\right) \times \left(Q_{\left(\frac{ft^3}{\sec}\right)} \times \frac{28.317L}{ft^3}\right) \times \frac{3{,}600sec}{Hour} \qquad [4]$$

Equation 5: Equation used to calculate dissolved chloride load using estimated Cl concentrations and discharge measurements. Where: *Cl load* is in kg/Hour; *Cl* is the estimated dissolved chloride concentration in mg/L; and *Q* is the discharge in CFS or ft^3/sec.

4.5.1 Dissolved Chloride Load Reliability Assessment

In order to evaluate the reliability of the calculated dissolved chloride load moving through the Saugus River and the Stillwater River, the dissolved chloride load discharged by each system is calculated using the data collected during the NAWQA study. The calculated dissolved chloride loads in each river are then compared to the estimated dissolved chloride load discharged by each system calculated using the linear equations used to estimate chloride concentration from specific conductance values (Section 4.4) recorded during the NAWQA study. The results of this reliability assessment can be found in Table 10. As can be seen in Table 10, the comparison of means t-test conducted on each river's datasets indicates that the null hypothesis cannot be rejected and the means are not different at the 99% confidence level. The average percent error incurred by estimating dissolved chloride load using specific conductance values and the linear equation between specific conductance and chloride concentration is 5.19% and 5.78% in the Saugus River and Stillwater River respectively. The results of the reliability assessment suggest that the calculated dissolved chloride load values are representative of the actual dissolved chloride load discharged by Stillwater River and Saugus River.

Dissolved Chloride Load Reliability Assessment		
	Saugus River	**Stillwater River**
Number of data points	39	38
Average absolute error (kg/hour)	25.51	6.28
Standard deviation absolute error (kg/hour)	42.26	9.47
Average % error	5.19	5.78
Paired t-test P value	0.88	0.94

Table 10: Data for the dissolved chloride load reliability assessment are from the USGS NAWQA program (Campo, Flanagan and Robinson, 2003). Error was calculated by subtracting the Cl load estimated using specific conductance measurements in each river from the dissolved chloride load calculated using chloride concentration values reported during each monitoring event at each river.

5. DATA

The stream gauge and conductivity sensors used in data collection are periodically calibrated and maintained by the USGS to provide high data quality for general public use (USGS, 2007). All data used in this study are available in the USGS archives.

The high-frequency (15-minute interval) datasets used in this study are assumed to capture the slightest changes in streamflows and specific conductivities. Using a similar sensor as the one used by the USGS to collect specific conductance and discharge values in Massachusetts rivers we have found that in general, streamflow and specific conductance values very slightly and linearly over small time intervals (less than 15 minutes) and larger variations are observed on the order of hours. This concept is graphically displayed in Figure 15, where streamflow discharge rate collected once per day do not accurately represent small variations in streamflow. The high-frequency datasets used in this study assures that we are capturing “real time” changes in streamflow discharge rate and specific conductance and the results of the study accurately characterize small changes in streamflow discharge rate and chemistry.

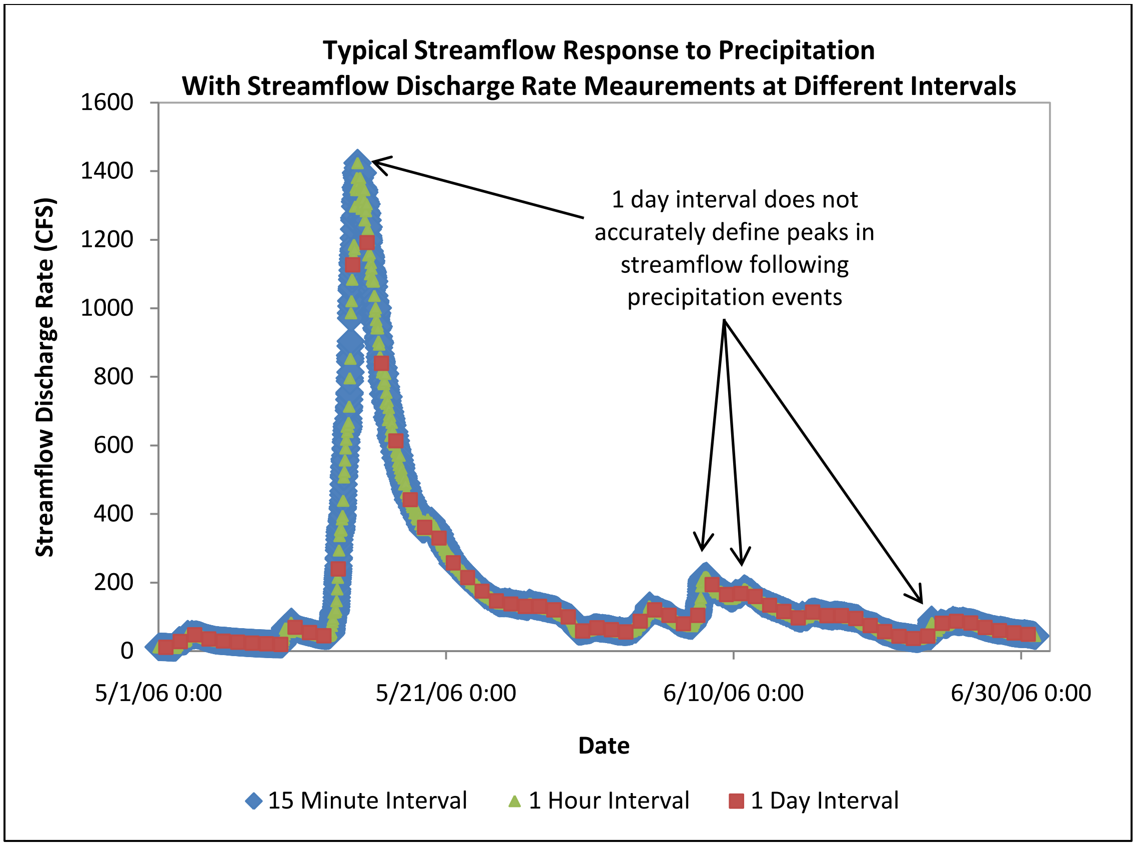

Figure 15: Streamflow discharge rate collected in the Saugus River from 5/1/2009 – 6/30/2009. Streamflow discharge rate is represented as if collected at different time intervals, 15 minute, 1 hour and 1 day intervals to demonstrate that 15 minute interval and 1 hour interval data can accurately characterize streamflow variation.

5.1 Significance of Event Flow Data

It is important to note that hydrograph separation techniques used in this study do not account for any fluctuation in baseflow specific conductance during periods of streamflow designated as containing both a baseflow and an event flow component. Therefore, the results of this study do not distinguish between; (1) increases in specific conductance due to increases in ion concentrations in event flow; (2) increases in specific conductance in baseflow discharge due to deep mixing of groundwater sources (deep groundwater sources likely have higher specific conductivities due to density of brine solutions) resulting from an increased water table gradient during precipitation events; and (3) possible increased specific conductance in event flow due to removal of re-crystallized salts stored in the vadose zone due to evapotranspiration, which leaves any dissolved solutes behind. The fact that these three potential sources of increased specific conductance in streamflow during precipitation events are all designated as changes in specific conductance in event flow alone indicate that the results of this analysis represent the maximum estimated dissolved chloride load that is transported as event flow. Subsequently, the estimated dissolved chloride loads transported as baseflow are conservative estimates.

5.2 SAUGUS RIVER WATERSHED

5.2.1 General Seasonal Chloride Concentration Patterns

The complete four-year calculated chloride concentration for the Saugus River is displayed in Figure 16. The record is broken up by season, winter (December, January, and February), spring (March, April, and May), summer (June, July, and August) and fall (September, October, and November), in order to see the general patterns of chloride concentrations throughout each calendar year and identify seasonal patterns over the four-year record. The Saugus River displays peaks in chloride concentration during the winter seasons, with the highest concentration seen during the winter of 2004 at 1,300 milligrams per liter (mg/l). Over the four-year record, the Saugus River has an average winter season chloride concentration of 160 mg/l (Table 11). The lowest chloride concentrations in the Saugus River are during the summer and fall months with the lowest concentration during the fall of 2003 of 0.9 mg/l. Over the four-year record, the Saugus River has an average fall season chloride concentration of 110 mg/l (Table 11), the lowest average chloride concentration of any season. The chloride concentration record from the Saugus River displays a general baseline chloride concentration from which positive and negative departures can be seen throughout the calendar year. This apparent baseline chloride concentration is between 125 and 175 mg/l and remains within this range over the four-year record. The departure from the baseline chloride concentration during the winter seasons is generally positive in the Saugus River. Figure 17 displays an example of chloride concentration fluctuation in the winter season in the Saugus River. During the spring, summer, and fall the chloride concentration in the Saugus River generally displays a decrease in concentration during periods of increased streamflow. Figure 18 displays an example of chloride concentration fluctuation during non-winter seasons in the Saugus River. The positive departures from the baseline chloride concentration during the summer are associated with extended periods of little change in streamflow and explain the fact the summer season has the second highest average chloride concentration for the Saugus River (Table 11). In general, the Saugus River chloride concentration shows an overall increase during the winter months when deicing agents are used within the watershed.

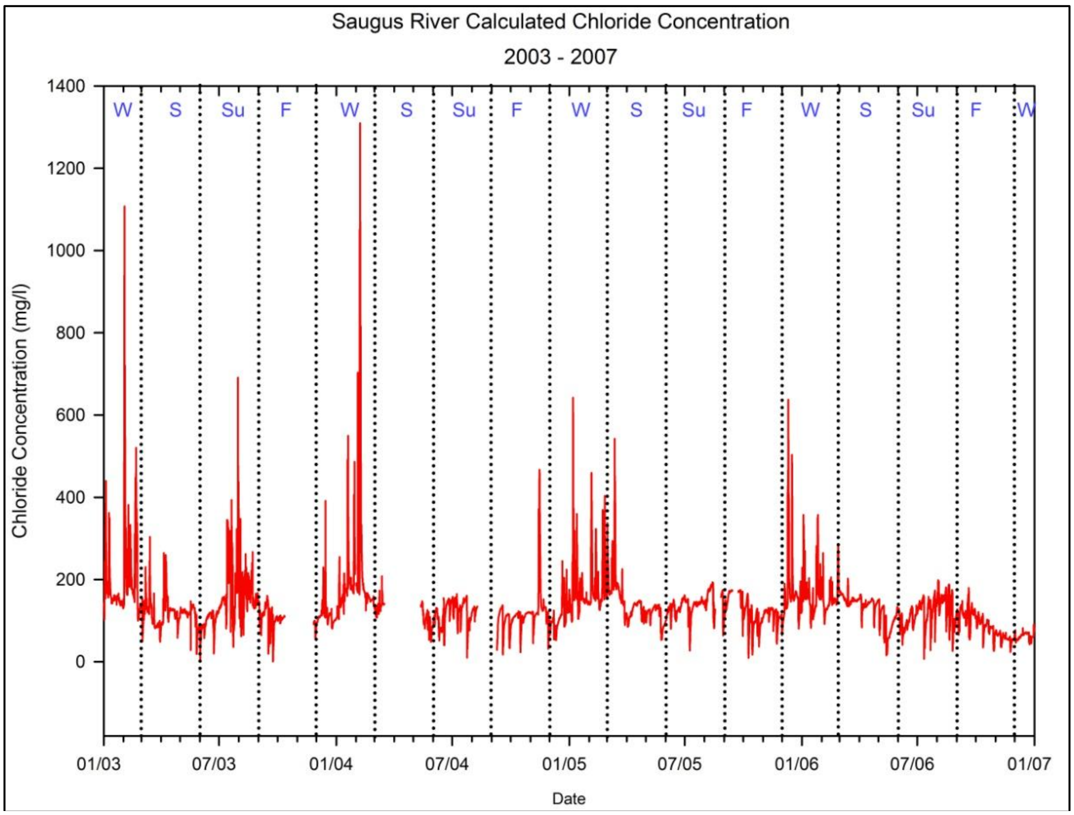

Figure 16: Calculated chloride concentration for the Saugus River from 2003 – 2007. All abnormal data has been removed (Section 4.2.1). Dotted lines represent change in season, W stands for Winter (December, January, and February), S stands for Spring (March, April, and May), Su stands for Summer (June, July and August), F stands for Fall (September, October, and November).

Saugus River Average Seasonal Chloride Concentration 2003 - 2007	
Season	**Average Chloride Concentration (mg/l)**
Winter (W)	160
Spring (S)	130
Summer (Su)	130
Fall (F)	110

Table 11: Four-year average seasonal calculated chloride concentration for the Saugus River from 2003 – 2007. Seasons are split as follows: Winter (W) is December, January, and February, Spring (S) is March, April, and May, Summer (Su) is June, July and August, and Fall (F) is September, October, and November.

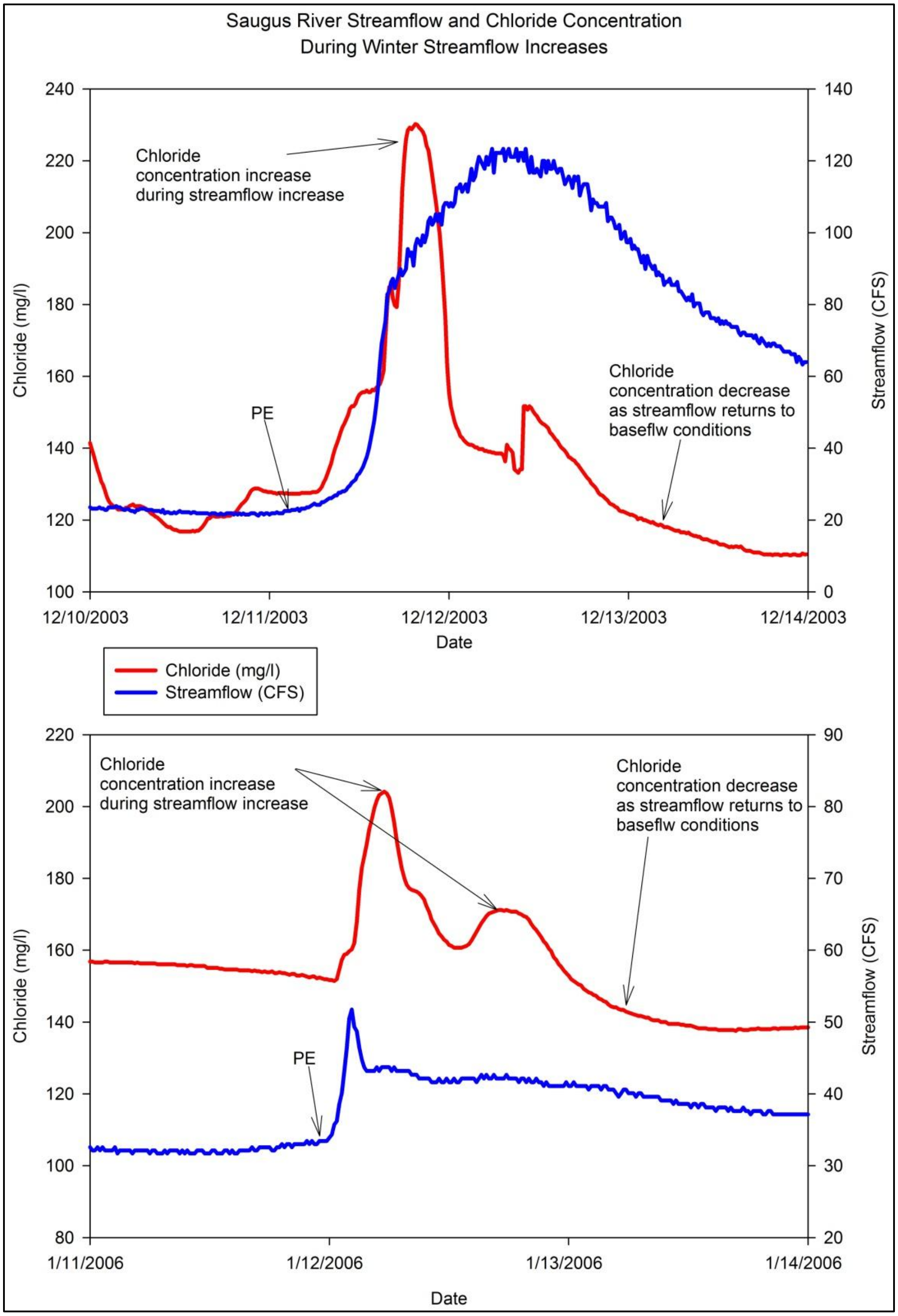

Figure 17: Example of Saugus River chloride concentration response to increased streamflow from precipitation during the winter season. PE stands for the approximate beginning of precipitation event

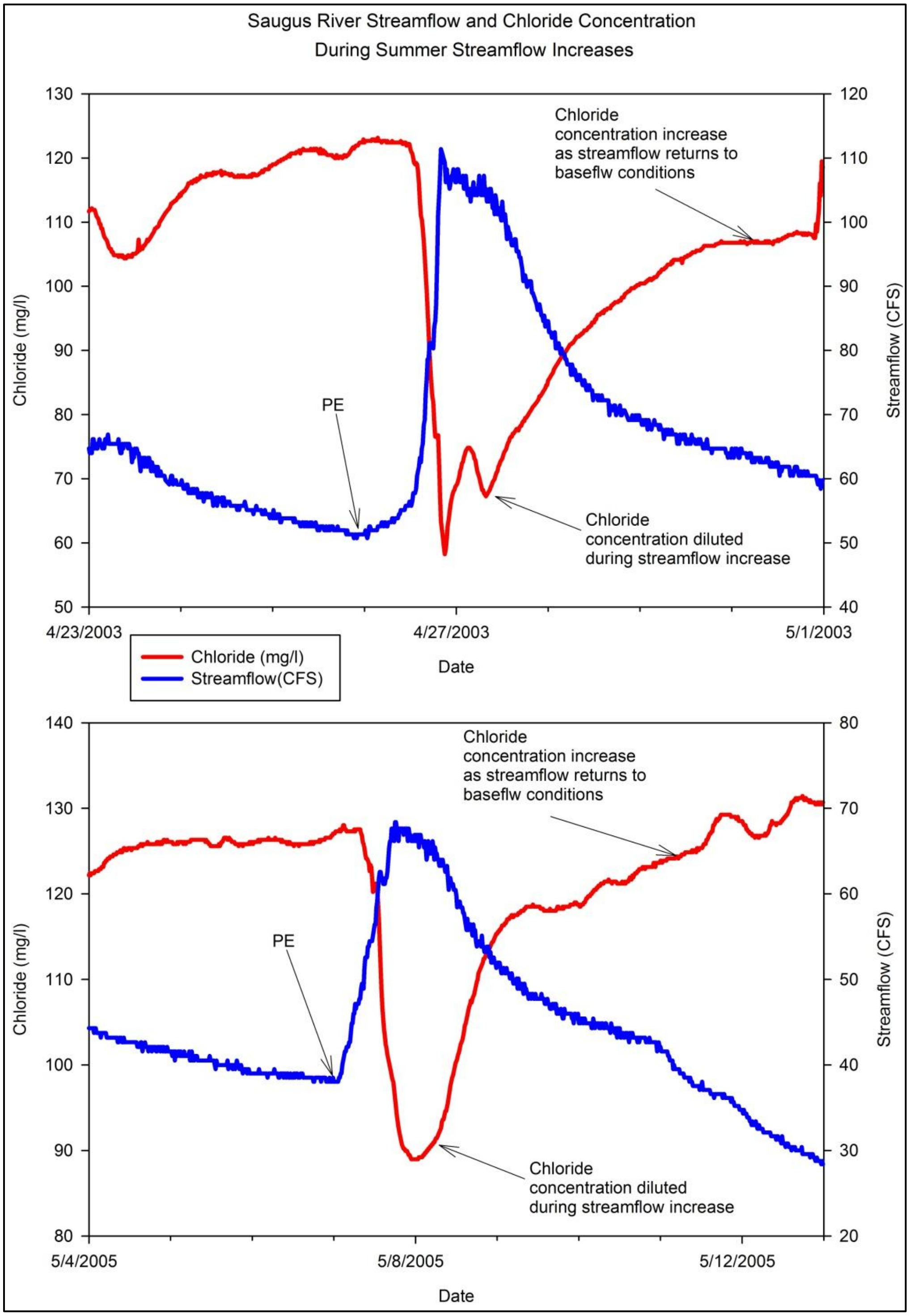

Figure 18: Example of Saugus River chloride concentration response to increased streamflow from precipitation during the non winter seasons. PE stands for the approximate beginning of precipitation event

5.2.2 Dissolved Chloride Load Patterns

5.2.2.1 Seasonal and Monthly Patterns

Using the chloride concentrations calculated for the Saugus River and streamflow discharge rate recorded at the Saugus River, the dissolved chloride load can be calculated using Equation 5 (Section 4.5). Dissolved chloride load data for the four-year dataset are then averaged over 2 week periods in order to account for any missing data points over each 2 week interval. Figure 19 displays the 14-day average dissolved chloride load discharge rate from the Saugus River along with the 14-day average streamflow rate for the Saugus River. Figure 19 has been split up into winter (December, January, and February), spring (March, April, and May), summer (June, July, and August) and fall (September, October, and November) seasons in order to visually assess how the dissolved chloride load discharge rate fluctuates between seasons. Table 12 displays the average dissolved chloride discharge rate per season over the four-year record. Gaps in Figure 19 are 14-day averages missing over 75% of the record due to missing or abnormal data during that 14-day time periods (see Section 4.2.1.1). In general, the Saugus River displays dissolved chloride load discharge patterns that correlate with increasing and decreasing stream discharge rate over the four-year period (Figure 20). The second order polynomial trend line in Figure 20 is meant to show the general relationship between streamflow rate and dissolved chloride load, a second order polynomial fit is used to account for increased dilution effects at high flow rates. The Saugus

River peak dissolved chloride discharge rate is seen in the spring of 2006 with a dissolved chloride discharge rate of approximately 1,300 kg/hour. The Saugus River 14-day average dissolved chloride discharge rate minimum occurred during the fall of 2005 of approximately 11 kg/hour. The Saugus River exhibits peaks in dissolved chloride discharge rate primarily during the winter and spring seasons and the Saugus River discharges an average of 390 kilograms of dissolved chloride per hour during the winter season, the highest average discharge rate of any season over the four-year record (Table 12). Each year, the Saugus River discharges the least amount of dissolved chloride during the summer and fall months when streamflow is also at the yearly minimum, and the season with the lowest dissolved chloride discharge rate for the Saugus river over the four-year record is the fall, when the Saugus river discharges an average of 100 kilograms of dissolved chloride per hour (Table 12).

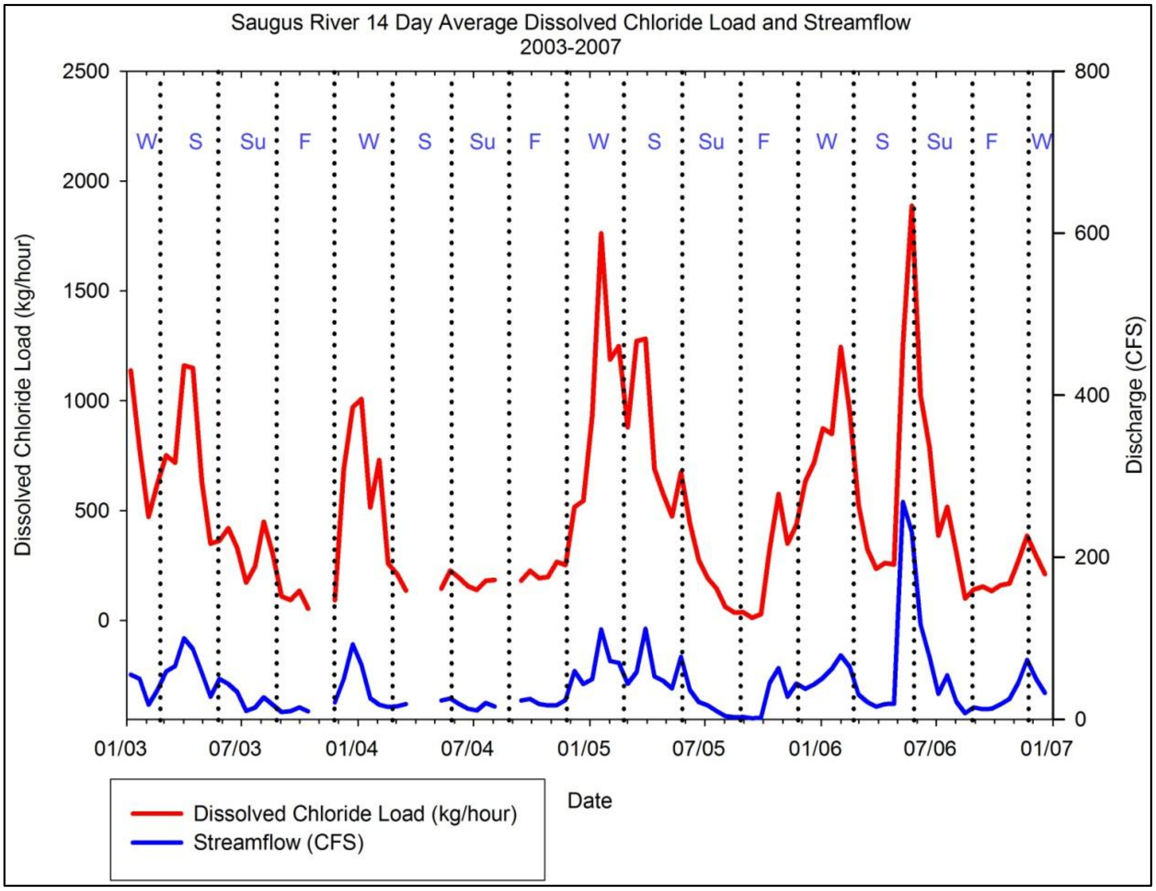

Figure 19: 14-day average dissolved chloride load discharge rate from the Saugus River is displayed in kg/hour. River discharge rate is also displayed as 14-day averages in CFS. Dotted lines represent change in season, W stands for Winter (December, January, and February), S stands for Spring (March, April, and May), Su stands for Summer (June, July and August), F stands for Fall (September, October, and November).

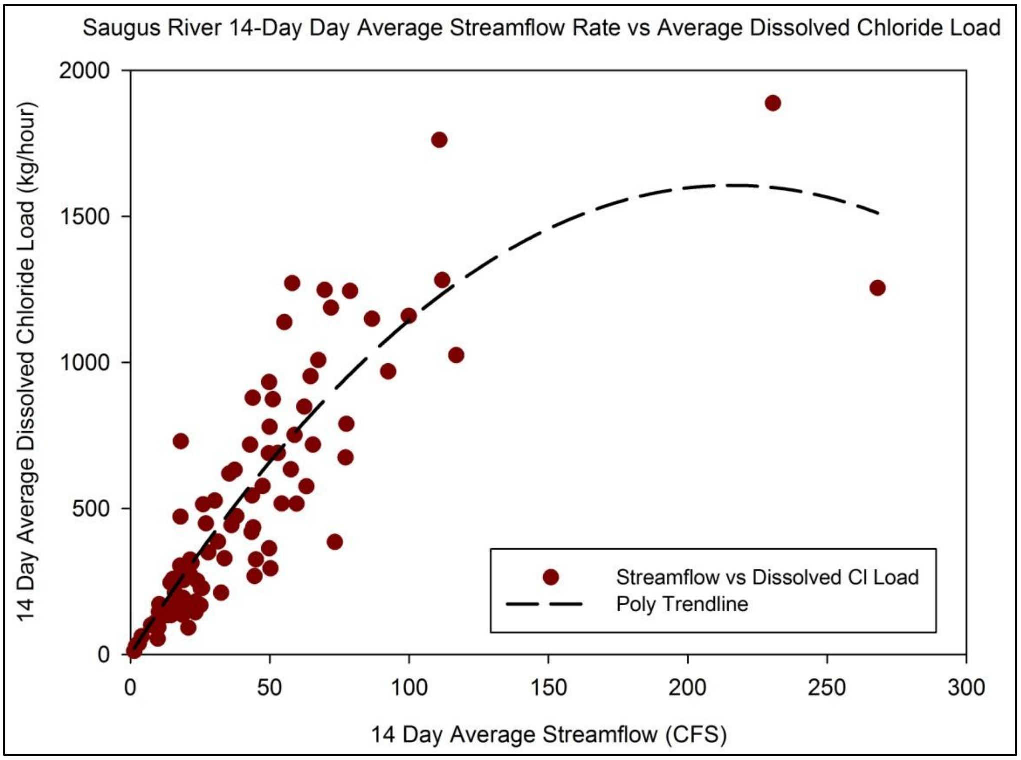

Figure 20: 2nd order polynomial trend analysis graph, 14-day average streamflow rate vs 14-day average dissolved chloride load rate for the Saugus River. Data from 2003 – 2007.

Saugus River Average Seasonal Dissolved Chloride Load Discharge Rate 2003 - 2007	
Season	**Average Dissolved Chloride Load (kg/hour)**
Winter	390
Spring	320
Summer	150
Fall	100

Table 12: Seasonal four-year average dissolved chloride discharge in kg/hour from the Saugus River from 2003 - 2007. Seasons are split as follows: winter is December, January, and February, spring is March, April, and May, summer is June, July and August, and fall is September, October, and November.

To analyze the monthly transport of dissolved chloride by the Saugus River over the four-year record, the total amount of dissolved chloride discharged per month is calculated for the Saugus River, and monthly averages are created to determine which month is responsible for transporting the most dissolved chloride. The results can be found on Figure 21 and Table 13. All values in Figure 21 and Table 13 are normalized to drainage area extent for comparison between different watershed sizes. On average, the Saugus River transports nearly 180,000 kg of dissolved chloride per square mile of drainage per year with 18% (32,000 kg) of the total discharged during the month of January and less than 3% (3,700 kg) during the month of September (Table 13). Overall, the Saugus River removes the majority of the total yearly amount of dissolved chloride from the watershed during the winter and the spring months, when over 80% of the total dissolved chloride is removed. This is due to high streamflow rates during the spring months (Figure 19), the fact that dissolved chloride loading rates increases with increasing flow rates (Figure 20), and the application of road deicing chemicals during the winter season that are flushed directly into the Saugus River during the winter months.

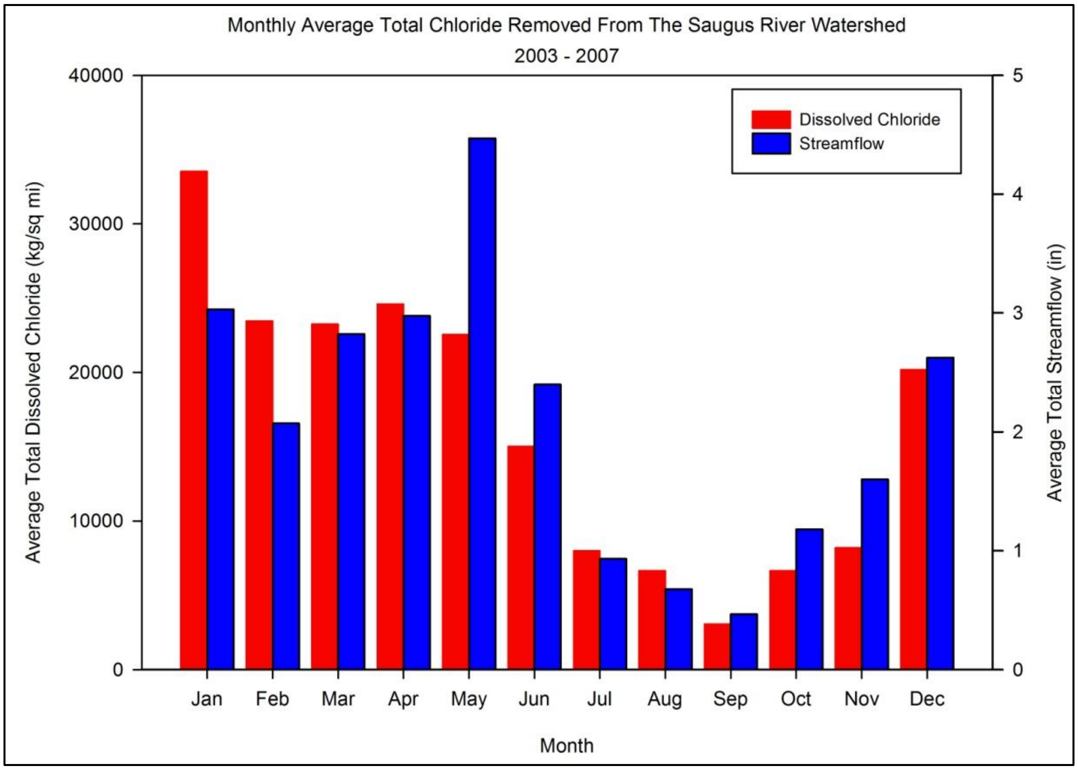

Figure 21: Monthly four-year average total dissolved chloride load discharged by the Saugus River from 2003 – 2007 normalized to drainage basin area and displayed as kilograms per square mile (kg/sq mi) and monthly four-year average total streamflow normalized to drainage area extent and displayed as inches (in) of streamflow.

Saugus River Monthly Average Total Dissolved Chloride Load 2003 - 2007		
Month	**Saugus River Average Total Dissolved Chloride Load (kg/sq mi)**	**Average Monthly Percent of Total Yearly Dissolved Chloride Discharged**
January	32,000	18%
February	22,000	12%
March	19,000	11%
April	19,000	11%
May	22,000	12%
June	14,000	8%
July	7,600	4%
August	5,800	3%
September	3,700	2%
October	7,100	4%
November	8,800	5%
December	18,000	10%

Table 13: Monthly four-year average total dissolved chloride discharged by the Saugus River from 2003 – 2007. Dissolved chloride load values are normalized to drainage area extent.

5.2.2.2 Distribution by Flow Components

To determine how dissolved chloride is transported in the Saugus River watershed after roadway deicing chemicals are used within the watershed, the dissolved chloride load dataset is split into baseflow and event flow components (see Section 4.3). The average chloride concentration in baseflow and event flow in the Saugus River are 140 $\pm$ 40 mg/l and 70 $\pm$ 110 mg/l respectively (Table 14). The average dissolved chloride loading rates in baseflow and event flow in the Saugus River are 290 $\pm$ 210 kg/hour and 270 $\pm$ 470 kg/hour respectively (Table 14). The lower standard deviations in baseflow chloride concentration and dissolved chloride loading rates when compared to event flow chloride concentrations and loading rates indicate more consistent chloride concentrations and loading rates in the baseflow component of stream discharge.

Saugus River Average Chloride Concentrations and Dissolved Chloride Loading Rates in Flow Components		
	Average	**Standard Deviation**
Baseflow dissolved chloride concentration (mg/l)	140	40
Event flow dissolved chloride concentration (mg/l)	70	60
Baseflow dissolved chloride loading rate (kg/hour)	290	210
Event flow dissolved chloride loading rate (kg/hour)	270	470

Table 14: Four-year average chloride concentrations and dissolved chloride loading rates in baseflow and event flow for the Saugus River from 2003 – 2007.

The total dissolved chloride discharged by the Saugus River via baseflow and event flow over the four-year record is averaged per month, and the results are displayed in Figure 22. Monthly average total dissolved chloride discharged by each hydrograph component is also displayed in Table 15. In the Saugus River, approximately 60% total dissolved chloride discharged per year is removed from the watershed as baseflow, while approximately 40% of the total dissolved chloride load removed from the Saugus River watershed each year is removed from the watershed via event flow. The month with the highest amount of dissolved chloride removed as event flow in the Saugus River is January, with an average of approximately 15,000 kg/sq mi of dissolved chloride removed (Table 15). The month with the lowest monthly average dissolved chloride discharged from the Saugus River via event flow is September, with approximately 1,000 kg/sq mi (Table 15) of dissolved chloride being discharged per year. The baseflow contribution of the total dissolved chloride discharged per month changes throughout the year depending on season. The baseflow contribution to the total amount of dissolved chloride discharged each month by the Saugus River ranges from approximately 75% of the total dissolved chloride discharged from August to November coming from baseflow to approximately 40% of the total dissolved chloride discharged in May contributed from baseflow. This discrepancy is in part accounted for by the larger number of precipitation events during the spring months and the melting of winter snowpack, more storms during a given month will increase the amount of streamflow designated as event flow and will transport more dissolved ions (including dissolved chloride) via event flow. The winter months, December, January and February also have lowered baseflow percent contribution of the total amount of dissolved chloride discharged in a given month (52% in January). This is due to the increased chloride concentration in event flow, as deicing chemicals are also being flushed into the Saugus River after application during winter storms.

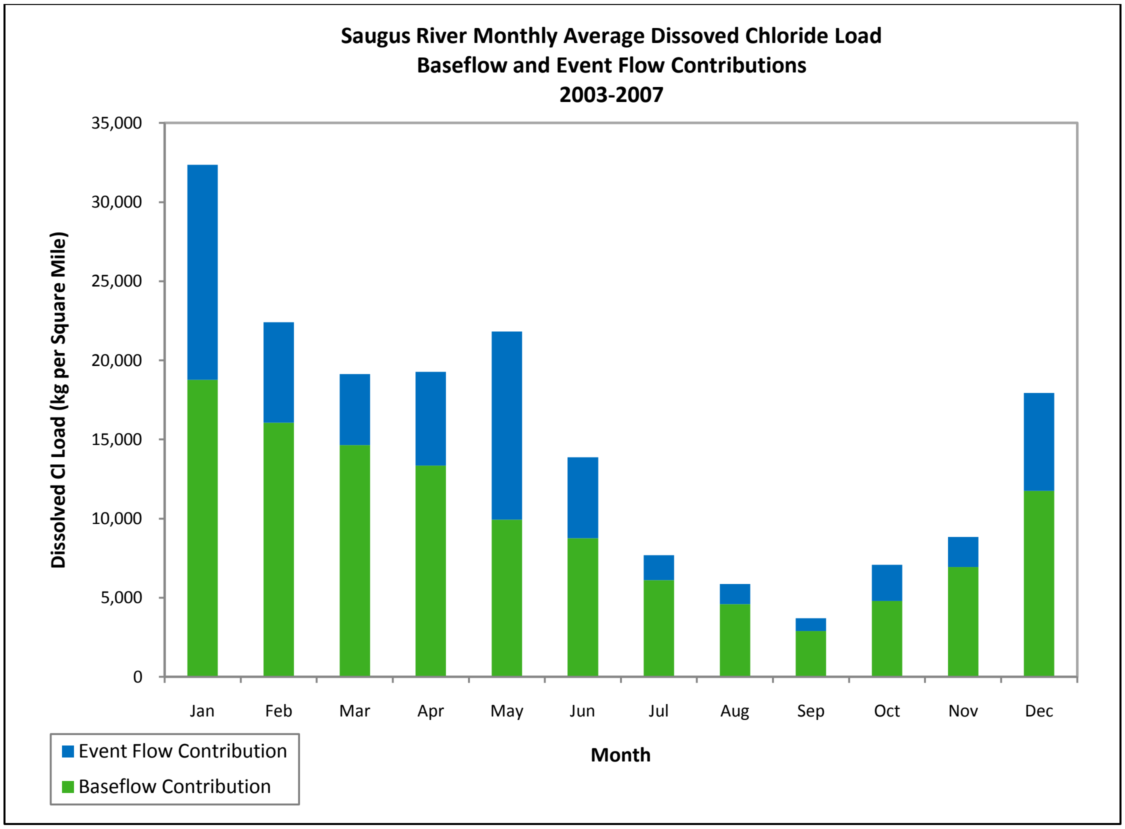

Figure 22: Four- year average monthly total dissolved chloride discharged via baseflow and event flow in the Saugus River. Dissolved chloride loads are normalized to drainage area extent.

Saugus River Total Monthly Average Dissolved Chloride Load By Flow Component 2003 - 2007		
Month	**Baseflow Contribution (kg/sq mi)**	**Event flow Contribution (kg/sq mi)**
January	17,000	15,000
February	14,000	8,100
March	14,000	5,400
April	11,000	7,900
May	9,100	13,000
June	7,200	6,600
July	5,600	2,100
August	4,400	1,400
September	2,700	1,000
October	4,600	2,500
November	6,900	2,000
December	11,000	6,700
Average % Contribution	**60%**	**40%**

Table 15: Baseflow and event flow four -year average monthly dissolved chloride loads discharged from the Saugus River normalized to drainage area extent.

5.3 STILLWATER RIVER WATERSHED

5.3.1 General Seasonal Chloride Concentration Patterns

The complete four-year calculated chloride concentration for the Stillwater River is displayed in Figure 23. Like the Saugus River chloride concentration figure (Figure 16), the Stillwater River calculated chloride concentration record is broken up by season, winter (December, January, and February), spring (March, April, and May), summer (June, July, and August) and fall (September, October, and November), in order to see the general patterns of chloride concentration throughout each calendar year and identify seasonal patterns over the four-year record. The Stillwater River displays peaks in chloride concentration during the summer seasons, with the highest concentration seen during the summer of 2005 of approximately 105 (mg/l). Over the four-year record the Stillwater River has an average summer season chloride concentration of 35 mg/l (Table 16), the highest average of any season. The lowest chloride concentrations in the Stillwater River are generally found during the spring and winter months, however, the lowest chloride concentration in the Stillwater River (approximately 7 mg/l) is found in the fall of 2005 during a large increase in streamflow associated with precipitation event. Over the four-year record, the Stillwater River has an average spring and winter season chloride concentration of 21 mg/l and 19 mg/l respectively (Table 16), with winter having the lowest average seasonal chloride concentration of any season. The chloride concentration record from the Stillwater River displays a general baseline chloride concentration from which positive and negative departures can be seen throughout the calendar year. This apparent baseline chloride concentration is between 15mg/l and 30 mg/l and remains within this range over the four-year record. The departure from the baseline chloride concentration during increases in streamflow during all seasons is generally a negative one. Both winter (Figure 24) and non-winter (Figure 25) chloride concentrations decrease from pre streamflow chloride concentrations during streamflow increases associated with precipitation events. Both winter (Figure 24) and non-winter (Figure 25) chloride concentrations increase briefly at the onset of precipitation events followed by a decrease in chloride concentration during the precipitation event. The higher chloride concentrations in the Stillwater River during the summer and early fall months seen on Figure 23 are associated with extended periods of little change in streamflow, and explain the fact the summer season has the second highest average chloride concentration for the Stillwater River (Table 16). In general, the Stillwater River chloride concentration shows an overall increase during the summer months when precipitation is scarce and temperatures are the highest. The lowest chloride concentrations are found during the winter and spring months when precipitation is more abundant and temperatures are cooler. The use of deicing agents within the watershed does not seem to have a direct effect during winter storms in the Stillwater River, as with the Saugus River.

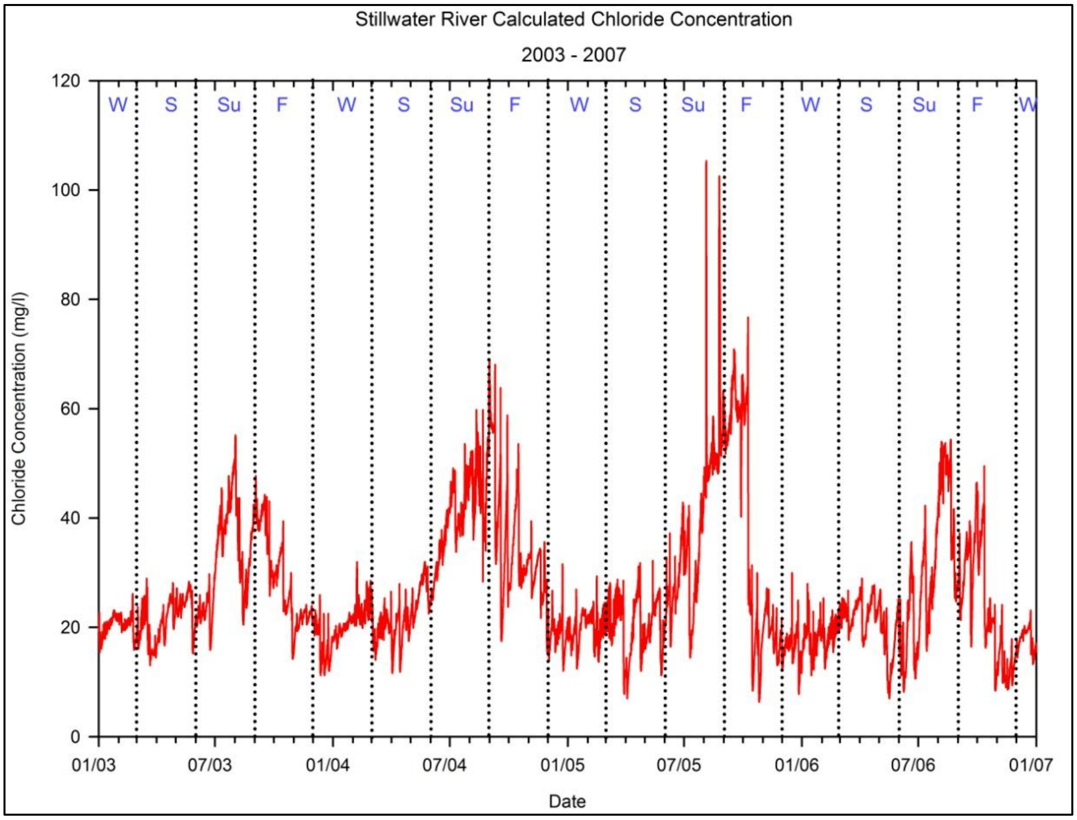

Figure 23: Calculated chloride concentration for the Stillwater River from 2003 - 2007. All abnormal data has been removed (Section 4.2.1). Dotted lines represent change in season, W stands for Winter (December, January, and February), S stands for Spring (March, April, and May), Su stands for Summer (June, July and August), F stands for Fall (September, October, and November).

Stillwater River Average Seasonal Chloride Concentration 2003 - 2007	
Season	**Average Chloride Concentration (mg/l)**
Winter (W)	19
Spring (S)	21
Summer (Su)	35
Fall (F)	30

Table 16: Four-year average seasonal calculated chloride concentration for the Stillwater River from 2003 – 2007. Seasons are split as follows: Winter(W) is December, January, and February, Spring (S) is March, April, and May, Summer (Su) is June, July and August, and Fall (F) is September, October, and November.

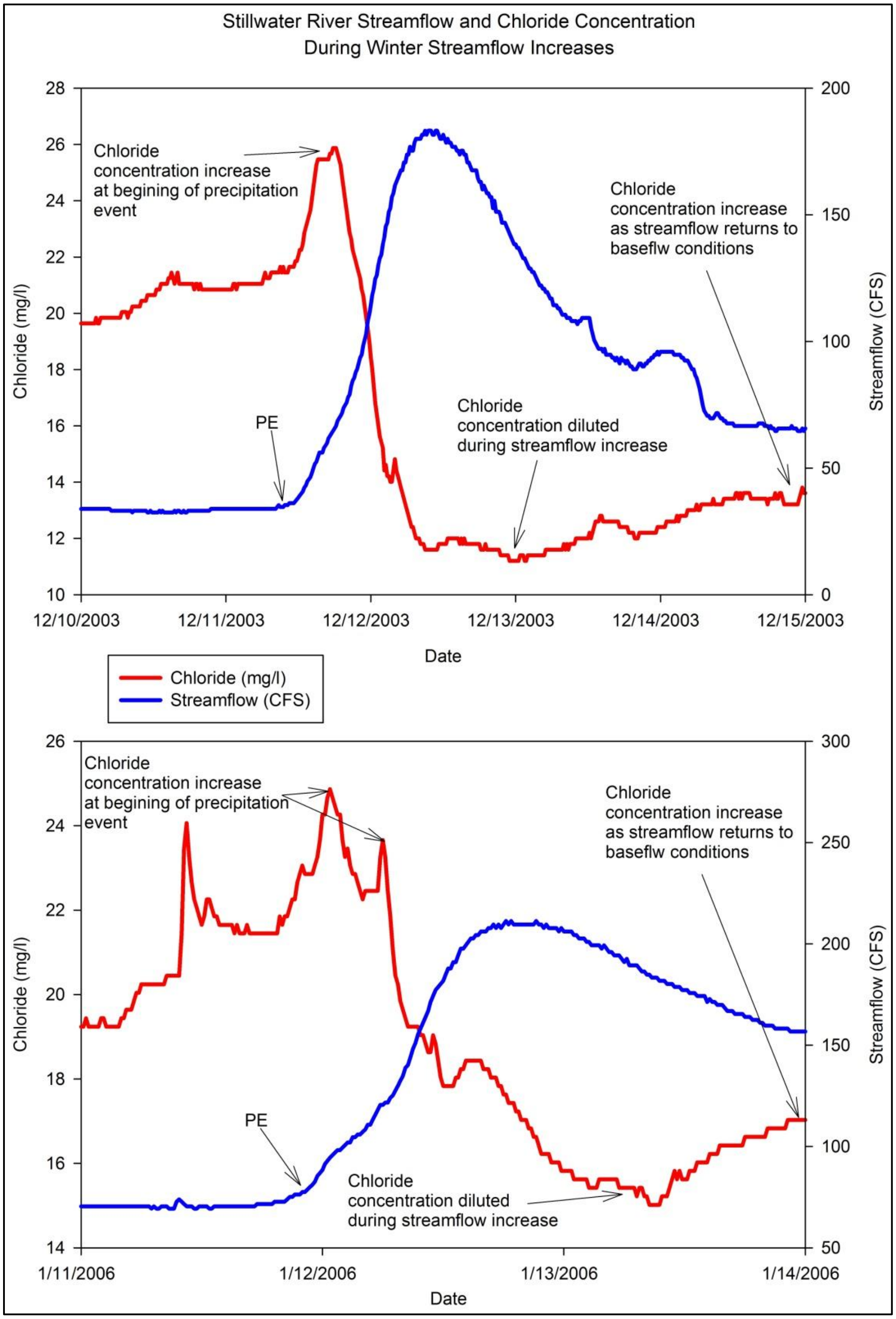

Figure 24: Example of Stillwater River chloride concentration response to increased streamflow from precipitation during the winter season. PE stands for the approximate beginning of precipitation event

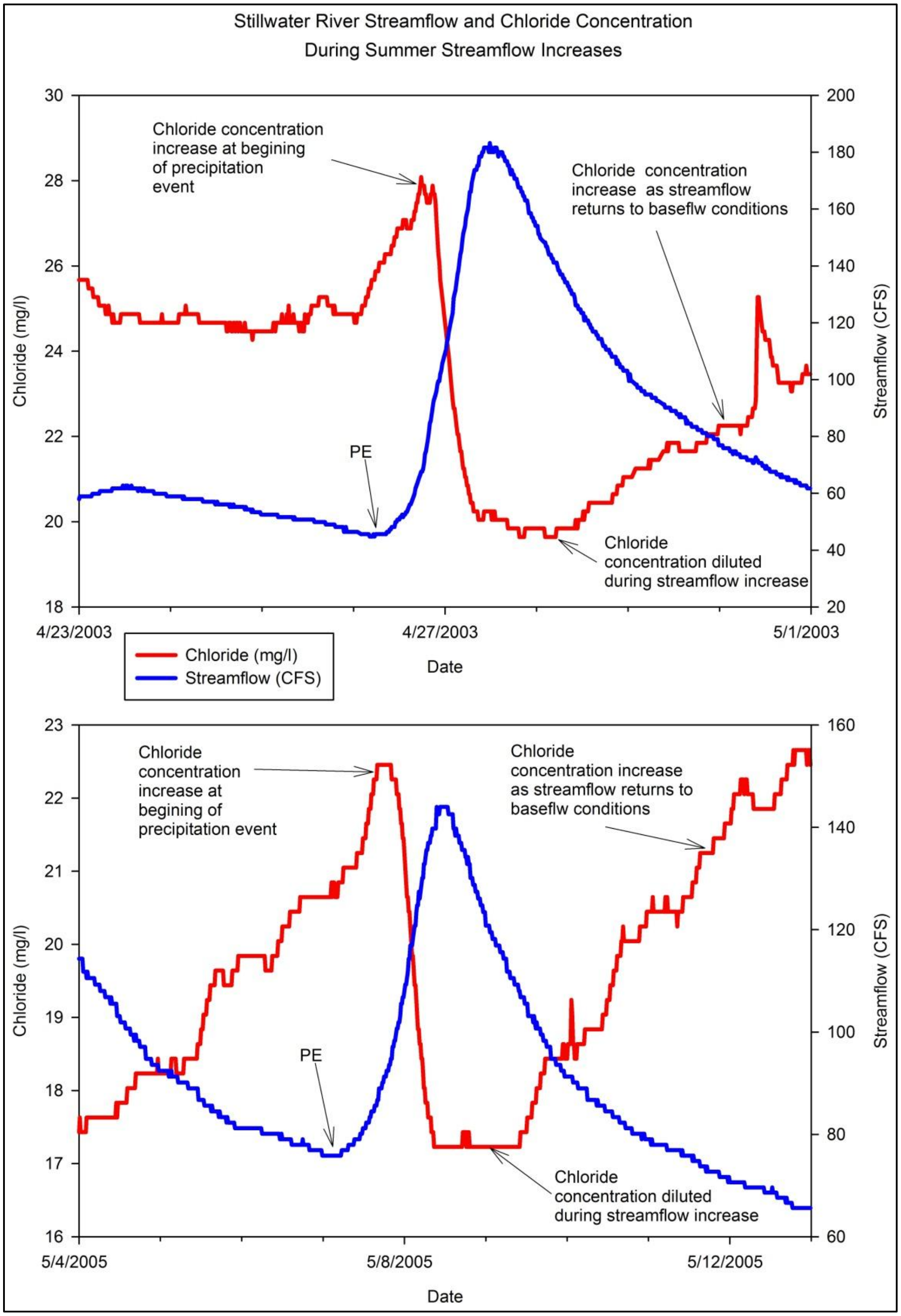

Figure 25: Example of Stillwater River chloride concentration response to increased streamflow from precipitation during the non winter seasons. PE stands for the approximate beginning of precipitation event

5.3.2 Dissolved Chloride Load Patterns

5.3.2.1 Seasonal and Monthly Patterns

Using the chloride concentrations calculated for the Stillwater River and streamflow discharge rate recorded at the Stillwater River, the dissolved chloride load can be calculated using Equation 5 (Section 4.5). Dissolved chloride load data for the four-year dataset are then averaged over 2 week periods in order to account for any missing data points over each 2 week interval. Figure 26 displays the 14-day average dissolved chloride load discharge rate from the Stillwater River along with the 14-day average streamflow rate for the Stillwater River. Figure 26 has been split up into winter (December, January, and February), spring (March, April, and May), summer (June, July, and August) and fall (September, October, and November) seasons in order to visually assess how the dissolved chloride load discharge rate fluctuates between seasons. Table 17 displays the average dissolved chloride discharge rate per season over the four-year record. In general, the Stillwater River displays dissolved chloride load discharge patterns that correlate with increasing and decreasing stream discharge rate over the four-year period (Figure 27). The second order polynomial trend line in Figure 27 is meant to show the general relationship between streamflow rate and dissolved chloride load, a second order polynomial fit is used to account for increased dilution effects at high flow rates. The Stillwater River peak dissolved chloride discharge rate is seen in the spring of 2005 with a dissolved chloride discharge rate of 332 kg/hour. The Stillwater River 14-day average dissolved chloride discharge rate minimum occurred during the fall of 2005 of 1.5 kg/hour. The Stillwater River exhibits peaks in dissolved chloride discharge rate primarily during the spring seasons when the Stillwater River discharges an average of 91 kilograms of dissolved chloride per hour, the highest average discharge rate of any season over the four-year record (Table 17). Each year the Stillwater River discharges the least amount of dissolved chloride during the summer and fall months when streamflow is also at the yearly minimum. The season with the lowest dissolved chloride discharge rate for the Stillwater River over the four-year record is the summer, when the Stillwater River discharges an average of 45 kilograms of dissolved chloride per hour (Table 17).

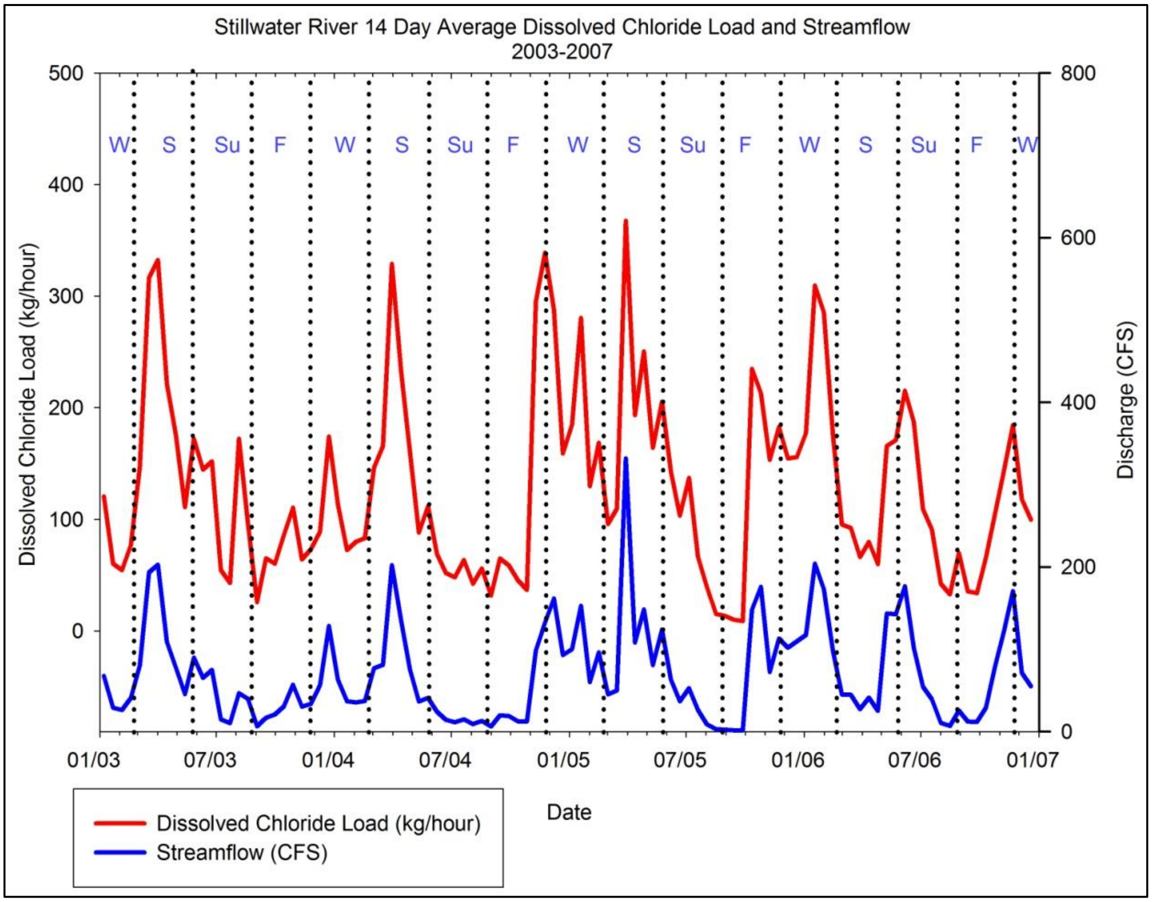

Figure 26: 14-day average dissolved chloride load discharge rate from the Stillwater River is displayed in kg/hour. River discharge rate is also displayed as 14-day averages in CFS. Dotted lines represent change in season, W stands for Winter (December, January, and February), S stands for Spring (March, April, and May), Su stands for Summer (June, July and August), F stands for Fall (September, October, and November).

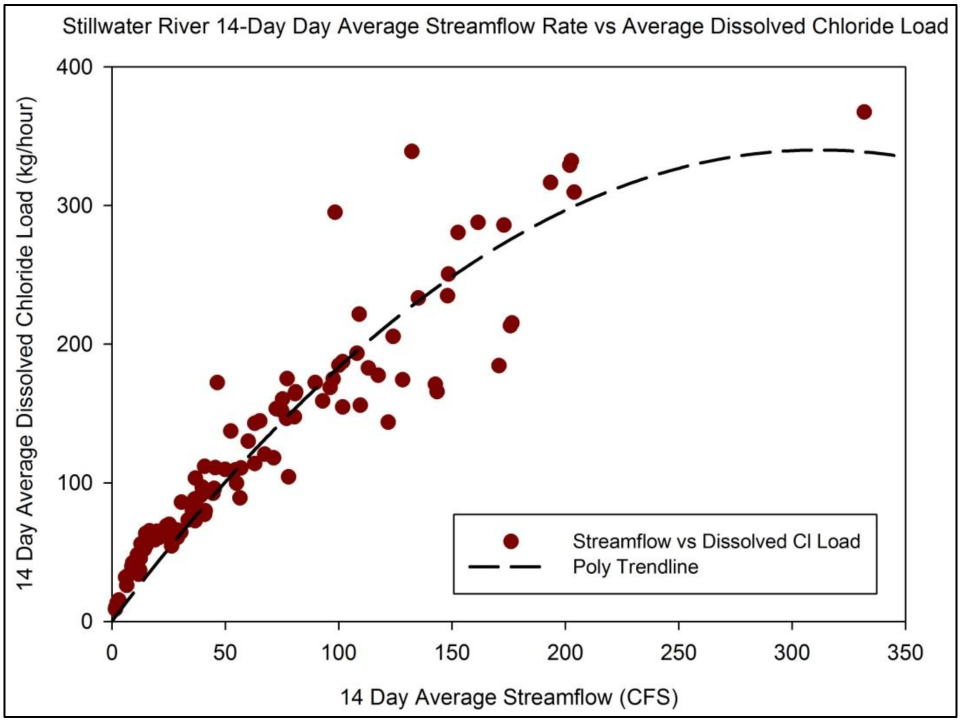

Figure 27: 2nd order polynomial trend analysis graph, 14-day average streamflow rate vs 14-day average dissolved chloride load rate for the Stillwater River. Data from 2003 – 2007.

Stillwater River Average Seasonal Dissolved Chloride Load Discharge Rate 2003 - 2007	
Season	**Average Dissolved Chloride Load (kg/hour)**
Winter	76
Spring	91
Summer	45
Fall	55

Table 17: Seasonal four-year average dissolved chloride discharge in kg/hour from the Stillwater River from 2003 – 2007. Seasons are split as follows: winter is December, January, and February, spring is March, April, and May, summer is June, July and August, and fall is September, October, and November.

In order to analyze the monthly transport of dissolved chloride by the Stillwater River over the four-year record, the total amount of dissolved chloride discharged per month is calculated for the Stillwater River, and monthly averages are created to determine which month is responsible for transporting the most dissolved chloride. The results can be found on Figure 28 and Table 18. All values are normalized to drainage area extent for comparison between different watershed sizes. On average, the Stillwater River transports approximately 38,000 kg of dissolved chloride per square mile of drainage per year, with over 34% (over 13,000 kg) of the total discharged during the spring months of March, April and May. During the summer months of June, July and August, the Stillwater River only transports 17% (6,500kg) of the total dissolved chloride removed per year on average over the four-year record. The high streamflow rates during the spring months (Figure 28) allow for more dissolved chloride to be removed from the Stillwater River Watershed during the springtime, opposed to the summer and fall months when streamflows are lower.

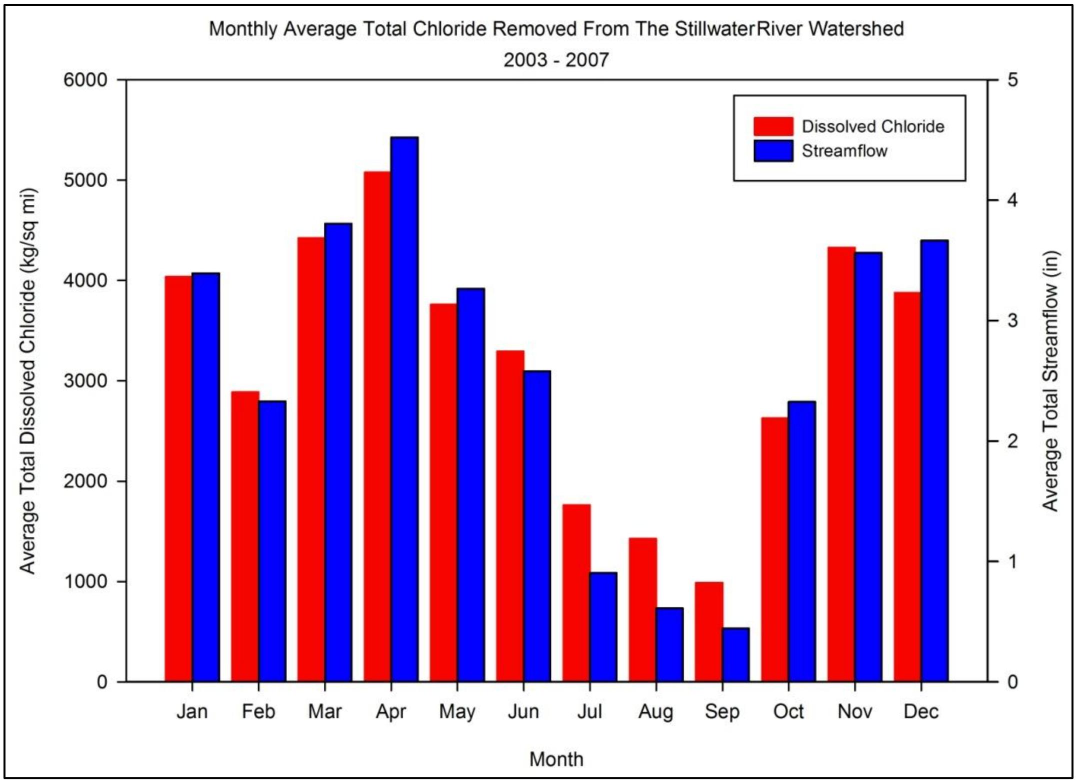

Figure 28: Monthly four-year average total dissolved chloride load discharged by the Stillwater River from 2003 – 2007, normalized to drainage basin area and displayed as kilograms per square mile (kg/sq mi) and monthly four-year average total streamflow normalized to drainage area extent and displayed as inches (in) of streamflow.

Stillwater River Monthly Average Total Dissolved Chloride Load 2003 - 2007		
Month	**Stillwater River Average Total Dissolved Chloride Load (kg/sq mi)**	**Average Monthly Percent Of Total Yearly Dissolved Chloride Discharged**
January	4,000	10%
February	2,900	7%
March	4,400	11%
April	5,100	13%
May	3,800	10%
June	3,300	9%
July	1,800	5%
August	1,400	4%
September	1,000	3%
October	2,600	7%
November	4,300	11%
December	3,900	10%

Table 18: Monthly four-year average total dissolved chloride discharged by the Stillwater River from 2003 – 2007. Dissolved chloride load values are normalized to drainage area extent.

5.3.2.2 Distribution by Flow Components

To determine how dissolved chloride is transported in the Stillwater River watershed after roadway deicing chemicals are used within the watershed the dissolved chloride load, the dataset is split into baseflow and event flow components (see Section 4.3). The average chloride concentration in baseflow and event flow in the Stillwater River are 29 $\pm$ 10 mg/l and 5 $\pm$5 mg/l respectively (Table 19). The average dissolved chloride lading rates in baseflow and event flow in the Stillwater River are 75$\pm$ 35 kg/hour and 67 $\pm$

170 kg/hour respectively (Table 13). This indicates that the bulk of the dissolved chloride removed from the Stillwater River Watershed is removed via baseflow recharge to the Stillwater River.

Stillwater River Average Chloride Concentrations and Dissolved Chloride Loading Rates in Flow Components		
	Average	**Standard Deviation**
Baseflow dissolved chloride concentration (mg/l)	29	10
Event flow dissolved chloride concentration (mg/l)	5	5
Baseflow dissolved chloride loading rate (kg/hour)	75	35
Event flow dissolved chloride loading rate (kg/hour)	67	170

Table 19: Four-year average chloride concentrations and dissolved chloride loading rates in baseflow and event flow for the Stillwater River from 2003 – 2007.

The total dissolved chloride discharged by the Stillwater River as baseflow and event flow over the four-year record is averaged per month and the results are displayed in Figure 29. Monthly average total dissolved chloride discharged by each hydrograph components are also displayed in Table 20. In the Stillwater River, approximately 83% of the total dissolved chloride is removed from the watershed as baseflow. The month with the highest average dissolved chloride discharged from the Stillwater River watershed as event flow is October, with an average of 1,200 kg/sq mi of dissolved chloride discharged during the four-year record. The month with the lowest monthly average dissolved chloride load discharged from the Stillwater River as event flow is September with an average of 40 kg/sq mi of dissolved chloride discharged over the four-year record (Table 20). It should be noted that the average event contribution of dissolved chloride discharged from the Stillwater River for October is skewed from an average of approximately 400 kg/sq mile to a monthly average of approximately 1,200 kg/sq mi due to multiple October 2004 streamflow discharge increase likely associated with a large precipitation events and resulting streamflow increase in that month (see Figure 26). The discharge increases caused the month of October 2004 to have an average event flow dissolved chloride discharge amount of approximately 4,000 kg/sq mi, while the average event dissolved chloride discharge for October 2003, 2005, and 2006 is approximately 400 kg/sq mi for the Stillwater River.

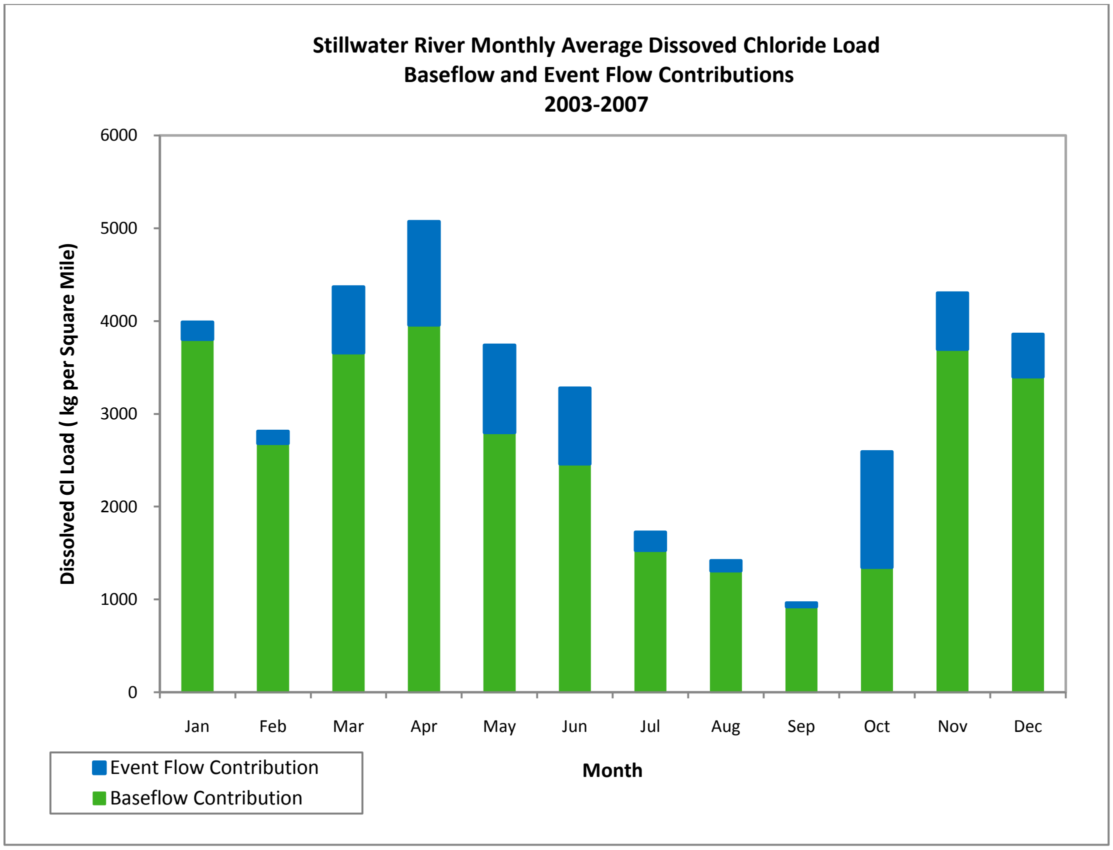

Figure 29: Four-year average monthly total dissolved chloride discharged via baseflow and event flow in the Stillwater River. Dissolved chloride loads are normalized to drainage area extent.

Stillwater River Total Monthly Average Dissolved Chloride Load By Flow Component 2003 - 2007		
Month	**Baseflow Contribution (kg/sq mi)**	**Event flow Contribution (kg/sq mi)**
January	3,800	190
February	2,700	130
March	3,700	710
April	4,000	1,100
May	2,800	900
June	2,500	820
July	1,500	200
August	1,300	110
September	920	40
October	1,300	1,200
November	3,700	610
December	3,400	460
Average % Contribution	**83%**	**17%**

Table 20: Baseflow and event flow four-year average monthly dissolved chloride loads discharged from the Stillwater River normalized to drainage area extent.

5.4 SAUGUS RIVER WATERSHED AND STILLWATER RIVER WATERSHED COMPARISON

5.4.1 Seasonal Differences in Chloride Concentration Patterns

The Saugus River and Stillwater River exhibit similar summer and fall trends in chloride concentration patterns, with overall chloride concentrations in each river increasing during summer and fall months (Figure 16 and Figure 23). This general increase in stream water chloride concentration during the summer and fall months in both the Saugus River and Stillwater River is likely due to evapotranspiration effects. During periods of low flow in the late summer and early fall, the chloride concentration of the Saugus River and Stillwater River increases with decreasing flow rate. During periods of low stream discharge rate, it can be assumed that the flow in the stream is due to groundwater discharge to the stream (Pettyjohn and Henning, 1979). During this time, the chloride concentration of both streams increases due to concentration effects by evapotranspiration. Evapotranspiration is the combination of water loss from the stream due to direct evaporation from the stream and water loss due to photosynthesis by plant life. Thus, evapotranspiration can lessen streamflow and also concentrate the solutes present in the stream (Zhang, Dawes and Walker, 1999). Water loss from the streams due to evapotranspitation leaves solutes, such as chloride, behind, which increases the chloride concentration in the stream. The effects of evapotranspiration are seen predominantly during the summer months when temperatures are highest and vegetation is most active (Zhang, Dawes and Walker, 1999). Figure 30 is an example of the effect evapotranspiration has on the chloride concentration of the Stillwater River during July of 2006. The effect of evapotranspiration in the Stillwater River can also be seen in Figure 23, where the chloride concentration of the stream increases every year during the late summer and early fall, then decreases again in the late fall and early winter, most likely due to increased precipitation, cooler temperatures and less active vegetation. The effect of evapotranspiration on the chloride concentration of the Saugus River is less prominent than that seen in the Stillwater River (Figure 16 and Figure 23). This is most likely related to land use differences within the watershed with increased impervious surfaces and less vegetation using water during photosynthesis.

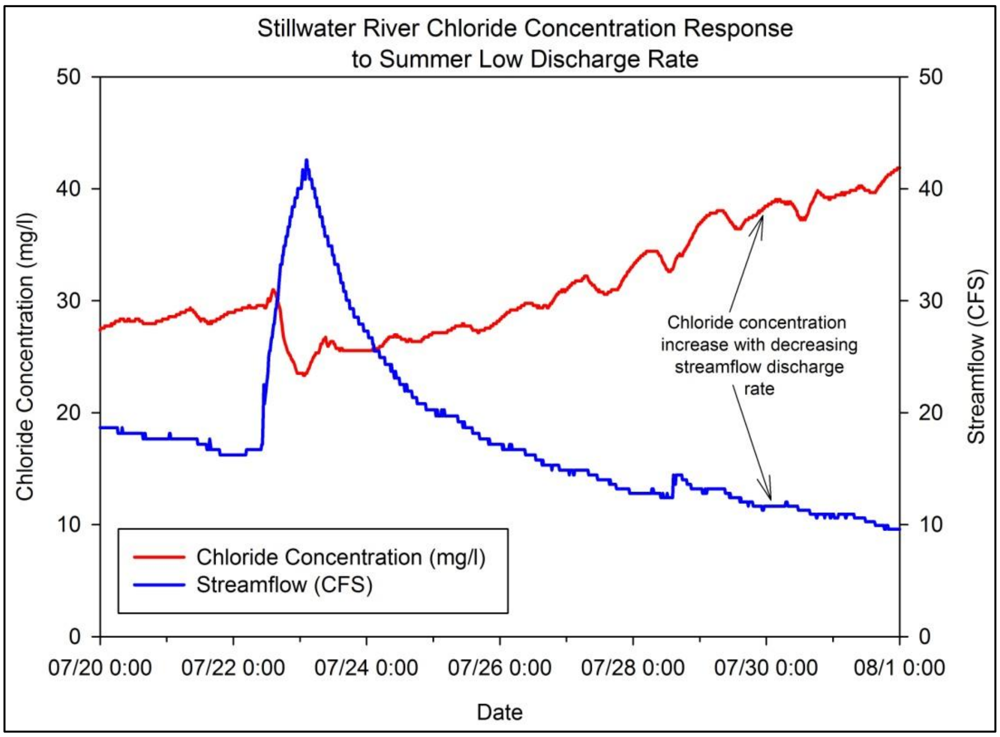

Figure 30: Chloride concentration and discharge records during a period of low streamflow discharge rate in the July, 2006

Both rivers display varying effects of stream discharge rate on chloride concentrations. Each river displays a baseline chloride concentration from which the chloride concentration increases or decreases throughout the year responding to discharge rate differences and evapotranspiration. This baseline chloride concentration seen throughout the year in each system indicates a reservoir of chloride in the subsurface that is discharged to streams throughout the year. The low standard deviation (less than ½ the average) of baseflow chloride concentrations over the four-year record (Table 14 and Table 19) also provides evidence of a consistent reservoir of chloride present in each system throughout the year. The affect of streamflow discharge rate on chloride concentration values increasing or decreasing from their respective baseline values depends not only on the total amount of stream discharge at the time of measurement but is also affected by the time of year the measurement is made. During spring, summer, and fall months when road salt is not being applied to roadways within the Saugus River or Stillwater River watersheds, the chloride concentration of the stream decreases with increasing flow rate (Figure 18 and Figure 25). This dilution effect is due to the influx of low chloride concentration rainwater to the stream (Visocky, 1970), which lowers the overall concentration of chloride present in both systems. During winter months, when road salt is being applied to roadways during precipitation events, the chloride concentration of the stream is influenced not only by the amount of precipitation but also land use within the watershed and the proximity to major roads (Ostendorf et al., 2001). The Saugus River and Stillwater River each display different responses to winter precipitation events (Figure 17and Figure 24). The increase in chloride concentration in the Saugus River during winter storms, where there would normally be dilution, indicates an increase of dissolved ions within the stream, most likely due to roadway deicing chemical runoff after application. In the Stillwater River, this increase in chloride concentration during winter storms is not seen. During the winter season, streamflow increases in the Stillwater River correspond to chloride concentration records that increase briefly at the onset of stream discharge increase but quickly decreases, indicating a dilution of the dissolved ions by low conductivity rain water (Figure 24). The brief increase when the stream discharge first begins to increase is also seen in summer increases in stream discharge in the Stillwater River (Figure 25) and could potentially be due to a pulse of contaminants that have collected on the ground surface near the stream between precipitation events, or during the winter season only, the result of salt from roadways entering the stream directly. While the overall increase of chloride concentration in summer months due to evapotranspiration effects is easily explained, the cause for the small increases in chloride concentration at the onset of precipitation events is not as easily rationalized. Further study of the increases of chloride concentration at the onset of precipitation events is needed to accurately quantify the exact dissolved constituents in these brief spikes. The Saugus River also displays a slight increase in chloride concentration before a decrease in chloride concentration corresponding to increased stream discharge during non-winter storm events (Figure 18). Both the Saugus River and the Stillwater River chloride concentration records during winter and non-winter storms show that as the discharge rate in each river reaches pre-storm event levels (before any discharge increase) the chloride concentration levels also trend toward values seen before the increased discharge rate (Figure 17, Figure

18, Figure 24, and Figure 25). This trend provides further evidence for the presence of a chloride concentration baseline value in each River.

The opposite patterns in chloride concentration in the Saugus River and Stillwater River during winter precipitation events can be linked to land use differences and differences in the way road salt (or chloride) move through each environment in each watershed. The Saugus River watershed is densely populated, over 50% urban and has 369 miles of roadway within its boundaries (Table 1). While the Stillwater River watershed is mostly forested with a low population density and only 166 miles of roadway within its borders (Table 1). The increased population and road density increase the overall amount of impervious surfaces subject to roadway deicing within the Saugus River watershed, causing more chloride to be applied within the Saugus River watershed than is applied within the Stillwater River watershed. This additional load of chloride applied in the Saugus River watershed is removed from the watershed differently than how it is removed from the Stillwater River watershed due to the increased amount of impervious surfaces which cause more direct runoff to streams during precipitation events. High-frequency chloride concentration records from Saugus River and Stillwater River provide the databases necessary to track the movement of road salt within the urban Saugus River watershed and rural Stillwater River watershed and the resolution necessary to quantify how the movement of chloride in the environment differs between these two sites.

5.4.2 Comparison of Dissolved Chloride Load and Dissolved Chloride Load Distribution

The calculation of dissolved chloride load discharged by the Saugus River and Stillwater River removes the dilution and concentration effects that fluctuating stream discharge rates cause on the dissolved chloride concentrations. After normalizing the total volume of dissolved chloride removed by each river to each river's drainage area, the Saugus River discharges an average 79% more total dissolved chloride per year than the Stillwater River (Table 13 and Table 19). The 79% increase in total dissolved chloride discharged per year by the Saugus River is equal to over 140,000 kg (140 metric tons) of dissolved chloride per square mile over what is discharged by the Stillwater River (see section 6 for discussion of amount of chloride applied to roadways within each watershed). On average, the Saugus River discharges over 75% more dissolved chloride per month than the Stillwater River per unit area over the four-year period of record (Table 13and Table 18). Aside from transporting more dissolved chloride, the Saugus River displays similar seasonal dissolved chloride loading rate patters when compared to the Stillwater River. Both Rivers have their highest dissolved chloride discharge rates during the winter and spring seasons (Table 12 and Table 17); however, the Saugus River has the greatest loading rate during the winter season while the Stillwater River has the greatest loading rate during the spring season. The increased dissolved chloride loading rate in the Saugus River and greater amount of total dissolved chloride removed by the Saugus River when compared to the Stillwater River can most likely be accounted for by the road density differences between the Saugus River and Stillwater River watersheds. The urban Saugus River watershed has more roadways subject to roadway deicing chemical application and has more dissolved chloride that will eventually be removed from the Saugus River watershed when compared to the rural Stillwater River watershed.

In order to assess whether or not the Saugus River and Stillwater River transported dissolved chloride differently, the hydrographs from each river are separated into a baseflow and event flow component as described in section 4.3. Both the urban Saugus River watershed and the rural Stillwater River watershed remove the majority of dissolved chloride from their respective watersheds as baseflow discharge. Over the four-year record, the Saugus River discharged 60% of the total dissolved chloride load as baseflow (Table 15). In contrast, the Stillwater River discharged over 80% of the total dissolved chloride as baseflow (Table 19), with the remainder being discharged during event flow periods. It is important to note that during the hydrograph separation analysis, the Stillwater River has a larger event flow component when compared to the Saugus River, with over 50% of the discharge from the Stillwater River being designated as event flow, compared approximately 45% being designated as event flow in the Saugus River hydrograph separation analysis (Table 7 and Table 8). This indicates that the increased dissolved chloride transported by the Saugus River, when compared to the Stillwater River, as event flow is not caused by the Saugus

River having more of its hydrograph trace designated as event flow. The difference that caused the Saugus River to discharge more dissolved chloride as event flow is the average dissolved chloride concentration in the Saugus River event flow compared to the Stillwater River event flow average dissolved chloride concentration (Table 14 and Table 19). The Saugus River event flow has an average dissolved chloride concentration of 70 mg/l, while the Stillwater River event flow has an average chloride concentration of 5 mg/l. Both of these values are above average chloride concentration for precipitation in this area of Massachusetts of 0.76 mg/l (Illinois StateWater Survey, 2009), however, the event flow chloride concentration in the Saugus River suggests significant road salt runoff directly into the Saugus River, especially during the winter months. This assumption is supported through the winter-time chloride concentration response to precipitation in the Saugus River (Figure 17), opposed to the Stillwater River (Figure 24). The Stillwater River does not display an increase in dissolved chloride concentration during winter storms. This observation is supported by the fact that event flow in the Stillwater River has a lower dissolved chloride loading rate average (67 kg/hour for the Stillwater River opposed to 270 kg/hour for the Saugus River), indicating a smaller amount of road salt is transported via event flow in the Stillwater River throughout the year. The Saugus River most likely receives more direct storm runoff containing elevated concentrations of chloride from deicing chemical use during winter storms.

6. DISCUSSION

Using the direct relationship between specific conductance and chloride concentration in natural water, high-frequency (15-minute interval) specific conductance datasets can be accurately calibrated to estimate chloride concentrations. Many studies have shown that chloride present in natural waters is a result of anthropogenic inputs, most notably roadway deicing chemical runoff (Kelly, 2008; Howard, et al., 1993; Nimiroski, et al., 2002). With roadway deicing chemicals (road salt) contributing the majority of chloride to the environment and the fact that chloride is found in all forms of road deicing salt, chloride can reasonably be used as a proxy for the movement of road salt in the environment. High-frequency chloride concentration datasets, when coupled with simultaneously collected streamflow datasets, provide the dissolved chloride load datasets needed to track how road salt moves through the environment in rural and urban areas.

Urban environments, represented by the Saugus River, and rural environments, represented by the Stillwater River, transport dissolved chloride in different ways resulting in different degrees of dissolved chloride retention in each environment. The increased dissolved chloride loading rate in the Saugus River and greater amount of total dissolved chloride removed by the Saugus River (79% more dissolved chloride removed by the Saugus River than the Stillwater River) is the result of differing land use with each watershed. The

Saugus River and Stillwater River have a total of approximately 626 lane miles and 329 lane km of roadway respectively, within their watershed boundaries (Mass GIS, 2007). The use of lane miles is important because road salt application rates are calculated per lane mile (Mattson, et al., 1994; Massachusetts Highway Department, 2009). The amount of road surface subject to winter road salting in each watershed would indicate that the Saugus River watershed receives approximately 48% more road salt per year than the Stillwater watershed, assuming application rates remain constant throughout the state. The discrepancy between the additional percentage of salt applied on roadways within the Saugus watershed and the additional percentage of dissolved chloride discharged from the Saugus River compared to the Stillwater River is 31% (79% more dissolved chloride discharged from the Saugus River while receiving only 48% more road salt than the Stillwater River watershed). This means that the either the Saugus River has additional sources of dissolved chloride that are discharged throughout the year, the drainage area extent of each watershed is less important than road density when relating dissolved chloride discharged in two separate systems, the pathways of road salt transport are different in the Saugus River compared to the Stillwater River, or a combination of the 3 possible explanations.

In order to assess whether or not the Saugus River and Stillwater River transported dissolved chloride differently, the hydrographs from each river are separated into a baseflow and event flow component as described in section 4.3.

The results found in this study represent a conservative estimate of the amount of dissolved chloride removed each year as baseflow and a maximum amount of chloride removed as event flow by each system (see section 5.1). It is clear from hydrograph separation analysis and the partitioning dissolved chloride transport in event flow and baseflow components that the two watersheds are transporting the road salt they receive during winter seasons in different manners. Both rivers are removing the majority of dissolved chloride as baseflow, however the Saugus River removes significantly more dissolved chloride as event flow (over 65,000 kg/sq mi per year) (Figure 22 and Figure 29). This difference in transport mechanism and roadway density differences within each watershed could explain why the Saugus River discharges 79% more dissolved chloride than the Stillwater River per year when normalized to drainage area extent. To see the effect road density has on the monthly average totals of dissolved chloride loads for the Saugus River and Stillwater River, the total average dissolved chloride loads are normalized per roadway lane mile, opposed to drainage area extent, for their respective watersheds. The results are displayed in Table 21. As can be seen on Table 21, the amount of dissolved chloride discharged as baseflow per lane mile in the Saugus River and Stillwater River are within 25% of each other while the amount of dissolved chloride discharged as event flow in each system differ by more than 75%. This indicates that the length of roadway in each watershed is more closely linked to the amount of dissolved chloride removed as baseflow than removed as event flow.

Clearly the total length of roadways must play a part in the amount of dissolved chloride discharged to the stream as event flow, due to the fact that more roadway length means more dissolved chloride applied per year. However, other factors, including street curbing, stormwater drainage to the river systems, and proximity of drainage ditches to streams may be more important when calculating the percentage of road salt that leaves a watershed via event flow. If the Saugus River receives direct stormwater drainage from curbed road areas, it could explain why the Saugus River discharges 40% of the total dissolved chloride leaving the watershed each year as event flow while the Stillwater River discharges less than 20% of the total the dissolved chloride discharged each year as event flow. It should be noted that after normalizing to roadway lane mile, the total amount of dissolved chloride discharged (event flow dissolved chloride + baseflow dissolved chloride) by the Saugus River is an average of 48% higher than the Stillwater River over the four-year period of record (Table 21). With road salt application rates remaining equal within each watershed per lane mile, the Stillwater River watershed must be storing the additional 23% of dissolved chloride per year that is discharged via event flow in the Saugus River (Saugus River discharges 40% of the total chloride via event flow while the Stillwater River discharges 17%). The results of a mass balance calculation estimating the input and calculated output of dissolved chloride to each watershed as event flow can be found on Table 22. Dissolved chloride inputs are calculated using a conservative estimate of road salt application rates reported from the in

Massachusetts from 1984 – 1986 of 18,185 kg dissolved chloride per lane mile per year (Mattson and Godfrey, 1994) and conservatively assuming that all road salt used is NaCl , which is 60.7% dissolved chloride by weight. This is considered a conservative estimate due to the fact that the mass balance calculation uses road salt application rates from over 20 years ago and, in general, application rates have increased since the mid 1980's in cold weather climates (Howard, et al., 2007; Kelly, 2008). Road salt generally also contains $CaCl_2$ and small amounts of $MgCl_2$ so therefore assuming all road salt is NaCl also makes the estimate of dissolved chloride input via road salt use a conservative one. Using the average amount of road salt removed via event flow from 2003 – 2007 in the Saugus River and Stillwater River, we are able to estimate the amount of dissolved chloride that enters the groundwater of each watershed per year (Table 22). This number is then normalized by roadway lane mile, and it is found that the groundwater within the Stillwater watershed should receive approximately 18% (1,800 kg) more dissolved chloride per year per lane mile than the Saugus River watershed groundwater due to the fact that over the four-year record the Saugus River discharges approximately 25% of the chloride applied to roadways in the same year in which it was applied via overland flow, as opposed to the Stillwater River which only discharges approximately 5% of the chloride applied to roadways via overland flow in the same year in which it was applied (Table 22). If steady state is reached in the Saugus River and Stillwater River with respect to dissolved chloride transport, the estimated kg of dissolved chloride per lane mile per year entering the groundwater in each watershed displayed in Table 22 should equal the amount of dissolved chloride removed from each watershed as baseflow per lane mile per year (Table 21). In the case of both the Saugus River and Stillwater River, the conservative estimate of the amount of dissolved chloride entering the groundwater is greater than the average amount of dissolved chloride removed from each watershed as groundwater recharge to each stream. This indicates that a steady state condition has not been reached with respect to dissolved chloride inputs from road salt and dissolved chloride outputs via baseflow discharge in either watershed. The finding that neither watershed is in steady state with respect to dissolved chloride inputs and outputs is corroborated by two studies conducted in Toronto, Canada that estimated that the time to reach steady state with respect to dissolved chloride inputs from road salt and outflow via stream discharge could take up to 100 years from the time of the studies in 2006 and 2007 Bester, et al. and Howard, et al. respectively. The four-year records used for this study lack the temporal change needed to estimate dissolved chloride concentration increases in groundwater or calculate the estimated time for each system to reach steady state. However, the fact that rural systems, such as the Stillwater River watershed, discharge significantly less dissolved chloride via event flow per year when compared to urban watersheds like the Saugus River watershed, indicate that future estimates of steady state conditions need to take the difference in transport mechanism of dissolved chloride in urban and rural settings into account when calculating approximation of time each system will take to reach steady state.

Saugus River and Stillwater River Monthly Average Total Dissolved Chloride Load 2003- 2007				
	Saugus River		Stillwater River	
Month	**Average Dissolved Chloride Load Baseflow Contribution (kg/lane mi)**	**Average Dissolved Chloride Load Event Flow Contribution (kg/lane mi)**	**Average Dissolved Chloride Load Baseflow Contribution (kg/lane mi)**	**Average Dissolved Chloride Load Event Flow Contribution (kg/lane mi)**
January	620	570	350	17
February	530	300	250	12
March	510	200	340	66
April	420	290	370	100
May	340	470	260	87
June	270	250	230	75
July	210	80	140	18
August	170	54	120	10
September	100	37	85	4
October	170	92	120	110
November	260	73	340	56
December	410	250	310	43
Total Yearly Contribution	**4,010**	**2,664**	**2,915**	**599**

Table 21: Monthly average dissolved chloride discharged by the Saugus River and Stillwater River normalized to roadway lane mile within each watershed.

Saugus River and Stillwater River Road Salt Application Rate Estimates and Chloride Retention Estimates		
	Saugus River Watershed	Stillwater River Watershed
Roadway lane miles	626	329
Estimated kg road salt applied per year	11,000,000	6,000,000
Estimated chloride kg from road salt	6,900,000	3,600,000
Average dissolved chloride discharged via event flow (kg/yr)	1,700,000	200,000
Estimated dissolved chloride entering groundwater (kg/yr)	5,200,000	3,400,000
Average dissolved chloride discharged via event flow (kg/lane mile per yr)	2,700	600
Estimated dissolved chloride entering groundwater (kg/lane mile per yr)	**8,200**	**10,000**

Table 22: Estimated chloride addition to each watershed due to roadsalt application within each watershed. Total roadway lane km obtained from Mass GIS(Mass GIS, 2007), estimated road salt application rate of 18,185 kg/lane mile per year after (Mattson and Godfrey, 1994). Average dissolved chloride discharge rates via event flow calculated from Table 21.

The fact that nearly 95% (Table 22) of the road salt applied in rural areas (where most drinking water aquifers are located) is entering the groundwater can potentially impact public drinking water supplies in a worse way than previously thought. This is due to the fact that it could take rural watersheds a longer time to reach steady state with respect to salt inputs and outputs when compared to urban environments. The timeframe of rendering the groundwater in rural areas unfit for drinking depends on many factors, including aquifer thickness, road salt application rates, and road density. However, it is important to note that a steady state of salt in and salt out for rural watersheds may happen slower than previous estimates of 100 years (Bester, et al., 2006; Kaushal, et al., 2005) due to the lack of dissolved chloride transport in event flow. Which results in higher dissolved chloride concentrations in groundwater than would be estimated assuming a portion of road salt applied to the roadways is leaving the system via event stream discharge during and directly after application. Even though the groundwater concentrations of dissolved chloride in urban groundwater will generally be higher than rural watershed groundwater, the difference in transport mechanisms could cause dissolved chloride concentrations in groundwater in both systems to be above the secondary maximum contaminant level for drinking water of 250 mg/l. This elevated concentration of dissolved chloride in groundwater could detrimentally affect streams and public water supply areas for centuries to come.

7. CONCLUSION

- High resolution (15-minute interval) dissolved chloride records allow for the accurate quantification of seasonal and yearly chloride transport trends. These records remove potential data biasing that could occur using manual sampling techniques due to the time of year sampling takes place, recent precipitation events, and drought periods.

- Annual trends and hydrograph separation of dissolved chloride load transport mechanisms suggests the existence of a large homogeneous chloride reservoir within the subsurface of both urban and rural watersheds. This reservoir of chloride is continually discharged to streams in all seasons via groundwater discharge, designated as baseflow in stream hydrographs.

- Streamflow discharge rate controls the total amount of dissolved chloride removed from both urban and rural watersheds with the majority of dissolved chloride (over 60% of the yearly total removed) being removed as baseflow in both environments.

- Rural watersheds are retaining as much as 95% of the chloride applied to roadways, and transport the chloride to streams and rivers predominately as groundwater discharge to streams. Urban watersheds transport chloride more evenly as both event flow and baseflow, discharging over 25% of the chloride applied to roadway surfaces in the same year in which it is applied.

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