Assessment of the Effects of Urbanization on Water Quality along a New England Stream

By

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Abstract.

Urbanization has a significant impact on water quality. Urban drainage systems and impervious surfaces accelerate the delivery of pollutants from land areas in watersheds to streams and rivers. The harmful pollutants include sodium and chloride associated with the application of road salts during the winter, metals and oils associated with vehicles and impervious surface. The goal of this project was to access impacts of urbanization on River Meadow Brook and validate a chloride assessment tool. The first phase of this research was a part of a chloride study sponsored by the Massachusetts Department of Environmental Protection (MassDEP). The second phase of the projects included flow and water quality monitoring. The first phase of the project involved the development of a linear regression equation to validate a chloride assessment tool that MassDEP had developed and implemented based on historical data. River Meadow Brook, a Massachusetts stream that flows from a non-urban, rural area with relatively low pollutant concentrations to highly urbanized area in Lowell, MA, was chosen for that purpose because of the area's large concentration of roadways and highways and historically high concentrations of chloride. Water samples and continuous conductivity data were collected for a 7-month period. Using 24 grab samples analyzed at the United States Environmental Protection Agency (USEPA) laboratory in Chelmsford, MA, the model was validated with 99.37% confidence using a linear regression equation. Therefore, the relationship between conductivity and chloride was validated. Calculated chloride was used to identify chloride violations of ambient water quality standards in River Meadow Brook.

In addition to MassDEP study, the relationship between the percent of imperviousness and various trace metals, anions and total suspended solids was developed to show impacts of urbanization on the stream. The research approach included collection of both water samples and flows to calculate daily pollutant loads. Water monitoring included grab samples and unattended continuous conductivity with a 30-minute recording intervals. Discharge monitoring included collection of flows in River Meadow Brook using a brad- crested dam and the area- velocity technique.

A wide variety of cations from a sampling of 5 sites along River Meadow Brook were analyzed using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Cl, sulfate and nitrate were analyzed using the Dionex ICS-2100 Ion Chromatography System. Laboratory results of water quality parameters showed that pollutants associated with impervious surface increase as the stream flows from its headwaters to downstream. The result from the Pearson correlation analysis revealed that sodium, chloride, potassium, vanadium, nickel, copper, arsenic, TSs and pH had a positive relationship with imperviousness while DO and nitrate had negative relationship. The combination of laboratory and field analysis helped to assess the impacts of urbanization and checked against ambient water quality standards.

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Abbreviations

NPS- Non-point source pollution

USEPA- The United States Environmental Protection Agency

BMPs- Best management practices

CWA- The Clean Water Act

TMDL- the total maximum loads

MassDEP- The Massachusetts Department of Environmental Protection

NURP- The Nationwide Urban Runoff Program

TSS- Total suspended solids

QC- Quality Control

QA- Quality Assurance

1. Introduction

1.1. Background and Problem Overview

According to a United Nations report published in 2013, it is projected that the human population will increase by 2.4 billion people by 2050 (United Nations, 2013). This increase will require additional development of cities, towns and associated infrastructure.

The associated increase in these urban areas will lead to large amount of paved area and impervious surfaces. The increases in impervious area will result in reduction in infiltration and significant increases in volumes of stormwater runoff that are discharged directly into receiving water bodies.

The traditional way of managing storm water runoff has been to construct a storm drainage networks to carry away this runoff volume to receiving streams. Surface water bodies that receive storm water runoff degrade because of the variety of pollutants have been discharged directly into water bodies, resulting in human health impacts and physiological impairment of aquatic biota.

Contaminants commonly found in urban stormwater runoff are summarized in Table 1.1. The pollutants generated in urban water runoff may come from different sources: residential, commercial and residential activities, construction sites, parking lots, and atmospheric deposition. These pollutants include sediments, oil, grease and toxic chemicals from motor vehicles, road salt and heavy metals from roadways, highways, and other impervious surfaces. The heavy metals typically include lead copper, cadmium, chromium and zinc (Davis el at. 2001; International stormwater BMP database 2011). Road salt, which is particularly prevalent in the Northeast, is the main cause of elevated concentrations of sodium and chloride (Copper el at. 2014; Godwin el at. 2003; Harte el at. 2010). The impacts of these constituents on surface water bodies is difficult to quantify.

Table 1.1. Sources of surface water pollution

Pollutant	Contamination source
Metals	Automobiles, bridges, atmospheric deposition, industrial areas, soil erosion, corroding metal surfaces, combustion processes
Total Suspended Solids	Streets, lawns, driveways, roads, construction activities
Nutrients	Lawn fertilizers, atmospheric deposition, automobile exhaust, detergent

1.2. Study Goal and Objectives.

The overall goal of this project was to determine changes in water quality as the stream flows from its headwaters to highly urbanized area with multiple highways and roads. The specific objectives are as follows:

- Determine the relationship between conductivity and chloride present in River Meadow Brook using continuous conductivity data
- Re- validate fresh water chloride assessment tool developed by MassDEP
- Determine concentrations of pollutants present in different catchment areas along River Meadow Brook to assess urbanization impact
- When available, calculate flows and pollutant loads using area- velocity technique and broad-crested weir
- Compare pollutant concentrations against water quality standards

There were several hypothesis developed in the beginning of the project, which include:

- A highly polluted small stream can affect the water quality of a larger water body
- Surface water quality degrades as the amount of paved surfaces increase
- Percent of impervious coverage was expected to be strongly correlated with a variety of metals, anions and TSS

To meet the objectives and address the hypotheses, this project concentrated on a river system that included varying levels of urbanization along its length. River Meadow Brook was chosen for this purpose. River Meadow Brook is a 6.4 mile tributary located in the Concord watershed in Massachusetts, which flows through Chelmsford, MA and Lowell, MA. This river, which flows through regions of increasing urbanization and impervious surface, was monitored for water quality parameters, including conductivity, toxic heavy metals, anions, dissolved oxygen (DO), pH and TSS to assess urbanization impacts on the stream. Water quality parameters were collected over a 7- month period including winter time. Background material is summarized in Chapter 2 and the methodology is summarized in Chapter 3. The results, including the development and validation of the chloride assessment tool and the relationship between concentrations of various inorganics and impervious surface, are presented in Chapter 4, and a summary and conclusion are provided in chapter 5.

2. Background.

This chapter provides background information on non-point source pollution, categories, sources and regulations of pollutants associated with impervious surface based on previous studies. In this chapter, each pollutant of interest was reviewed separately to identify its adverse impact on ambient water quality and relationship to impervious coverage.

2.1. Non-Point Source Pollution.

2.1.1. NPS Pollution Overview

Surface water pollution refers to the contamination of a surface water body by substances that can adversely impact aquatic life and human health. Urban surface runoff is considered to be non- point source (NPS) pollution. NPS pollution, unlike pollutant discharges from industrial and sewage treatment plants, is caused by rainfall or snowmelt, transporting pollutants over and through the ground. As the runoff flows over surfaces, it transports pollutants, depositing them into rivers, lakes, wetlands, coastal and ground waters ("What is nonpoint source pollution", 2016). Since land area in many urban areas is covered with asphalt pavement with asphalt and concrete, water is not able to filtrate into the soil and flows into rivers and streams as runoff. This process can impact ambient waters adjacent to urban areas, especially in the winter time when road salt is applied in large quantities. Another example of NPS pollution includes agricultural runoff. In agriculture, land is typically plowed to grow crops. Plowing the land exposes the soil for fertilizers and pesticides to escape, and to be deposited into nearby waterbodies during rainfalls. The primary NPS pollution of concern from agricultural activities are nitrogen and phosphorus. Both are essential for plant growth, but if too much of these substances enters a waterbody, it can lead to eutrophication. With NPS pollution, water quality can vary with season and can be significantly affected by precipitation events (Mallin et al., 2009). NPS pollution is not directly regulated and considered the leading remaining cause of water quality problems in the United States. The United States Environmental Protection Agency (USEPA) addresses NPS pollution problem through best management practices (BMPs). BMPs are the primary method for reducing pollution concentration from storm water runoff (U.S. EPA 2012e). Each state is required to submit a management program for waters that cannot meet water quality standards without controlling NPS pollution.

2.1.2. NPS Pollution Management

2.1.2.1. Federal Regulations

Potential problems caused by pollutants from non- point sources such as urban and highway runoff are addressed by policies and laws such as the Clean Water Act (CWA) of 1972 and amendments and non-point source management programs. The state transportation agencies have a responsibility to identify and minimize impacts from highway pollutants that are being washed off from highways to nearby water bodies.

In 1972, USEPA was charged to implement pollution control programs under the CWA to protect the condition of national water resources. CWA is a reorganized and expanded version of the Federal Water Pollution Control Act, 1948. The objective of the CWA is to "restore and maintain the chemical, physical and biological integrity of the Nation's waters" (33 U.S.C §1251(a)). The CWA establishes the basic structure for regulating water quality standards and discharges of pollutants into the waters of the United States. Under the CWA, Section 304 (a)(1), the EPA requires water quality criteria to be developed based on the latest scientific knowledge that accurately indicate the impacts of pollutants on human health and the environment. Water quality parameters can be numeric and narrative (the desired conditions of a water body). Under Section 303 (c) of the CWA, states have the responsibility for adopting water quality standards as laws and regulations. If it is determined that water quality parameters in a waterbody are above standards, it is added to the 303d list. Section 303d of the CWA is known as a list of impaired waters in the United States. This list is updated every 2 years. For water bodies added to the 303d list, the total maximum loads (TMDLs) are established.

Aquatic life criteria are developed under Section 304(a) of the Clean Water Act to set up a safe upper limit of toxic chemicals present in water that do not pose a significant risk to the majority of aquatic species. The USEPA recommends that states should use aquatic life criteria as guidance in developing their own ambient water quality standards. Table 2.1 summarizes the aquatic life criteria of pollutants often associated with urban and highway runoff based on previous studies described in section 2.2.

Sometimes these criteria can be adopted directly from USEPA. For example, in 1998, EPA defined chronic chloride toxicity as “the 4-day average concentration of chloride, when associated with sodium, does not exceed 230 mg/l more than once every 3 years on average”, and acute chloride toxicity as “the 1 hour average chloride concentration does not exceed 860 mg/l more than once every three years on average” (USEPA 1986). MassDEP Surface Water Quality Regulations (314 CMR 4.00) do not specifically include water quality standards for chloride for the protection of aquatic life. However, section 4.05 (5) (e) of the regulations states that USEPA’s recommended numerical criteria will apply for any pollutant where the Department has not otherwise listed a specific criterion or standard for such pollutant. Therefore, MassDEP utilizes USEPA’s recommended chronic and acute standards to assess water bodies for impairment due to elevated chloride concentrations.

Table 2.1. Aquatic Life Criteria

Priority Pollutant (dissolved)	Freshwater Aquatic Life		Saltwater Aquatic Life		Freshwater criteria hardness based standard
	acute (µg/L)	chronic (µg/L)	acute (µg/L)	chronic (µg/L)	
Arsenic, total	340	150	69	36	No
Cadmium	1.8	0.72	33	7.9	Yes
Chloride	860000	230000	—	—	No
Sodium					
Chromium (III)	570	74	—	—	Yes
Copper	—	—	4.8	3.1	no
Iron	—	1000	—	—	Yes
Lead	65	2.5	210	8.1	yes
Nickel	470	52	74	8.2	yes
Zinc	120	120	90	81	yes

2.1.2.2. Best Management Practices

Because NPS pollution poses many threats to environmental and human health, it is important to effectively manage the associated pollution problems. In 1996, the MassDEP issued a Stormwater Policy aimed at preventing stormwater discharges from causing and contributing to the pollution of the surface waters of the Commonwealth. In 1997, MassDEP published the Massachusetts Stormwater Book as guidance on the Stormwater Policy (MassDEP 2014). Chapter 2 of the Stormwater Handbook presents strategies, BMPs, to improve already existing practices for capturing pollutants from stormwater discharge.

BMPs may include structural and nonstructural methods of reducing pollutant content. The following BMPs often used in urban areas throughout Massachusetts:

- *Deep sump catch basin*- an underground retention system designed to remove large debris and coarse sediment. Provides 25% TSS removal
- *Oil/grit separator*- an underground storage tank with three chambers to remove heavy particulates and hydrocarbons from stormwater
- *Sediment forebay*- usually consists of an excavated pit, or cast structure combined with a weir to slow down stormwater and provide the environment for sedimentation of suspended solids
- *Buffer strips*- strips of grass located between and around impervious paving materials such as parking lots and sidewalks, and a body of water. This method helps to absorbs soil, fertilizers, and other pollutants before they can reach the water.
- *Retention ponds* typically an excavated pit that captures runoff and stormwater. Sediments and contaminants settle out of the water when they are trapped in the retention pond.
- *Constructed wetlands* a relatively recent innovation in which an area is made into a wetland; the land is then used to slow runoff and absorb sediments and contaminants. The constructed wetland also provides habitat for wildlife.
- *Porous paving materials*- often used in parking lots and highways. The porous pavement allows rainwater and stormwater to drain into the ground beneath it, reducing runoff

In some cases, there is also a stone reservoir underneath the pavement to allow filtration of the water before it reaches the groundwater.

2.2. Impact of Urban Land Use on Water Quality

This section describes the key physical and chemical influences on ambient water quality associated with urban land use and imperviousness, based on a review of the information summarized from previous studies. Monitoring for specific chemicals helps states assess surface waters against ambient water quality criteria, as well as to identify and trace the source of the impairment.

Urbanized areas directly affect ambient water quality because these areas often have high percentage of impervious area, which results in direct pollutant discharges into streams. For many years, urban water runoff has been the subject to numerous studies to characterize its nature and impacts on aquatic life. The Nationwide Urban Runoff Program (NURP) conducted the most comprehensive study of urban runoff. The program was focused on the characteristics of urban runoff from different urban land use categories. Sampling was conducted for 28 NURP projects which included 81 specific sites and more than 2,300 separate storm events. From NURP, it was concluded that all 13 metals of USEPA's priority pollutant list were detected in urban runoff samples (Appendix A); Nutrients were present but concentrations did not appear to be high compared to other possible sources. Total suspended solids (TSS) were highly correlated with percentage of impervious surface in catchment areas. They also found that there were no significant differences between pollutant concentrations resulting from different urban land use categories such as commercial and residential. There was a significant difference, however, in pollutant concentrations in urban runoff generated from nonurban areas (USEPA 1983).

In another study, the Federal Highway Administration (FHWA), analyzed stormwater runoff from 31 highways in 11 states during the 1970s and 1980s. It was determined that pollutants originating from urban water runoff included heavy metals, nutrients, TSS, sediments and other constituents (Newberry and Yonge 1996). However, it can often be challenging to understand the fate and transport of physical and chemical impairments in a watershed due to the variety of inputs from different sources and spatial variability (Barber *et al*., 2006).

2.2.1. Impervious Surface and Heavy Metals

In wooded or natural areas, water pounded on the forest floor infiltrates into the soil, converts to groundwater, is utilized by plants, and evaporates or transpires into the atmosphere. In urban areas, on the other hand, that water is converted directly into surface runoff due to the large amount of impervious surface coverage. The larger the amount of impervious surface present, the higher the percentage of direct runoff.

As stated previously, impervious surfaces are described as pavements such as roads, sidewalks, driveways and parking lots that are covered by impenetrable materials. Imperviousness is one of the most important characteristics describing the extent of urbanization (Lee and Heaney 2003). Previous studies on urban runoff were to correlate urban runoff water quality in areas with different land uses and impervious surface. Initial studies of the effects of urbanization noted that there were four interrelated but separable effects on the hydrology of an area associated with urbanization: changes in peak flow, changes in total runoff, changes in the hydrological amenity, and changes in water quality (Leopold 1968). Later studies were conducted to proof that theory. Metasaranta et al. (2005) looked at the rainfall-runoff relationship and stormwater quality in three different urban areas with different percentage of impervious surface: <20%, 20% and 50% respectively. Runoff water quality results showed that the area with highways and road construction (50% impervious surface) led to poor water quality. Maximum average concentrations of total nitrogen, total phosphorous and total suspended solids were the highest compared to other two locations with lower percentage of impervious surface.

Another research investigation that followed a similar approach was completed by Valtanen et al. (2014). Runoff water quality was continuously measured in three catchment areas with 19%, 62% and 89% of impervious coverage. From the water quality results, it was concluded that TSS, tot-N, Mn, Co, Ni and Cu increased with increasing imperviousness. Total- phosphorous (tot-P), Al, Cr, Zn, Pb varied in city center catchments compare to low populated areas. Increased volume of runoff with larger pollutant loads are appeared to be more significant during warmer seasons especially during spring.

A number additional reports investigated the sources of metals in urban areas. Davis et al. (2001) investigated various sources of lead, copper, cadmium, and zinc in urban water runoff. The authors determined that all four metals came from building siding, and vehicle brake emissions the sources of copper, and tire wear of zinc. These four metals were found in the final report of the U. S. EPA's NURP as the most prevalent constituents found in urban runoff (U.S.EPA 1983).

Bannerman et al. (1993) studied critical urban source areas, which were defined as areas that produced large contaminant loadings. Contaminant concentrations and simulated runoff volumes were used to determine source-area loads. The samples were analyzed for 16 constituents including TSS, Cd, Co, Pb and Zn. Runoff from parking lots had the largest loads of solids and Co. Runoff from industrial roofs contributed the most of the Zn load. From this study, the majority of the runoff loads for many contaminants were from streets in every land use where the most of the pollutants come from parking lots.

Van Matre and Mahler (2003) recognized that rooftops from urban contributed to loadings of zinc and lead. 20% and 18% of the total watershed load of zinc and lead, respectively, came from rooftops. The concentrations of zinc were in the range 141- 6200 mg/kg and lead from 36- 390 mg/kg over 22 sampling dates.

Tiefenthaler et al. (2001) evaluated samples of stormwater runoff from 8 different land use types in southern California for a number of metals including Fe, Zn, Cu and Pb. These metals had the highest mean concentrations of any constituents analyzed. The research showed that industrial land use sites contained highest concentrations of metal concentrations. Zinc was found in particularly high concentrations after dry periods.

In a study conducted by Lind and Karro (1995), heavy metal concentrations in the topsoil layers of urban roadside areas in Sweden to be 2 to 8 times higher when compared to rural areas. In areas with high infiltration ability, concentrations of metals, on average, were 200% less than in the area with the traffic intensity 34000 vehicles in 24 hours. A general conclusion was that the concentration of Zn, Pb, Cu increases with increasing impervious surface.

2.2.2. Sediments

As impervious surface coverage increases in urban areas, more sediments are generated. When rainfall or snowmelt event occurs, sediments are washed-off into nearby streams. Sediments may also come from stream channel erosion if large volumes of flow were generated. Solids in stormwater runoff, both suspended and dissolved, are classified using various approaches, with most dependent on size. Sediment pollutant levels can be measured as total suspended solids (TSS). TSS and total dissolved solids (TDS) are separated in practice by a 0.45-µm filter. TSS include all particles suspended in water which will not pass through a filter. There is no formal water quality criteria for TSS but it is generally accepted that water with TSS concentration less than 20 mg/L is considered to be relatively clear. One of the harmful effects of TSS on ambient water is that the solids tend to absorb heat from sunlight, which increases water temperature and, therefore, decreases levels of dissolved oxygen. Some fish such as trout are sensitive to changes in temperature (Meisner, 1990; Flebbe, 1994). Another negative impact from increased concentrations of TSS is reduction of vulnerable aquatic organisms such as benthic communities. Miserendino et al. (2008) conducted a study to assess urban impacts on benthic community and fish in Argentinian streams. From the study, he concluded that higher levels of TSS in urban areas degraded invertebrate species richness compare to reference sites (minimally disturbed). Another study by Hepp and Santos (2009) also confirmed that the diversity and evenness of sensitive organisms tended to decrease along land use gradient- from low to high.

A strong correlation between TSS and metals was observed in previous research because these elements tend to absorb onto sediments. That was a good observation because treating solids can actually reduce metal concentrations. Research study by Nasrabadi et al. (2016) linked concentrations of TSS to metal concentrations present in the South of Caspian Sea, Iran. In this study TSS and eight metals (Ni, Pb, Cd, Cu, Zn, Co and As) were analyzed from 10 locations within the catchment area. The robust relationship was achieved by linear regression with R^2 being 0.87 for copper and 0.95 cadmium.
EPA (1983) calculated that on an annual load basis, suspended solids contributions from urban runoff an order of magnitude or greater than those contributions from waste water treatment plants. Control

of urban runoff, as opposed to advanced waste treatment, should be considered where TSS-associated water quality problems exist.

2.2.3. Nitrate and Sulfate

Nitrogen pollution is one of the most common, expensive, and challenging environmental problems caused by increased concentrations of nitrogen. Nitrogen is naturally present in the air and are parts of aquatic ecosystem (EPA, Nutrient Problem). When these elements are in excess, they impact water bodies resulting in algae blooms. Algae harm water quality and decrease the oxygen present in water, which is needed for aquatic organisms to survive.

In stormwater, nitrogen can take different forms such as ammonium (NH_3-N), nitrate (NO_3-N), nitrite (NO_2-N), dissolved organic N (DON), and particulate organic N (PON) which makes nitrogen difficult to control (Li L. and Davis A. 2014). Any of these forms can contribute to eutrophication However, nitrogen in the form of nitrate is of the greatest concern because it is not absorbed by soil and usually moves with infiltrated water. Sources of nitrate in urban areas are include chemical fertilizers applied to lawns, landscaped areas, and gardens. Concentrations of nitrate can vary widely. Based on Shanley et al. (1995), nitrate concentrations were in the range from 0.06 to 0.6 mg/l in a Quabbin Reservoir, MA tributary. Concentrations of nitrate in rainwater of up to 5 mg/l have been observed in industrial areas (Van Duijvenboden & Matthijsen 1989). In rural areas, concentrations are somewhat lower. The nitrate concentration in surface water is normally low (0–18 mg/l) but can reach high levels as a result of agricultural runoff, refuse dump runoff or contamination with human or animal wastes.

To control inputs of nitrate, the EPA has set a drinking water Maximum Contaminant Level (MCL) of 10 mg/L for nitrate to prevent blue-baby syndrome in infants under the age of six months who could consume the water from surface waters that serve as sources of drinking water (USEPA, 2009).

Sulfate occurs naturally in rivers from weathering of rocks. Additional input of sulfate to surface waters can be from fuel combustion (Hem 1992).

Campo, K. el at. (2003) monitored nine rivers in the New England region for various constituents including sulfate. In the report, it was indicated that sulfate concentrations were generally highest in the intensely urbanized Aberjona River and lowest in the minimally urbanized Stillwater River. Therefore, the percentage of urban land use in the drainage basin affects sulfate concentrations Among the indicator median sulfate concentrations ranged from 6.9 (Stillwater River) to 25.8 mg/L (Aberjona River) in the indicators basins and from 7.1 (Kennebec River) to 12.25 mg/L (Charles River).

2.2.4. Road salt

In urban areas of the Northeast, road salt is an additional pollution contributor. When road salt is applied in large quantities, it may cause exceedances of the USEPA water quality standards, and has negative impacts on aquatic biota, plants and soils (Heath and Belaval, 2010; Novotny et al., 2008; Mattson and Godfrey, 1994; Trombulak and Frissell, 2000).

Road salt has commonly been used for several decades to maintain safety on roads. When applied on snowy or icy roads, the salt creates a solution with a lower freezing point than water, therefore turning the ice into a drivable slush (Hochbrunn, 2010). Sodium chloride (NaCl), more commonly known as table salt, is one of the most commonly used types of road salt in Massachusetts and many other states.

When the road salt interacts with water, it dissolves and the break down components are sodium (Na^+) and chloride (Cl^-) ions. These constituents, are transported via runoff and discharges into both surface water (streams, lakes and rivers) and the groundwater. Chloride and sodium ions have different physical and transportation paths in the environment. Chloride is a non- reactive, conservative ion that is soluble and very mobile. Sodium, on the other hand, is prompt to ion exchange in the subsurface releasing nutrients into the groundwater (NHDES).

Because of the non- reactivity of chloride ions, the presence of it in water becomes a good indicator of pollution due to application of road salt. Several recent research findings indicate negative environmental impacts from deicing practices particularly due to released chloride ions. One of the studies presented by Mattson and Godfrey (1994) found a correlation between the length of area of interstate highways and observed elevated levels of chloride in streams based on sampling results collected in April 1992 from 162 random stations across the Commonwealth.

Another study conducted in New Hampshire has documented increased chloride concentrations in four watersheds with the most development. The chloride concentrations in streams ranged from 149.0 mg/L to 308.7 mg/L where 8 to 31 percent of the watershed area consisted of commercial, industrial and transportation areas. Deicing of roadways and parking lots accounted for 91 percent of the chloride loading in each watershed (Throwbridge at el., 2010).

A 2008 study stated that the average chloride concentrations in a rural stream in southeastern New York increased from 15 mg/L to 40 mg/l over a 20 year period from 1986 to 2005 due to application of road salt (Kelly et al. 2008). The U.S. Geological Survey has reported that the mean annual chloride concentrations in the Merrimack River increased from 2.9 mg/L in the early 1900's to 24.9 mg/L as measured in 1995 (Robinson et al. 2003).

MassDOT has conducted several research studies along I-93 corridor where they have found exceedances in chloride concentrations both from major interstates and parking lots, municipal roads, and developed areas with high percentage of imperviousness (MassDOT, 2012).

2.2.4.1. Development of Chloride Assessment Tool

Measuring chloride in-situ is a process requiring frequent calibrations, and involves additional complications. The preferred method for determining chloride in water is ion chromatography. The method is reliable, and provides accurate results. However, this method is not suitable for field applications or real-time monitoring. Historically, chloride was based solely on grab samples. Alternately, people measure conductivity to estimate chloride concentrations in water. In 2015, MassDEP developed the chloride assessment tool which correlates conductivity and concentrations of chloride. However, as mentioned earlier, one time grab samples cannot provide reliable information about chronic or acute chloride concentrations in ambient waters because the toxicity levels are based on the 4-day- average and 1- hour- average chloride concentrations respectively.

Alternately, people have also measured conductivity to estimate chloride concentrations in water using correlations between conductivity and chloride. In 2015, MassDEP developed the chloride assessment tool which correlates conductivity and concentrations of chloride. MassDEP gathered 2442 historical data points collected from 249 stations statewide from June 7, 1995 to November 14, 2012 (Figure 2.1). These data were analyzed for chloride and specific conductance (SC) in co-located samples (i.e. collected at a single location). The Kolmogorov-Smirnov statistical test was used to examine whether or not statewide SC data were normally distributed (Daniel and Cross 2012). The results showed that the SC data has 15 points that are above 30,000 $\mu S/cm$ and 1 point in the 10,000 and 30,000 ranges that make the SC data precluded the use of a normal distribution. It was concluded that those points might be directly or indirectly influenced by the sea. Therefore, these points were excluded from the freshwater model because in Massachusetts, there is no inland freshwater stations with SC higher than 10,000 µS/cm (Health and Morse, 2013; Health, 2014).

Linear regression was used to develop the relationship between chloride concentrations and for SC less than 10,000 µS/cm in freshwater (Figure 2.2). Chloride concentrations and SC show a strong linear relationship with an equation: Y = 0.2753X – 18.987 with $R^2 = 0.9445$, $P<0.001$, N = 2,426 (Y=Chloride concentration, X= SC). The lowest chloride concentration was 1.0 mg/L and the highest was 2,400 mg/L. Threshold SC values that are associated with the chronic and acute exposures of dissolved chloride were calculated by plugging in Y= 230 mg/L (chronic level) and Y= 860 mg/L (acute level) into the equation, resulting in X = 904 µS/cm and X = 3,193 µS/cm, respectively.

The regression freshwater model was first validated using data for the USEPA Auburn, MA project (winter 2013-2014) (Health, 2014). For the Auburn study, 37 samples were collected by the USEPA and analyzed for chloride concentrations along with co- located SC measurements. The freshwater model developed by MassDEP was used to calculate predicted concentrations of chloride. The predicted numbers generated by the MassDEP model was put on a best fit line with real data collected from the USEPA study. The results showed that the model developed by MassDEP is 99.08% accurate and the regression line is also close to the 1:1 line with a slope of 0.9709 (Figure 2.3). All the statistics and model estimation were performed using SAS® (Version 9.4, SAS Institute Inc. Cary, NC)

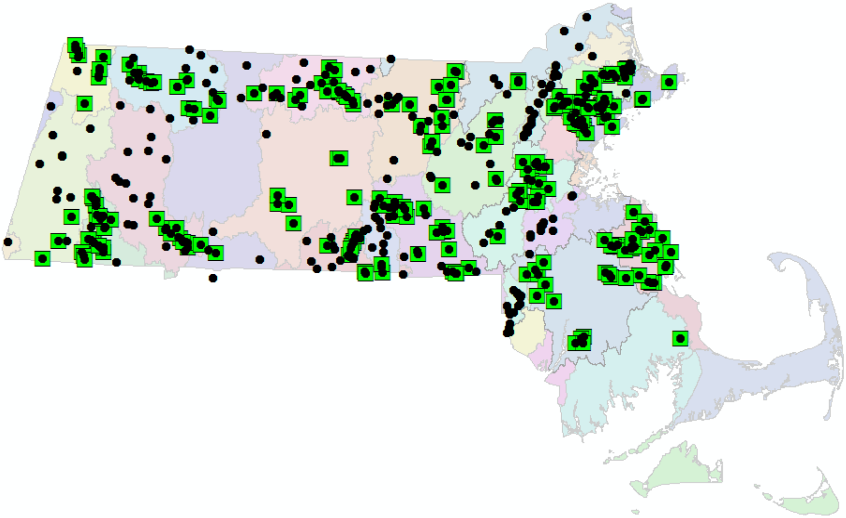


Figure 2.1. Chloride and co-located conductivity stations in Massachusetts

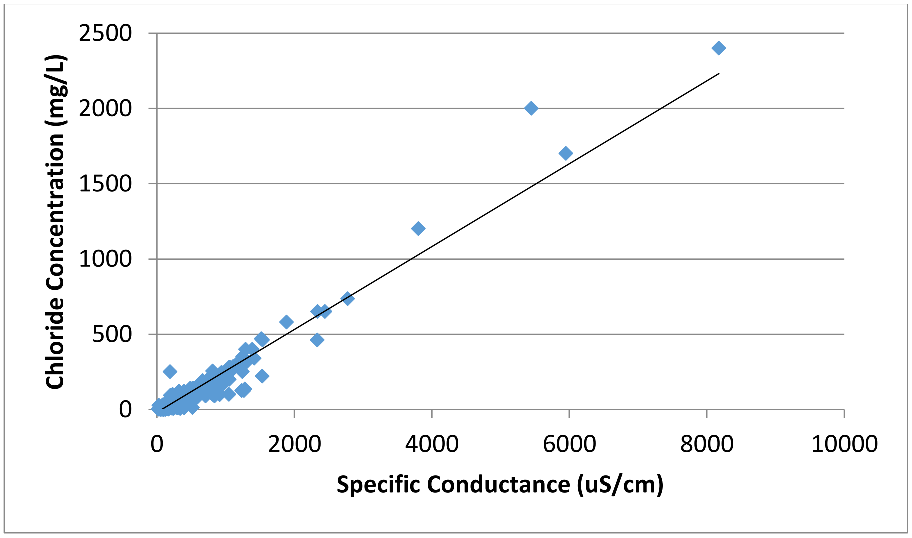


Figure 2.2. Relationship between Chloride and Conductivity

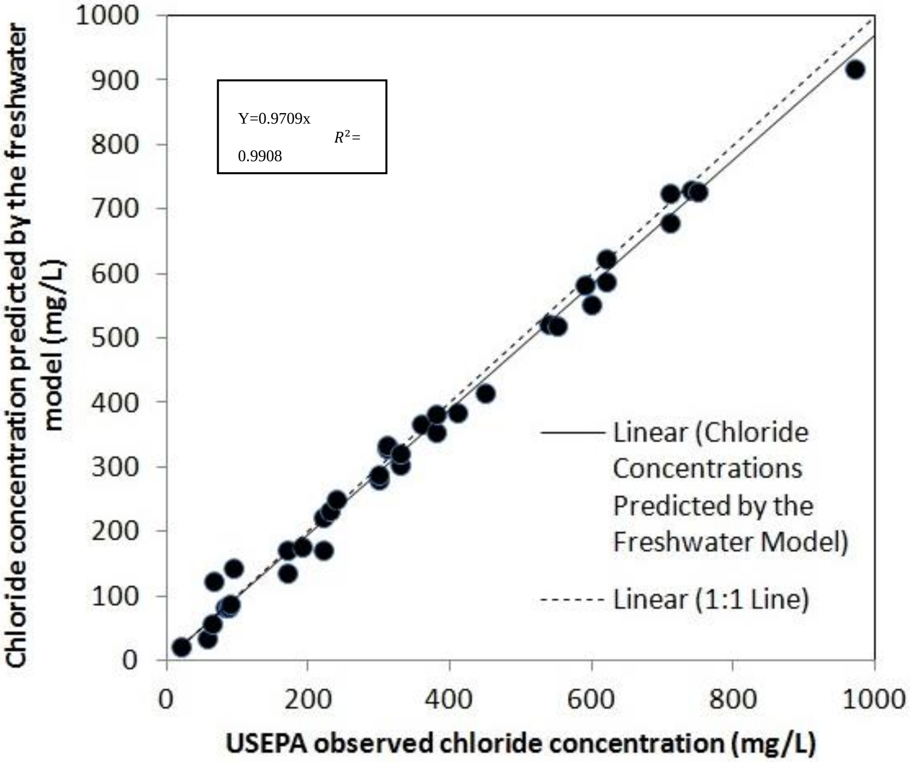


Figure 2.3. Validation of Freshwater Model using USEPA data

2.3. Flow monitoring

To understand to what extent urban runoff effects the receiving water bodies, in terms of pollutant loads, surface water discharge measurements and pollutant concentrations need to be collected. Surface water discharge (volumetric flow) is the rate of flow or the volume of water that passes through a channel cross section in a specific period of time. Discharge is reported as total volume of water in cubic feet per second (ft^3/s or cfs) or cubic meters per second (m^3/s) (USGS, 2007).

According to the USEPA, the first method of obtaining discharges in an open channel is to measure a cross sectional area of the channel and flowrates using a current meter. A second method is to use hydraulic structures such as weirs in a conjunction with an automated device such as mechanical or electronic flow meters. Additionally, a measurement of the stage needs to be used in determining the flow rate through the use of published equations. A stage (stream stage or gage height) is the height of the water surface relative to an established fixed point and is measured in meters or feet. For example, the

USGS uses different equipment and methodology for observation and recording of stage such as traditional still- well systems, bubble gages, submergible pressure, transducers, radar, acoustic and laser methods. These devices are used to collect stage height information continuously every 15 minutes, and automatically send data to office computers (USGS, 2010). It is often a challenge to establish a fixed point (datum) which is often set up as a zero height being near the river or stream bed. The distance between the water surface and the bottom of the stream is monitored using a rigid metal plate graduated in meters or feet attached to a secure backing usually related by survey to a fixed reference (e.g., a bridge deck). The application of stage measurements is the development of a stage-discharge relationship, also known as rating curve and computation of pollutant loads.

It is often necessary to measure an instantaneous discharge to develop a stage-discharge relationship. It can be achieved through the area-velocity technique or broad- crested weirs that will be described in Chapter 3.

2.4. Pollutant Loads

As mentioned above, establishing a solid relationship between discharge and pollutant concentrations can be used in pollutant load calculations for various nonpoint source parameters in urban areas. The pollutant load is the measure of mass of pollutant which passes through a cross-section of the river in a specific amount of time. Loads are expressed in mass units (e.g. tons, kilograms), but the interval of time over which the load occurs is always important to indicate.

Total pollutant loads can be calculated as follows:

$$L_T = \sum_{i=1}^{n} Q_i * C_i * \Delta T_i \qquad \text{(Equation 1)}$$

Where,

L_T- is the total load of a pollutant in units of mass

Q- is the flowrate in mass per time

C- is concentration in mass/volume

ΔT- is a time interval

In previous research, pollutant loads of different variables were correlated with imperviousness. For example, Hatt et al. (2004) estimated that the mean annual loads of several water quality parameters were strongly positively correlated with basin imperviousness. He also concluded that the percent of impervious surface coverage in drainage area controls water quality degradation, rather than the presence of impervious areas alone. Relationships between imperviousness and loads of water quality parameters were taken as a central assumption in most simple and complex pollutant loading models (Donigian and Huber, 1991). For example, Simsek, Uygun and Albek (2014) used the Hydrological Simulation Program-Fortran (HSPF) developed by USEPA to model the relationship between impervious surface and water quality parameters such as sediment, chloride and nitrate. The result showed that impervious segments have been found to be affecting all parameter concentrations.

2.5. River Meadow Brook. General overview and early history.

River Meadow Brook flows in a south-to-north direction from southwestern Lowell to the Concord River (Figure 2.4). The total length of the stream is 6.4 miles. River Meadow Brook's headwaters are located in a nutrient-rich wetland. As the stream flows north in Lowell, MA more urbanized area become predominant with several highway and roads intersections such as Route 3A, Lowell Connector, and highway 495. River Meadow Brook narrows and becomes more sinuous as it flows through a residential area. The final section of River Meadow Brook flows through an industrial complex and passes under a couple of large brick buildings, then discharges into the Concord River.

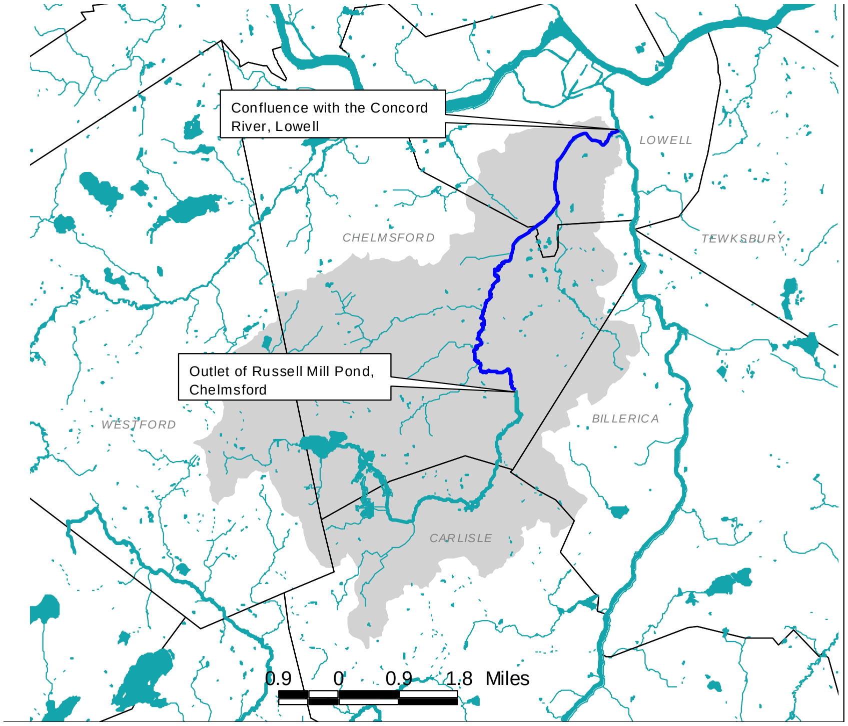


Figure 2.4. River Meadow Brook watershed

In the 19th century, River Meadow Brook was heavily polluted and considered a "sewer basin" according to the Lowell Board of Health (Figure 2.5). There was a small railroad repair shop, several cotton waste and batting mills, metal fabrication plants, bleaching industry, brewery, iron and steel boiler shops were located along the stream discharging their waste into the stream. For example, the Lowell-Bleachery discharged millions of gallons of chemical waste from washing, bleaching, and dyeing cloth on a daily basis, U.S. Bunting dumped 300,000 gallons of wastewater from scouring wool, washing cloth, and dyeing stock, and U.S. Cartridge released 60,000 gallons of oil-heavy wash water from shell production (Lowell History). In 1893, the Massachusetts Board of Health conducted a series of inspections of water ways in the Commonwealth due to outbreaks of typhoid fever and complaints of foul odors. They recommended a construction of sewer industrial waste and the wastes of factory workers. These recommendations were partially accepted; however, dumping of industrial water did not stop.

In the 1930's, during the Great Depression, River Meadow Brook was neglected and was subject to illegal garbage disposal, heavy junk and household and industrial chemicals disposal.

In 1960-62, River Meadow Brook experienced a dramatic change when the Lowell Connector highway was constructed. River Meadow Brook was straightened and rerouted to build a four-lane, divided highway. This project entailed the demolition of many residential buildings, as well as the removal of the dam at Hale's Mills, replacing it with a concrete dam at the same location.

In 1982, the Silresim Chemical Corporation located on Tanner Street was declared as a Superfund site due to thousands of abandoned steel drums contained highly toxic liquids (Fitzsimons, 2013).

Today, based on the last evaluation of water quality conditions conducted by MassDEP, River Meadow Brook is listed in the 303(d) list of impaired waterbodies (MassDEP 2015). The main known causes of impairment are fecal coliform and pathogens. However, the urbanization and highway corridor provides a source of road salt, metals, and other constituents as well. This project is intended to assess the impact of urbanization and the associated inorganic constituents on water quality in River Meadow Brook.

Figure 2.5 River Meadow Brook in the early 1900s. The scum floating at the surface of the intake pond to Ames Worsted Company's turbine building near the Middlesex Dam.

* Adopted from http://lowelllandtrust.org website

3. Materials and Methods

The goal of this study was to assess impact of urbanization on River Meadow Brook and validate a chloride assessment tool developed by MassDEP. To validate the tool, River Meadow Brook was chosen as the site containing historically high concentrations of chloride. The stream was continuously monitored for chloride and temperature. Conductivity was used to calculate chloride concentrations along River Meadow Brook. To assess impacts of urbanization, the stream was divided into 4 catchments areas. As the stream flows from upstream to downstream, the percentage of impervious surface increases, providing a useful basis for assessing the stream on urbanization impact. Inorganics associated with impervious surface and urbanization were analyzed using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Dionex ICS-2100 Ion Chromatography System. Additionally, laboratory analysis for pH, TSS and DO were performed.

3.1. Site Characterization

River Meadow Brook was broken down into 5 sampling sites. Additionally, 2 conductivity monitoring sites were chosen on the Concord River (Table 3.1, Figure 3.1). Historical data, collected by MassDEP personnel in 2006, showed that the downstream site (site 4) had a significantly higher concentration of chloride than the upstream site (site 2) (Figure 3.2). The variation in conditions showed that the stream provided a good representation of urbanization and degradation of water quality as the stream flows from less urbanized to highly urbanized areas. Stations 5 and 6 were located in the Concord River upstream and downstream of the confluence with the River Meadow Brook with an intention to test the hypothesis that the chloride concentration in the main stem of the Concord River can be affected by River Meadow Brook if chloride concentrations in this tributary is significantly different from the chloride concentrations in the Concord River.

Figure 3.1 River Meadow Brook monitoring sites (map)

Table 3.1 River Meadow Brook monitoring sites

Station #	Lat/Long	Waterbody	Description
1	N 42°56186´ W 071°33270´	Unnamed Tributary	About 1000 ft east from 26 Mt Auburn St, Chelmsford MA
2	N 42°57819´ W 071°33224´	River Meadow Brook	230 ft upstream from Mill road, Chelmsford MA
3	N 42°61485´ W 071°32236´	River Meadow Brook	50 ft downstream from Industrial avenue in Lowell, MA
4	N 42°63384´ W 071°30128´	River Meadow Brook	100 ft upstream from Concord River
4b	N 42°632348 W 071°309457´	River Meadow Brook	Along Gorham street
5	N 42°63379´ W 071°30132´	Concord River	50 ft upstream from the mouth of River Meadow Brook
6	N 42°63379´ W 071°30132´	Concord River	Approximately 100 ft upstream from the Rogers St bridge

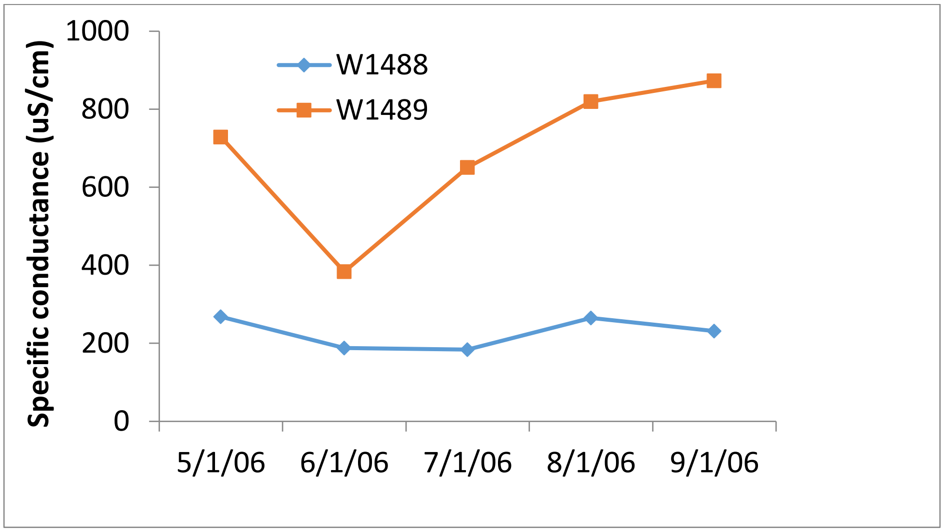


Figure 3.2 Specific conductance data for Station 2 (W1488) and Station 4 (W1489) in the River Meadow Brook collected in the summer 2006 (station 4 is downstream of station 4).

Because of the variations in land uses along the stream, the samples sites provide good conditions for assessing River Meadow Brook since the catchment areas can be used to identify variations in pollutant concentrations in the stream in the areas with different percentage of development. Basin characteristics for each sampling site were delineated by catchment area using StreamStats (Table 3.2). StreamStats is a map-based web application used to provide information such as drainage- basin boundary, stream flow statistics, basin characteristics and more. StreamStats showed that the percent of impervious coverage increased as the stream flows from upstream to downstream.

Table 3.2. General characteristics of the four catchment areas for River Meadow Brook

	Site 1	Site 2	Site 3	Site 4b	Site 4
Drainage area, mi^2	7.9	10	22	26.4	26.9
% area covered by forest	56.07	54.07	35.99	33.31	32.68
% impervious surface	6.14	7.45	18	22.9	23.7
% land use, class 21-24*	21	24.6	47.9	53.1	54
% wetlands	22.28	20.36	16.24	15.37	15.08

* Classes 21-24 indicate various intensities of development

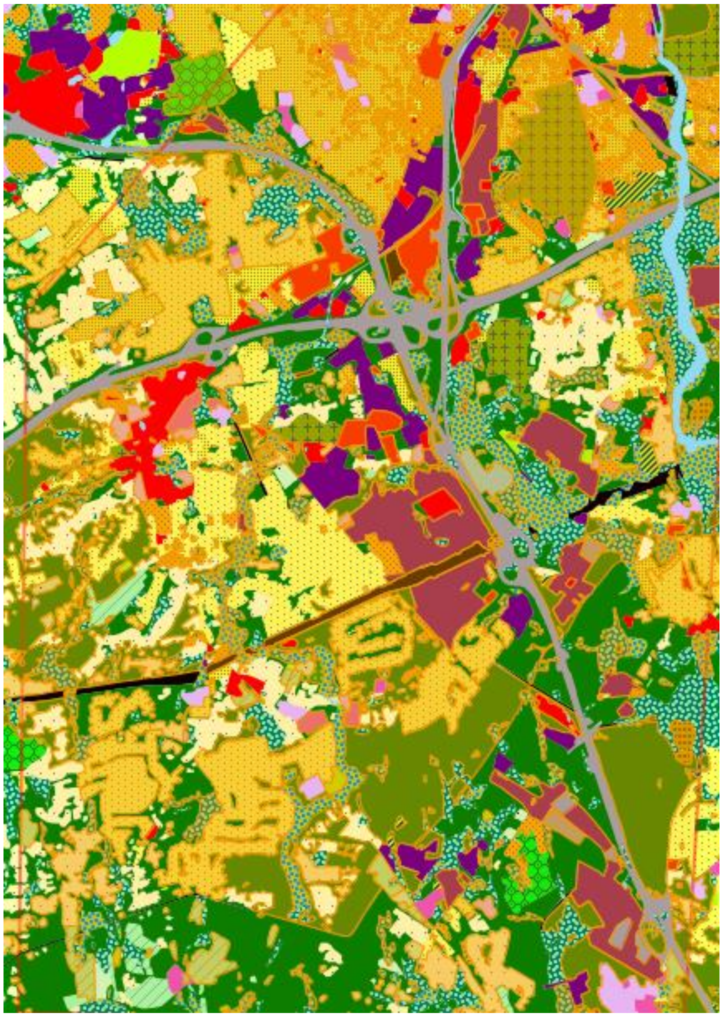


Figure 3.3. Land use map for River Meadow Brook

The land use map for River Meadow Brook catchment area was created using MassGIS online and applying the land use 2005 data layer. The map is shown in Figure 3.3. Within the boundaries of River Meadow Brook, there are different types of land uses, including commercial, industrial, transportation, residential, power/ utility and forest.

3.2. Field Program

This section describes the field part of this study, particular, the sample and flow collection that was needed to validate a chloride assessment tool and assess water body for urbanization impacts.

3.2.1. Water sample collection and analysis

All analyses were performed in accordance with MassDEP Standard Operating Procedure (MassDEP 2015) and within allowable holding times (Rice et al. 012). Duplicates were taking at each sampling site based on rotating schedule. Water samples were analyzed for aluminum (Al), arsenic (As), cadmium (Cd), cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), potassium (K), sodium (Na), magnesium (Mg), nickel (Ni), vanadium (V), zinc (Zn), sodium (Na), chloride (Cl), sulfate (SO_4), nitrate (NO_3), total suspended solids (TSS), pH and dissolved oxygen (DO). The abbreviations listed here are used throughout the remainder of this document. A digestion process was also used to determine total cation concentrations, but these are not included for the purpose of this thesis. Laboratory water quality results are reported in Chapter 4.

3.2.1.1. Water sample collection

Grab samples were collected on average once a month from October 2015 through April 2016 on a monthly basis (47 samples) using wade-in techniques. Sampling dates are presented in Table 3.4. New sample bottles were rinsed two-three times in ambient water before grabbing the samples. Sampling containers were obtained while facing upstream, with the bottles plunged into the water to about 6 inches below water surface to avoid collecting surface scum. The current climate, current site conditions, the use of any non-routing sampling techniques, and other observations were also noted on field sheets to help assess collected data. Water sample collection was guided by the MassDEP Standard Operating Procedure

CN1.21 (MassDEP 2015). All samples were stored in insulated coolers packed with ice to achieve the temperature of approximately 4℃ and transported to ether the EPA Region I New England Office of Environmental Measurement and Evaluation in North Chelmsford, MA as part of the Chloride Assessment Tool Project, and to the WPI Laboratory as part of the Master's Thesis research.

Twenty field visits were used to obtain 20 sets of samples including 12 dry and 8 wet weather sampling days. For the purpose of this study, a wet weather sample was defined with consideration to the total amount of rainfall (in inches) 24 hours prior to sampling. The rainfall amount are listed in Table 3.3. Rainfall/snowfall data was obtained from the National Oceanic and Atmospheric Administration (NOAA).

Table 3.3 River Meadow Brook sampling summary

Date	Site1					Precipitation, in (24-hr prior sampling)	Condition	Season
	1	2	3	4	4b			
10/23/2015	x	x	x	x		0.07	wet	Fall
11/3/2015	x	x	x	x		0	dry	Fall
12/3/2015	x	x	x	x		0.97	wet	Fall
1/8/2016			x	x		0	dry	Winter
1/9/2016		x				0	dry	Winter
1/11/2016	x	x	x	x		0.93	wet	Winter
2/24/2016	x	x	x	x		0.2	wet	Winter
3/5/2016		x	x	x		0	dry	Winter
3/7/2016`	x	x	x	x		0	dry	Winter
3/8/2016		x				0	dry	Winter
3/15/2016						0.01	dry	Winter
3/16/2016				x	x	0.26	wet	Winter
3/20/2016				x	x	0	dry	Spring
3/21/2016						0.26	wet	Spring
3/22/2016					x	1.12	wet	Spring
3/30/2016						0.3	wet	Spring
4/1/2016	x	x	x	x	x	0	dry	Spring
4/11/2016				x	x	0	dry	Spring
4/17/2016					x	0	dry	Spring
4/20/2016	x	x		x		0	dry	Spring

3.2.1.2. Unattended continuous conductivity data

HOBO conductivity loggers were deployed at 6 sites (except for site 4b) in October 2015 for collecting continuous conductivity and temperature information in River Meadow Brook and the Concord River (Appendix B). The resulting conductivity readings are the *actual conductivity* "raw" data, without temperature compensation (i.e. not in terms of specific conductance (SC) at 25^0C). These data were converted to SC using Equation 2 below. The data loggers were inserted in pipes and placed vertical. Sensor faces were cleaned as part of each monthly download.

Specific conductance or conductivity obtained from an assessment of a water body is often used to develop a linear regression model to estimate chloride in water (Mattson 1994). Conductivity (in microsiemens per centimeter) is the specific conductance @25°C. Conductance/conductivity is a measure of water's capability to pass electrical flow. This ability is directly related to the concentration of ions in water. These conductive ions come from dissolved salts and inorganic materials such as alkalis, chlorides, sulfides and carbonate compounds. There is a direct relationship between conductivity and the presence of ions in the water. The high number of ions in a water body is associated with a higher conductivity. Sudden increases in conductivity can indicate a change in water quality. If conductivity is measured, the specific conductance @ 25^{o}C can be obtained using the following conversion equation:

$$Specific\ conductance = \frac{\text{Measured conductivity}}{(1+r*(T-25)} \quad \text{(Equation 2)}$$

Where,

r is the temperature coefficient correction

T is temperature in degrees Celsius

And the conductivity is measured in µs/cm

Conversion from specific conductance to chloride using a linear regression equation in surface waters is presented in several research papers (Table 3.5). In this equation, n represents the number of samples used to develop the model, x represents the specific conductance @ 25C° collected in- situ, and y represents estimated chloride concentration.

Table3.4 Previous studies used chloride and conductivity relationship

Water source	Equation	n samples	R^2	SC@230	SC@860	Reference
MassDEP	Y=0.2753*x-18.987	2426	0.9445	904	3193	
NH streams	Y=0.307*x-22	649	0.97	821	2873	Throwbridge
Dark Brook, Auburn,MA	Y=0.2864*x-21.9	37	0.9936	880	3079	Heath, D. 2014
Barrows Wellfield, Wellfield, MA	Y=0.3688*x-109.28	68	0.9932	920	2628	Heath, D. and Morse, D. 2013

3.2.1.3. Field use of Multiprobes to collect co-located SC data

A multiprobe was used approximately once a month to collect temperature, specific conductance, pH, DO and temperature for quality control (QC) purposes. To assure valid in-situ water quality data pre-survey calibration and post-survey checks were performed on the multiprobes monthly by MassDEP calibration laboratory supervisor.

3.2.1.4. Data quality assurance and quality control

Water sample data were quality assured using quality control (QC) check samples, field duplicates and field blanks. The ambient field blanks were deionized water samples treated the same way as other samples taken in the field. Field blanks were submitted double-blind to USEPA Laboratory along with other samples. Field duplicate samples were collected simultaneously adjacent (side-by-side) with water samples. The field replicates account for both analytical and field sampling error. In addition, QC check samples were submitted to the lab with each sample batch. These were known standards made from a KCl stock solution. Additionally, chloride samples results from the EPA lab were compared to chloride results obtained at WPI lab.

3.2.2. Flow Monitoring

The purpose of flow monitoring was to determine the volumetric flowrates in 5 catchment areas along River Meadow Brook, named site 1, 2, 3, 4 and 4b. The flow estimates could be used in conjunction with concentration data to estimate loads.

To measure instantaneous discharge at locations 1, 2, 3 and 4, the area-velocity technique was used, and for location 4b, a broad-crested dam equation was used.

- *Area-velocity technique.*

This is the most common method of measuring discharge in open channels. Discharge is typically calculated as the product of *velocity* and *cross-sectional area*. The product of these two measurements gives discharge in volume per unit time:

$$Q = V * A, \qquad \text{(Equation 3)}$$

Where,

V is the velocity in feet per second (ft/s) or meters per second (m/s)

A is the cross- sectional area in m^2 or ft^2

First, each catchment area was divided into segments (approximately 10 ft wide). The velocity of the water was measured at each segment using current meter. Current meters generally consist of a propeller or a horizontal wheel with small, cone-shaped cups attached to it which fill with water and turn the wheel when placed in flowing water. For segments with the stream depth less than 2.5 ft (0.8 m), a single velocity measurement at 60% of the total depth below the water surface was measured. For segments with the depths 2.5 ft or more, the average velocity was taken at 0.2 and 0.8 of depth.

Second, cross-sectional area for each segment was multiplied by corresponding velocity to obtain discharge. The total discharge in the catchment area was calculated by summing discharges.

- *Broad-crested weir*

At site 4b, a dam served as a control point to get relatively accurate flow estimates. The shape of the spillway was approximated by a broad-crested weir. A broad-crested weir is a weir that is not formed by a thin plate (with a sharp edge). For a broad crested weir, the depth of water over a dam can be converted to a continuous rate of flow if the length of the dam is known using the following general equation:

$$Q = CLH^{3/2}$$

$$C = (2/3)^{3/2}(g)^{1/2}$$

$$Q = 0.55 * \sqrt{g} * L * H^{1.5} \qquad \text{(Equation 4)}$$

Where,

Q is the discharge in cfs

G is the acceleration of gravity 32.2 ft/sec^2

L is the width of dam in ft

H is the upstream height of water above the weir (head)

For this case, the coefficient in the equation was calibrated using field flow measurement taken at site 4b. The final equation took the following form as indicated above.

The length of the dam at location 4b was measured 40 ft. A depth probe and a ruler was used to continuously monitor water depth over dam. The ruler was securely attached to the dam's abutment. A single reading on a ruler was recorded to a field journal during every depth probe installment or removal. Then continuous probe depth data was adjusted relative to the ruler. Adjusted depth value was used to calculate continuous water height over the dam.

Two different rulers were used: one ruler was used to adjust water depth for two time periods- 3/8-3/16 and 3/20-3/30. A new ruler was placed on 3/30 and was used for all measurements there-after. The 36 inch long ruler was placed such that readings increased with increasing depth. As per the ruler, the top of the dam was measured 12.375 inches. Every depth probe reading needed to be adjusted by the value d2 which was calculated according to the following equation:

$$d2 = d1 + (dm - dp1),$$

Where,

dp1 is the probe measurement at the sample time as measurement on the ruler

Dm is the measured depth on the ruler

d1 is the initial probe reading

d2 is the adjusted probe reading

Based on the ruler used, the height over dam was calculated using the following equation

$$H = d2 - 12.375 \text{ in}$$

3.2.3. Pollutant Loads

The stream discharge and pollutant concentrations can be used to in pollutant load calculations that provides information to understand nonpoint source loads in urban areas. Total pollutant loads were calculated as follows:

$$L_T = \sum_{i=1}^{n} Q_i * C_i * \Delta T_i \qquad \text{(Equation 5)}$$

Where,

L_T is the total load of a pollutant in units of mass

Q is the flowrate in mass per time

C is the concentration in mass/volume

ΔT is the time interval

3.3. Laboratory procedures

Surface water samples were analyzed for trace metals (Al, V, Cr, Fe, Co, Ni, Cu, Zn, As, Cd, Pb), cations (Na, Mg, K), anions (Cl, sulfate and nitrate), TSS, pH and DO. Not every sample was analyzed for each parameter. For example, TSS analysis were performed for 12 samples out of 46. A summary of laboratory analysis and methods is presented in Table 3.5.

Table 3.5 Laboratory analysis summary

Laboratory analysis	Method used	Standard
Anions	Dionex ICS-2100 RIFC,	Ion Chromatography
Cations and metals	NexION 350X ICP-MS Spectrometer	
Specific conductance	HOBO loggers	
Total Suspended Solids	Pump, oven, and Ohaus Discover scale	EPA 160.2
pH	Accumet Basic AB15 pH Meter	-
Dissolved oxygen	Thermo Electron Corp. Orion 3 star DO benchtop	-
TSS	Pump, oven, and Ohaus Discover scale	EPA 160.2

3.3.1. Anions

Chloride, sulfate, and nitrate were analyzed using ion chromatography in accordance with Standard Method 4110 (APHA *et al*., 1995) using a Dionex ICS-2100 RIFC (Figure 3.4). Prior to analysis, a calibration curve of anion standards was developed for concentrations ranging from 100 to 5,000 µg/L using a standard solution prepared in advance. The detection limits for chloride, nitrite, and sulfate analyses were assumed to be equal to 50 µg/L. Samples were diluted 1:100 due to high presence of chloride. Therefore, phosphate and bromide were below detection limits, and not considered for this study. Filtered samples were transferred to 5 mL sample cells with filter caps, which were loaded into the automatic sampler for analysis. The results of each sample analysis were integrated based on the calibration curve.

3.3.2. Heavy metals

Dissolved and total metals were determined by NexION 350X ICP-MS Spectrometer (inductively coupled plasma mass spectrometry) (Figure 3.5). Dissolved metals were determined after filtering with 0.45-µm membrane filter. Total metals were defined as the concentration of metals contained in unfiltered samples after vigorous digestion with nitric acid (HNO_3) to pH<2.

Figure 3.4. NexION 350X ICP-MS Spectrometer

- *Dissolved metals analysis*

Samples for analyzed for Mg, Na and K were diluted by 1:100. To dilute samples, a digital micropipette set to 500 microliters was used. A 500 µl of a sample was released in a 50 ml tube and filled up to a 50 ml mark with deionized water. For further analysis, some of those samples were poured into a 14ml tube (Figure 3.6).

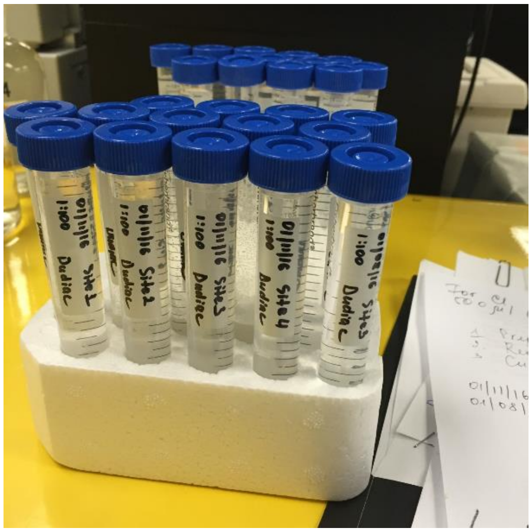


Figure 3.5. Water samples cut 1:100 for dissolved metal analysis

- *Total metals analysis*

To convert metals to a free metal form, a digestion technique was used. The digestion technique include using a 100 mg sample and 5ml of HNO_3. This mixture was transferred to a hot plate for evaporation. A sample was down approximately to 20ml clear solution. Then the volume was filtered and adjusted back to 100 ml before transferred to 14ml tube for further analysis (Figure 3.7)

Figure 3.6 Digested samples on a hot plate for total metal analysis

3.3.3. Total Suspended Solids (TSS)

A standard Method 2540 D “Total Suspended Solids dried at 103-105°C” (APHA *et al*., 1995) was used for determining the total amount of suspended material in a water sample. A new standard glass fiber filter disk was rinsed with reagent grade water, dried at 105°C, and weighted with/without aluminum weighting dish. That filter was inserted into the filtration apparatus with wrinkled side up to filter a measured volume of sample through using vacuum suction, and washed three times with 20mL portion of reagent-grade water (Figure 3.8-3.10). The residue retained on the filter was dried in the oven for 1 hour at a constant temperature 105°C to evaporate excess of water. Removed filters were transferred to an inert aluminum weighting dish and weighted. The increase in weight of the filter represented the total suspended solids.

To determine the TSS, the following equation was used:

$$TSS = 1000*(W_{fl}-W_i)/V \qquad \text{(Equation 6)}$$

Where,

TSS- is the total suspended solids

W_{fl}- is the final weight (mg)

W_i- is the initial weight (mg)

V- is the sample volume

Figure.3.7. Pump for TSS analysis

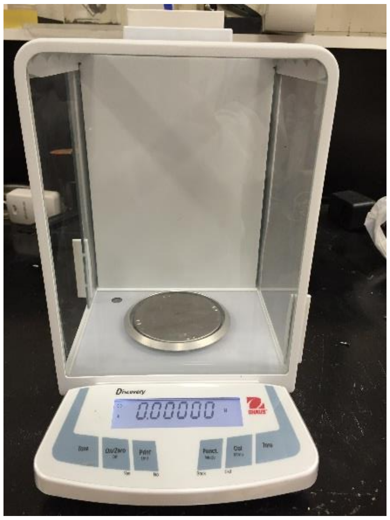


Figure 3.8. Ohaus Discover scale

Figure 3.9. TSS results

3.3.4. pH

An Orion 720 pH probe, Model 420A with an Accumet AB15 Benchtop pH Meter was used to measure pH in the laboratory in accordance with Standard Method 4500-H+ B (APHA *et al.*, 1995). Before analysis, the pH meter was calibrated using pH 4, 7, and 10 buffers (Figure 3.11). One pH measurement was taken for each sample by inserting the pH probe into a small volume (~50 mL) of sample and recording the resulting measurement.

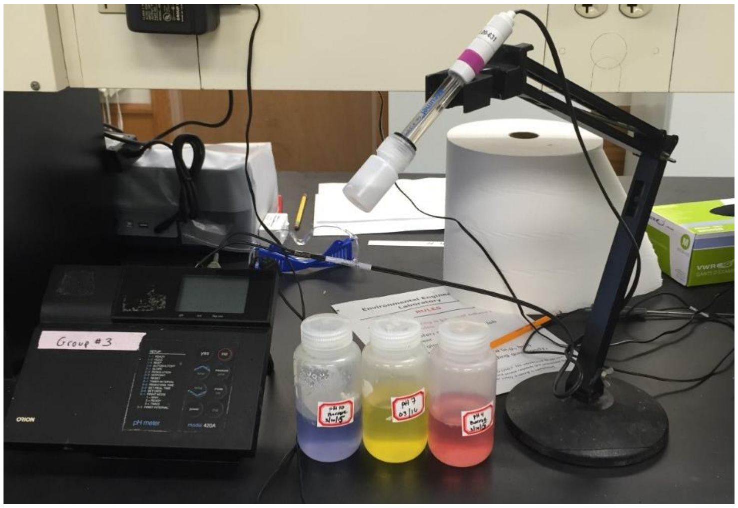


Figure 3.10. Orion 720 pH probe, Model 420A for pH analysis

3.4. Statistical Analysis

3.4.1. The Pearson's Correlation Analysis

The Pearson Correlation Analysis is a statistical test that measures the statistical relationship between two variables. Variables are not dependent on the data units. Therefore, all variables must be standardized before the analysis (meaning use the same units). Correlation analysis were performed using the CORR procedure of the SAS system to compute Pearson correlation coefficients. The correlation coefficient, r, is a value of the linear relationship between data pairs. Depending on the value of r, the significance of relationship for two values was determined. The correlation between the same two constituents is always 1. A negative sign of the r value indicates inverse correlation, whereas zero indicates no correlation. The confident interval was chosen to be 95% ($p \leq 0.05$), which is commonly used for research. The P-value is a measure how reliable the data is. The results of this test can be found in the "Results" section of this paper.

3.4.2. ANOVA Analysis

The analysis of variance (ANOVA) is a statistical test that determines the variation of the means of a group of data or variables to understand statistical significance. The Student-Newman-Keuls Test for values was performed using the SAS Statistical software. This test is a multiple comparison procedure used to identify sample means that are significantly different from each other. This test controls the Type I experiment wise error rate under the complete null hypothesis but not under partial null hypotheses. The null hypothesis states that there is no difference between groups of data. Type I error occurs when the null hypothesis is true, but rejected. It is asserting something that is absent, a false hit. Similar to the Pearson's Correlation Analysis, the significance level is set to 95% ($p \leq 0.05$).

4. Results and discussions

This project provided information on the impacts of urbanization on the water quality in River Meadow Brook, a New England Stream with varying land uses. In this chapter, the flow and quality of water in River Meadow Brook were characterized. Flow data and water samples were collected and analyzed along River Meadow Brook. This section on water quantity is divided into two sub-sections: one is for sites 1, 2, 3 and 4 and the other is for site 4b. The water quality section (Section 4.2) is also broken down into two major sub-sections: one is for chloride analysis based on continuous conductivity data and the other one is for the rest of inorganics.

4.1. Water quantity

In order to obtain total loads of constituents, concentration and discharge information were needed. Since the project had started as a chloride assessment tool study sponsored by MassDEP, the discharge information and estimating pollutant loads was not initially included within the scope and flowrates could not be obtained until January, 2016. The first flow measurements for site 1, 2, 3, 4 were performed on 01/11/2016. In February and March, streamflow information was not collected due to harsh weather conditions and ice coverage. To compensate for limited flow data, additional streamflow data were obtained in June, after the collection of previous water depth data. These data were used to estimate rating curves for the sampling stations along River Meadow Brook.

On March 8th, an additional site (Site 4b), located near Gorham Street, Lowell, MA, was chosen to collect flow information. The site, which was located a short distance upstream of Site 4, was included because a dam at this site provided an ideal control section and assured that there would be no backwater effect from the Concord River. The control section allowed for accurate flow estimation. A rating curve was constructed based on field flow measurements over the dam and the development of a rating curve (i.e. stage-discharge curve) based on a spillway relationship. Rating curves are intended to contain numerous discharge measurements at all ranges of stage and streamflow. Due to the limited time frame of this study, the rating curve did provide full range of flows, but it did provide sufficient flow information to provide approximate estimates of flow and loads.

4.1.1. Area-velocity technique

At each site, a distance across River Meadow Brook was measured and divided into zones. For each zone, velocity and stream depth were measured. Based on collected information, discharge for sites 1, 2 and 3 was calculated as described in Chapter 3. Detailed discharge calculations can be found in Appendix C. Discharge was not considered when developing rating curves due to lack of uniform flow and a consistent downstream control. Since the Concord River was the downstream control for River Meadow Brook, a constant relationship between stage and flow could not be maintained at Site 4.

Additionally, for each flow measurement, a distance from a designated point to water surface was measured and written in a field journal. A designated point at each site was chosen to be a centerline of the bridge. Based on collected information, rating curves for each location were constructed (Figure 4.1 through 4.3). Due to limited data, rating curves do not contain a full range of flows. For days when only a distance to water surface was measured, the discharge was retrieved from the rating curve. For example, the distance from a centerline of the bridge located at site 1 on the March 5, 2016 field trip was 1ft. From the rating curve for site 1, the discharge at stage 1ft is approximately equal to 0.5 ft^3/sec (5/19/16) . The same procedure was repeated for all days and summarized is Table 4.1. The curves for Figures 4.1 through 4.3 are shown with stage measured downwards from the reference. The distance between the references and the channel bottoms were 1.26 feet for Site 1, 4.65 feet for site 2, and 13.95 feet for site 3.

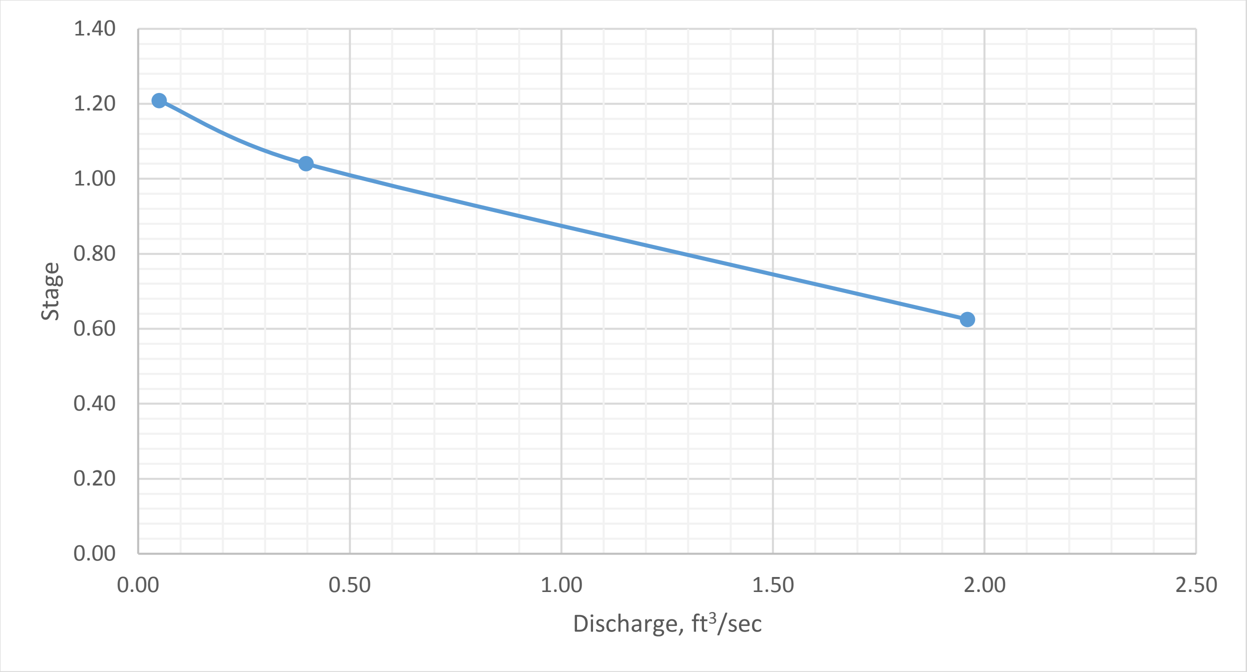


Figure 4.1. Rating curve for site 1

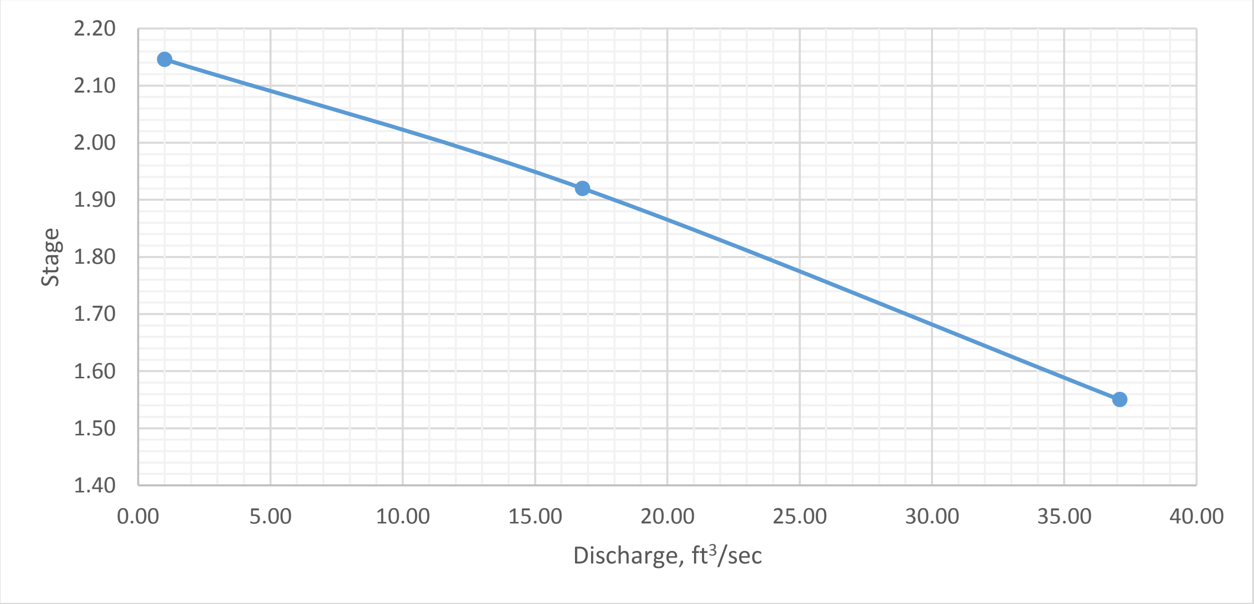


Figure 4.2. Rating curve for site 2

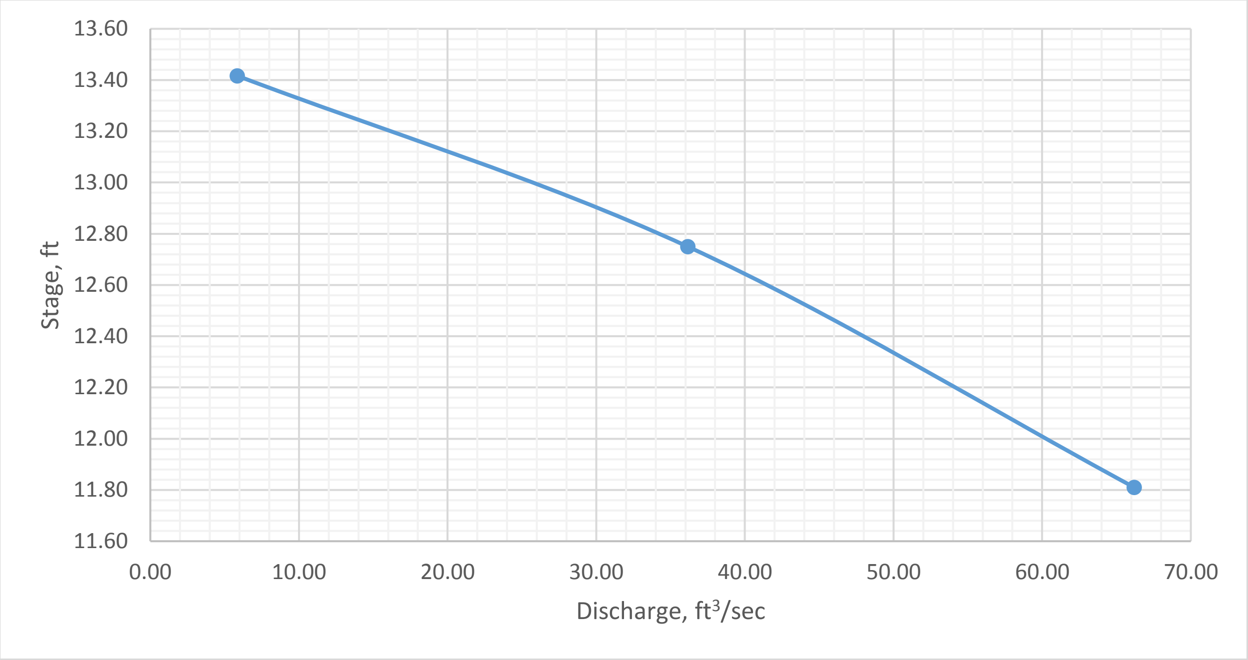


Figure 4.3. Rating curve for site 3

Table 4.1. Summary of area-velocity measurements and calculations

Site	Date	Discharge, ft^3/sec	Mean discharge, ft^3/sec
1	1/11/2016	2.0	0.7
	3/5/2016	0.5	
	4/1/2016	0.4	
	5/19/2016	0.5	
	6/22/2016	0.1	
2	1/11/2016	37.1	17.7
	3/5/2016	16.1	
	4/1/2016	16.8	
	6/22/2016	1.0	
3	1/11/2016	66.2	27.8
	2/24/2016	39.0	
	3/5/2016	30.0	
	4/1/2016	36.2	
	5/19/2016	11.0	
	6/10/2016	6.2	
	6/22/2016	5.9	
4	1/11/2016	96.8	70.8
	4/11/2016	44.9	

Discharge increases as the stream flows from upstream to downstream. The mean discharge was 0.7 ft^3/sec for site 1, 17.7 ft^3/sec for site 2, 27.8 ft^3/sec for site 3 and 70.8 ft^3/sec was for site 4.

4.1.2. Broad- crested weir

Because of the presence of the hydraulic structure (broad- crested dam), located near Gorham Street in Lowell, MA, site 4b was chosen to continuously monitor flows. The length of the dam was estimated to be 40 ft. The depth probe was set to continuously record water depth with a 15- minute interval. Depth probe data were adjusted relative to the ruler placed adjacent to the dam, and converted into continuous head values (water depth over dam). Adjusted head values over time periods from 3/8 to 3/16, 3/20 to 3/30, 4/1 to 4/11 and 4/17 to 5/1 were entered into the discharge equation. Based on stream discharge and stage information, a rating curve for site 4b was created (Figure 4.4).

Over the four flow monitoring periods, 5497 depth probe data points were recorded. The depth over the dam ranged from 0.859 in to 8.684 inches and the discharge 2.4 ft^3/sec and 76.8 ft^3/sec respectively. The average discharge was 49.5 ft^3/sec. This mean value falls between the mean discharge values for site 3 and site 4, which make sense. Field measurements confirmed that the flow at Site 4b closely matched the flows at Site 4.

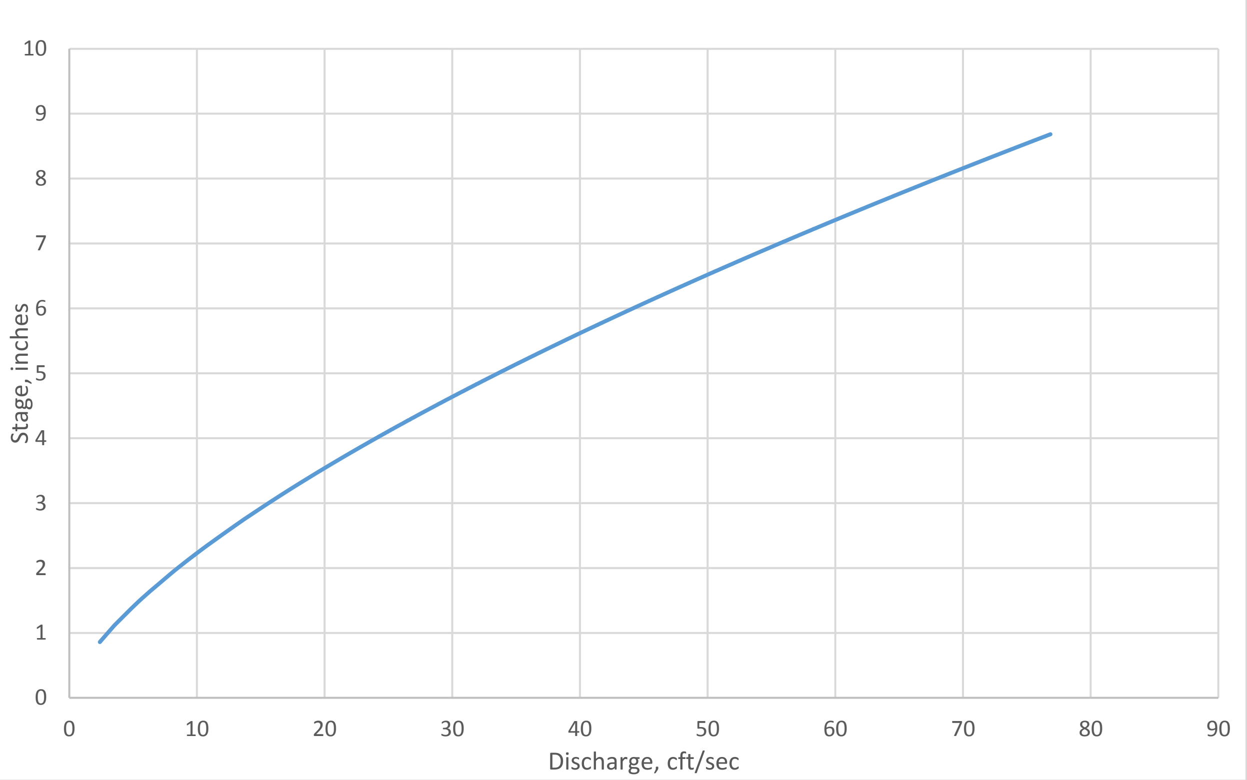


Figure 4.4. Rating curve for site 4b

The limitation of this approach are that the flow over weir is assumed to be well represented in terms of the discharge equation, and that the shape of the dam needed to be estimated because the engineering department for the city of Lowell, MA could not provide us the exact parameters of the dam. The field measurements indicated that the approach provided reasonable estimates for the flow.

4.2. Water Quality

Water samples were analyzed for metals, anions, TSS, pH and DO to capture water quality changes from upstream to downstream of River Meadow Brook. The results are present in this section, and are summarized into two subsections: chloride and other pollutants.

In the first part of the chloride section a chloride assessment tool developed by MassDEP was re-validated. The tool, which is an equation developed by MassDEP, was used to calculate chloride concentrations based on continuous conductivity data collected for a 7-month period. In the second part of the section the relationship between precipitation, chloride violations and spikes along River Meadow Brook were identified.

In the “Other Constituents” section, trace metals, anions, cations, TSS, DO, pH trends from site 1 through site 4 are shown. The Pearson correlation analysis was used to show the relationship between impervious surface and various water quality parameters.

4.2.1. Chloride

In this section, a chloride assessment tool was re-validated by evaluating results for River Meadow Brook. It was found to match the results with a 99.37% confidence. The tool was then used to estimate chloride concentrations and determine violations of chloride ambient water quality standards. The relationship between elevated chloride concentrations and snowfall is also discussed in this section. Finally, chloride concentrations results determined by USEPA and WPI laboratories are compared for QC/QA purposes.

4.1.1.1. Calculated Chloride Concentrations

As part of the MassDEP study, 24 grab samples collected along River Meadow Brook were analyzed for chloride by USEPA laboratory. These results were compared to 24 co-located chloride concentrations calculated using a linear regression equation. For example, a grab sample collected on October 6, 2015 at 10.00am and analyzed by USEPA laboratory showed a chloride concentration of 83 mg/l. A single conductivity reading for the same day and time extracted from the logger was 384.4 µs/cm @25ºC. The conductivity point was plugged into the equation developed by MassDEP ($Y = 0.2753X – 18.987$, where X represents conductivity and Y calculated chloride concentration). Therefore, $Y = 0.27553*384.4-18.987$ or $Y = 86.72$ mg/l, where “Y” represents a calculated chloride concentration. In Table 4.2, 24 grab samples and 24 calculated chloride concentrations were compared using a linear regression comparison in Excel. The goal was to check how calculated chloride values close to the real chloride concentrations measured by USEPA laboratory. It is demonstrated that the calculated chloride values explained 99.37% of the EPA measured results (Figure 4.5) and their linear regression line is very close to the 1:1 line. This result represents re-validation of the Tool developed by MassDEP.

Table 4.2 summarizes chloride concentrations predicted by the tool and analyzed by USEPA laboratory. The relative percent difference (RPD) was calculated to compare chloride concentrations. The comparison is expressed as a unitless ratio.

Table 4.2. Calculated chloride and EPA laboratory results

#	Date	Site	EPA lab Measurement, mg/l	Model Prediction, mg/l	RPD, %
1	10/6/2015	1	83	86.72	4.39
2		2	100	97.31	-2.73
3		3	390	336.98	-14.59
4		4	320	286.19	-11.16
5	11/3/2015	1	94	101.31	7.49
6		2	78	73.60	-5.80
7		3	270	247.48	-8.70
8		4	270	248.22	-8.41
9	12/3/2015	1	86	87.77	2.04
10		2	140	124.07	-12.06
11		3	180	167.26	-7.34
12		4	200	181.82	-9.52
13	1/21/2016	1	90	91.54	1.70
14		2	130	125.91	-3.20
15		3	220	214.26	-2.64
16		4	260	241.13	-7.53
17	3/7/2016	1	79	76.27	-3.52
18		2	97	90.69	-6.72
19		3	190	172.00	-9.94
20		4	220	204.40	-7.35
21	4/20/2016	1	81	79.63	-1.71
22		2	120	107.18	-11.29
23		3	230	196.25	-15.84
24		4	250	222.55	-11.62
	Average		**174.08**	**160.8**	**6.08**

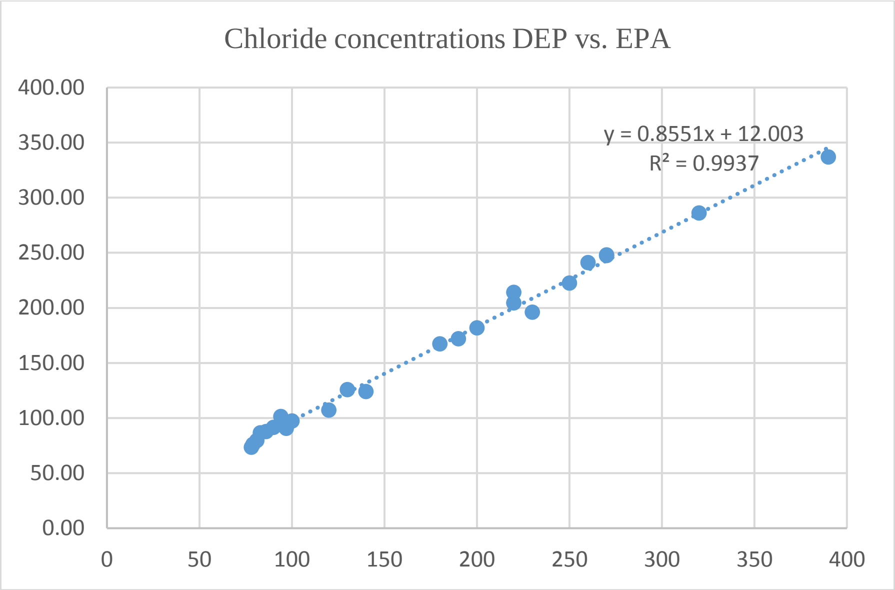


Figure 4.5. Chloride linear regression analysis

Because the tool/equation (Y = 0.2753X – 18.987) developed by MassDEP proved to be reliable, and validated twice through USEPA Auburn and MassDEP studies with a high percent accuracy, it was used to calculate chloride concentrations. Calculated chloride concentrations were used for estimating chronic and/or acute toxicity violations for each site. A chronic chloride violation considers whether the 4-day average concentration of chloride exceeds 230 mg/l. An acute chloride violation considers whether the one-hour average chloride concentration more than 860 mg/l. The following paragraphs summarize results for each site.

- ***Site 1***

Continuous monitoring of specific conductivity from 10/06/2015 to 04/20/2016 shows that the stream did not exceed chronic/acute standards for chloride. The maximum chloride concentration derived from conductivity was 118.78 mg/L (01/06/16) and the minimum concentration was 27.08 mg/L (01/10/16) (Table 4.3). Chloride from grab samples ranged from 83 to 94 mg/L (table 4.2). Based on logger measurements, the average concentration over the eight month period was 81.3 mg/L (Figure 4.6a)

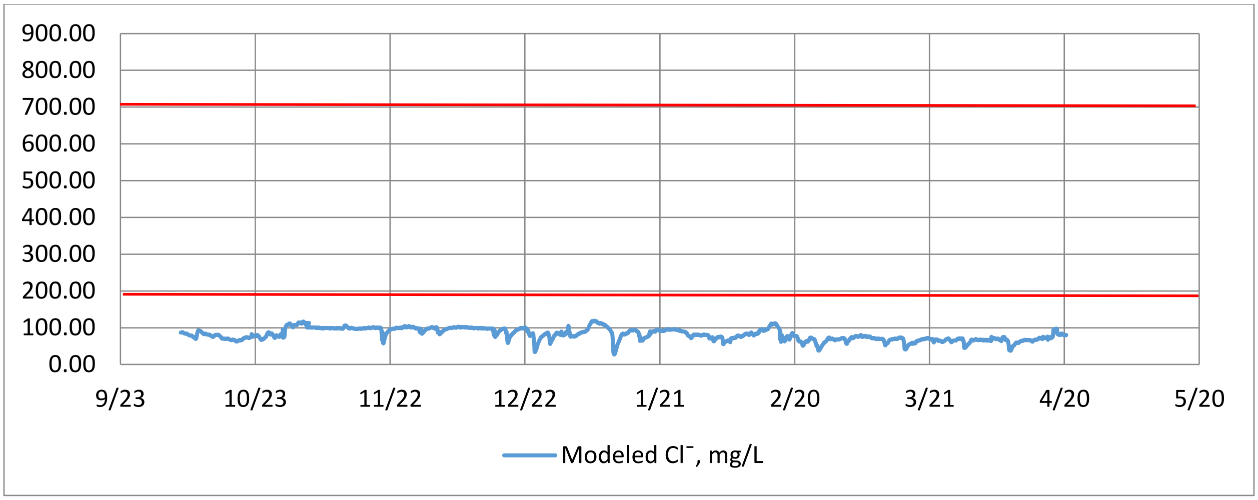


Figure 4.6a- Calculated chloride concentrations at site 1

- ***Site 2***

River Meadow Brook at Site 2 did not experience chronic/acute exceedances in chloride (Figure 4.6b). The maximum calculated chloride level was 212.0 mg/l (on March 8, 2016), the minimum concentration was 65.8 mg/l (on 02/28/2016), and the average concentration over the study period was 101.3 mg/l (Table 4.3). Grab samples analyzed for chloride ranged from 78 mg/l to 140 mg/l (Table 4.2).

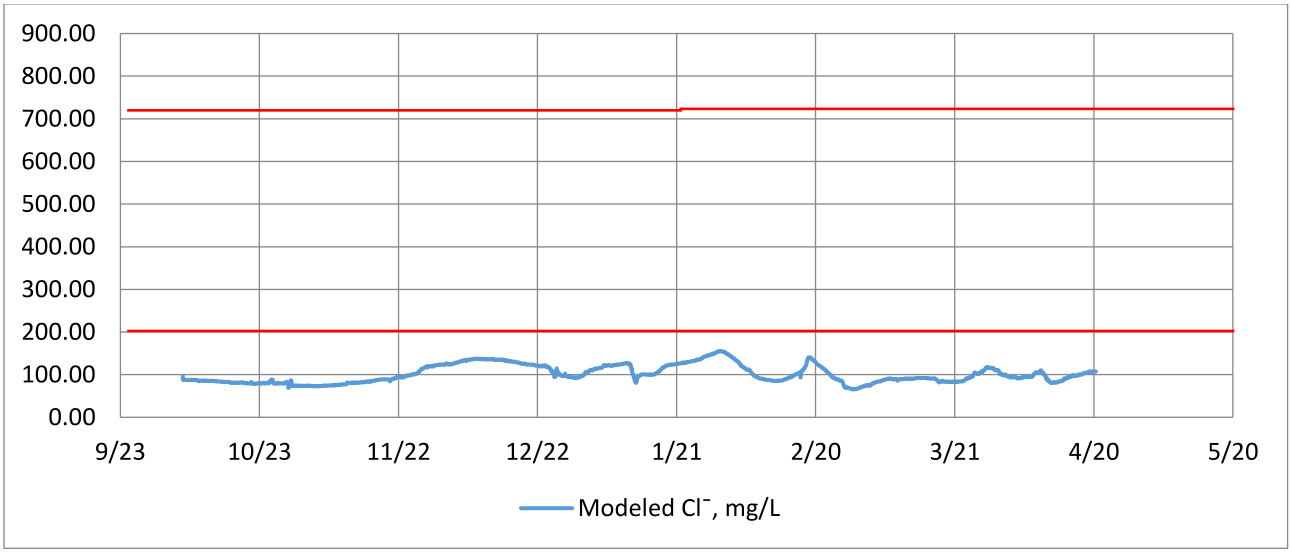


Figure 4.6b- Calculated chloride concentrations at site 2

- ***Site 3***

Site 3, has the most potential for impact by chloride due to close vicinity of State Highway 495, Road 3 and Lowell Connector S. Numerous outfalls connected to the catch basin bring flow and pollutants directly to the stream. The maximum concentration of calculated chloride was 1228.62 mg/l (02/16/16), the minimum concentration of chloride was 55.93 mg/l (10/29/15), and the average was 218.3 mg/l (Table 4.3). The seven months of monitoring showed that the chloride exceeded the 230 mg/l chronic standard for 22 days. The periods ranged in length from 5 days in November and December to 22 days in October (Table 4.4). Chloride concentrations at site 3 exceeded the acute water quality standard one time on 2/16/16 with the mean concentration 1062 mg/l.

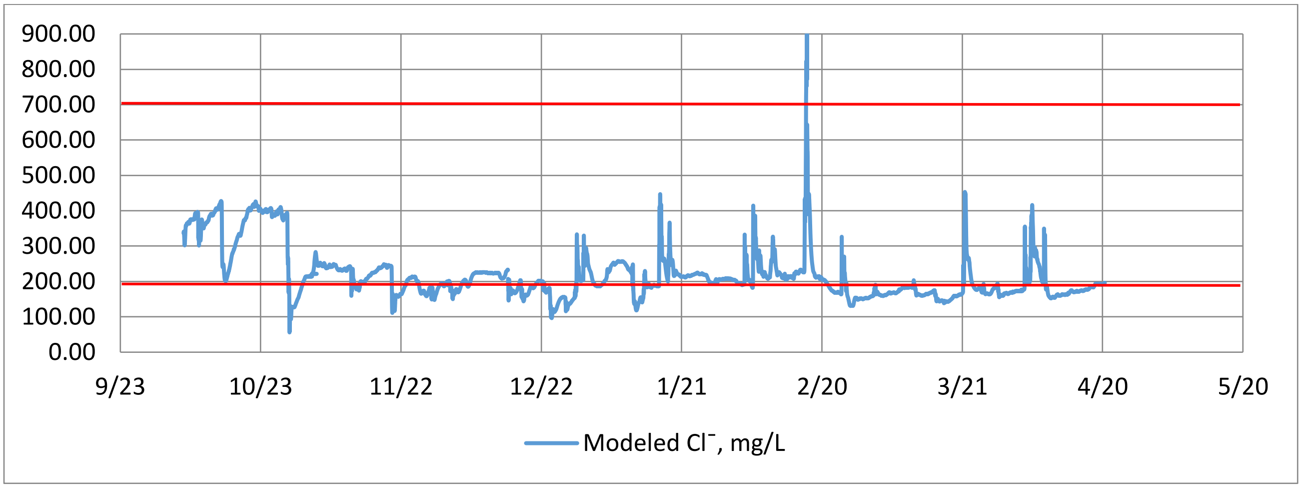


Figure 4.6c- Calculated chloride concentrations at site 3

- ***Site 4***

At its confluence with the Concord River, River Meadow Brook receives all inputs within the subbasin. As a result, this location can show the cumulative impacts from chloride. Site 4 had 13 episodes of calculated chronic chloride exceedance lasting for 49 days. The periods of violation ranged in length from 3 days in March to 24 days in October. (Table 4.4). The highest spike of chloride was 1035 mg/L which occurred on 02/16/16 and gradually stabilized. The minimum concentration of chloride for the seven-month period was 50.5 mg/l, and the average 240.4 mg/l (Figure 4.6d).

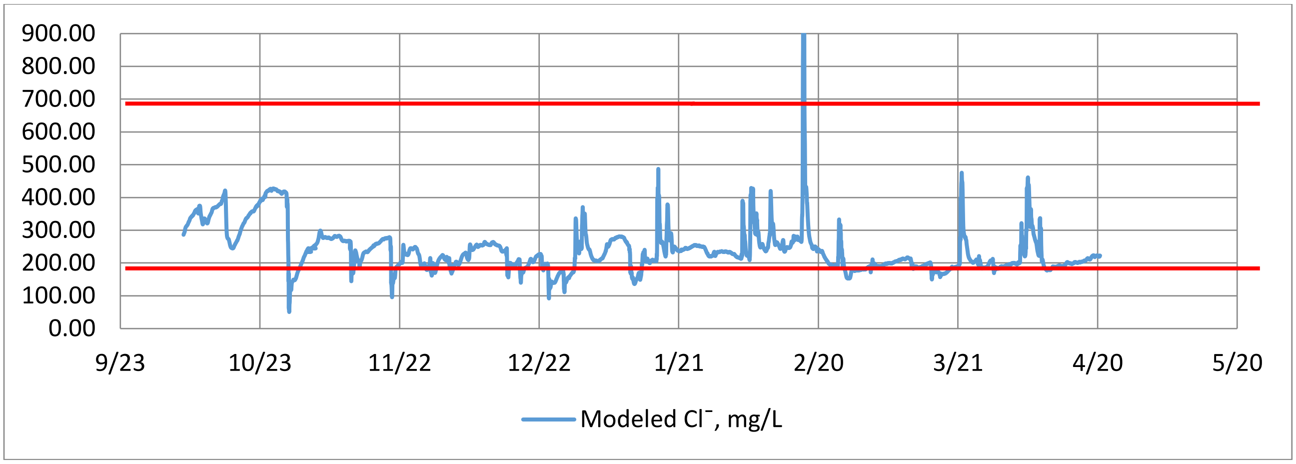


Figure 4.6d- Calculated chloride concentrations at site 4

- ***Site 5***

At site 5, upstream of the Concord River where River Meadow Brook discharges, the maximum chloride concentration was 251 mg/l, and the average 163 mg/l. Chloride from grab samples, ranged from 145 mg/l to 186 mg/l (Table 4.2). Data collected from continuous conductivity loggers showed the maximum calculated chloride concentration was 251 mg/l (02/16/16), the minimum was 105.17 mg/l (01/02/2016), and the average was 163 mg/l over the seven-month period (Figure 4.6e)

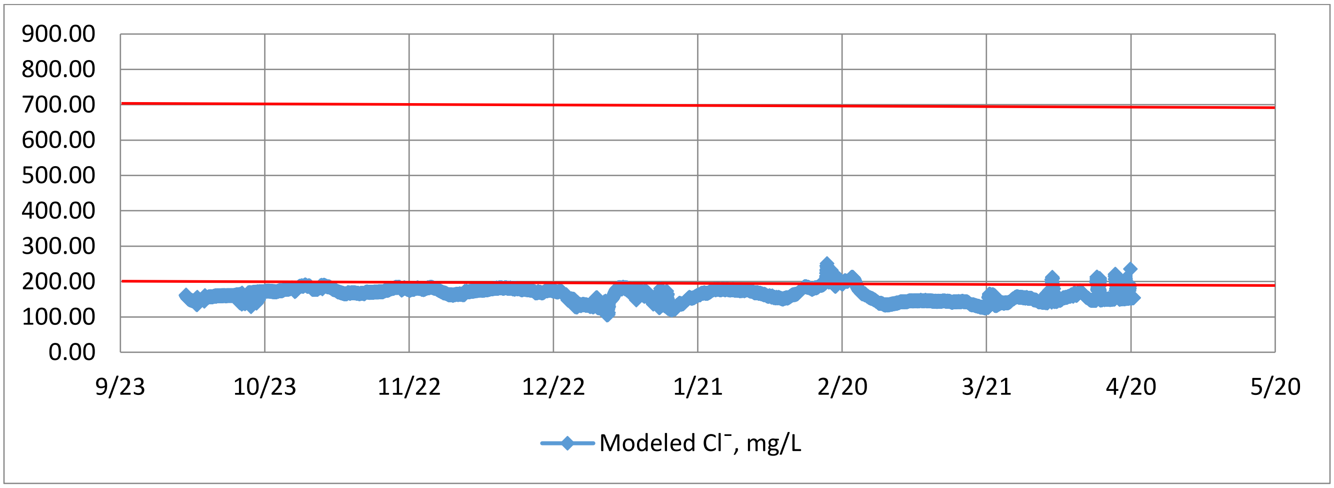


Figure 4.6e- Calculated chloride concentrations at site 5

- ***Site 6***

Site 6, was located in the Concord River, downstream of the confluence with River Meadow Brook. In February 2016, this site exceeded the 230 mg/l range twice. No other chronic or acute exceedances were observed. The maximum calculated chloride concentration was 468.82 mg/l, the minimum chloride concentration was 106.11 mg/l, and the average was 168.81 mg/l (Figure 4.6f). Five grab samples were collected during the study ranged from 160 mg/l to 190 mg/l for chloride (table 4.2).

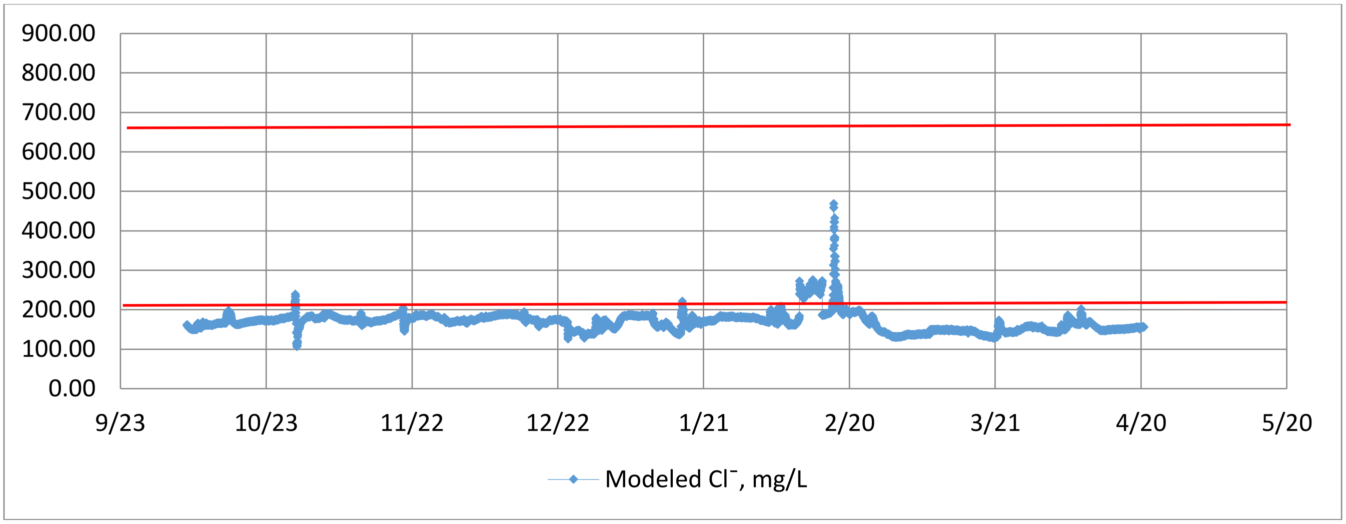


Figure 4.6f- Calculated chloride concentrations at site 6

Table 4.3. Min, max and average concentrations of chloride

Site	Chloride concentrations, mg/l		
	Min	Max	Average
1	27.1	118.8	81.3
2	65.8	212	101.3
3	55.9	1228.6	218.3
4	50.5	1035.1	240.4
5	105.2	251	162.8
6	106.1	468.8	168.8

4.1.1.2. Estimated Chloride Violations

The number of chloride violations of chronic and acute water quality standards were calculated using the model developed by MassDEP. Based on the number of violations, it was determined that River Meadow Brook was impaired according to ambient water quality standards. Violations of the acute and chronic water quality standards for chloride were calculated by rolling averages for all possible blocks of one and 96 hours, respectively. This method captured all occurred violations. The time increment for the rolling averages was 30 minutes; therefore, the time blocks by rolling averages overlapped. Each independent period of violation was identified by the beginning of the time block of the first overlapping violation and the end of the time of the last overlapping violation. The total duration of each independent period was calculated. The number of violations corresponding to each independent period was calculating by dividing the duration by one hour and 96 hours and rounding to the nearest integer. The number of violations for the period of record was summed for all the independent periods of violation (Table 4.3).

Analysis of the continuous monitoring data for specific conductance for the 7-month period showed that concentrations of chloride at site 3 exceeded the 230 mg/l mark for 22 days including 3 hours of the acute water quality standard of 860 mg/l. The maximum chloride concentration at site 3 was 1228 mg/l.

The accumulation of chloride at site 4 resulted in a chronic chloride violation that lasted for 49 days. The maximum calculated chloride concentrations was 1035 mg/l.

Three episodes of exceedances of chronic chloride concentrations were observed at site 6. The maximum average chloride concentration for these periods was 278 mg/l. No acute chloride exceedances were observed at this site. There was no violations observed at site 5 which provides some affirmation of the assumption developed in the beginning of this study that a small stream can affect water quality of a large stream.

Table 4.4. Chloride water quality violations, part 1

Site	Block Date start	Block Date end	Duration, days	# of Violations	Violation type	Mean [Cl^-], mg/l
3	10/6/2015 12:00	10/31/2015 7:30	22	1001	Chronic	342.0
3	11/3/2015 7:00	11/11/2015 23:00	8	343	Chronic	240.5
3	11/16/2015 15:00	11/20/2015 9:30	5	84	Chronic	235.4
3	12/28/2015 22:00	1/2/2016 12:30	5	33	Chronic	234.1
3	1/3/2016 18:00	1/11/2016 5:00	9	167	Chronic	243.8
3	1/13/2015 20:00	1/21/2016 23:30	9	201	Chronic	244.9
3	2/2/2016 4:00	2/13/2016 4:00	12	338	Chronic	239.6
3	2/12/2016 17:30	2/21/2016 5:30	10	229	Chronic	304.6
3	2/16/2016 18:30	2/16/2016 20:00	N/A	3	Acute	1062.5
3	4/1/2016 16:00	4/9/2016 0:00	8	161	Chronic	249.0
	Total # violations for site 3			2560 (22 days)		

Table 4.4. Chloride water quality violations, part 2

Site	Block Date start	Block Date end	Duration, days	# of Violations	Violation type	Mean $[\mathrm{Cl}^-]$, mg/l
4	10/6/2015 14:00	10/30/2015 23:30	24	1029	Chronic	351.3
4	10/31/2015 16:30	11/13/2015 6:30	13	464	Chronic	265.0
4	11/13/2015 9:00	11/21/2015 4:00	8	232	Chronic	252.7
4	11/22/2015 3:30	11/26/2015 23:00	4	89	Chronic	235.4
4	12/5/2015 4:00	12/15/2015 17:30	10	364	Chronic	249.7
4	12/28/2015 11:00	1/3/2016 20:00	5	164	Chronic	259.9
4	1/3/2016 11:00	1/11/2016 12:30	8	245	Chronic	260.9
4	1/16/2016 17:30	1/29/2016 4:30	13	599	Chronic	253.0
4	1/27/2016 19:30	2/2/2016 12:30	6	199	Chronic	232.1
4	1/31/2016 20:00	2/22/2016 3:00	23	962	Chronic	277.8
4	2/16/2016 17:00	2/16/2016 18:30	N/A	3	Acute	942.3
4	3/22/2016 1:00	3/25/2016 2:00	3	147	Chronic	259.2
4	4/1/2016 20:30	4/9/2016 5:00	8	211	Chronic	284.3
	Total # violations for site 4			4708 (49 days)		
6	2/9/2016 17:30	2/14/2016 10:00	5	35	Chronic	251.7
6	2/12/2016 10:00	2/18/2016 3:30	6	83	Chronic	269.0
6	2/16/2016 16:30	2/21/2016 3:30	5	25	Chronic	278.6
	Total # violations for site 6			143 days)		

4.1.1.3. Snowstorm and chloride exceedances relationship

To show the relationship between the applications of road salt, exceedances of chloride and snowfall along River Meadow Brook, daily snowfall data were retrieved and evaluated from the National Climate Data Center (NOAA). For this study, daily snowfall at each location was assumed to be associated with a potential road salt application (Table 4.5). Continuous conductivity data for the 7-month period did not reveal any particular trends associated with snowfalls and application of road salt at locations 1 and 2 (Figure 4.7a and 4.7b). This is most likely because of the absence of direct runoff and low application of road salt at these sites. At locations 3 and 4, on the other hand, chloride spikes occurred almost immediately after each snowstorm event resulting in multiple chronic and acute violations of water quality standards for chloride (Figure 4.7c and 4.7d). During multiple snowstorm events that occurred in the winter 2016, location 5 did not show any particular trend related to snowstorm events and chloride concentrations (Figure 4.7e). This might be due to high flows and dilution in the Concord River. Even though location 5 did not respond to a possible road salt application during snowfall events, spikes occurred at site 6 after the March and April snowstorm events were recorded (Figure 4.7f). This observation supports the assumption that a small stream may have an influence on a bigger river with high flows. Snowstorm observations supported the statement/assumption we had developed in the beginning of the study which was that urbanization and the close vicinity of roads have a negative effect on water quality in River Meadow Brook due to salt application.

Table 4.5. Snowfall data

Month	Date	Snowfall, in
October		N/A
November		N/A
December	12/29/2015	0.9
	12/31/2015	1.4
January	1/13/2016	2.6
	1/18/2016	2.4
	1/18/2016	0.8
February	2/6/2016	8
	2/9/2016	6.3
	2/11/2016	0.2
	2/16/2016	2.6
March	03/05/2016	0.1
	3/21/2016	3
	3/22/2016	1
April	4/5/2016	4
	04/12/2016	0.22

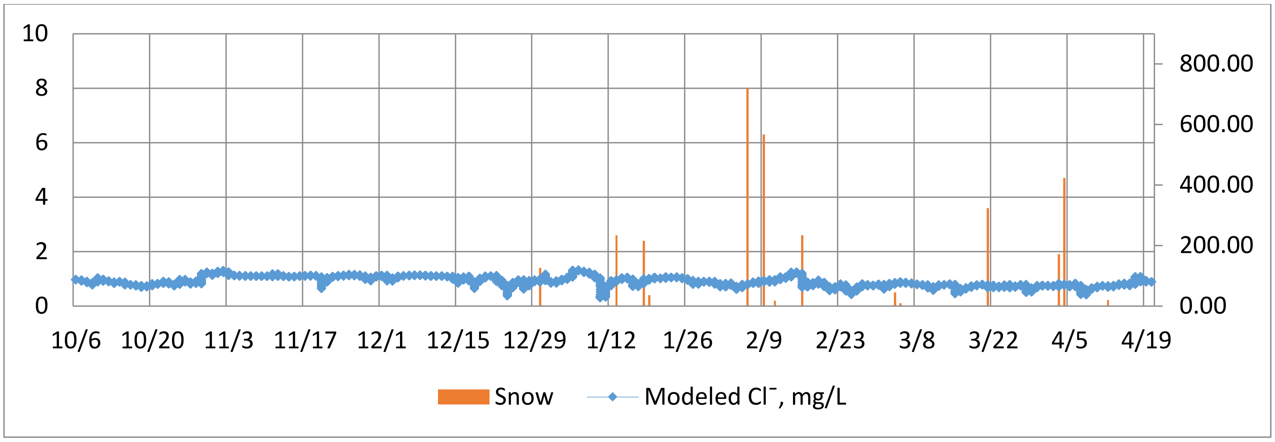


Figure 4.7a- Snowfalls and calculated chloride at site 1

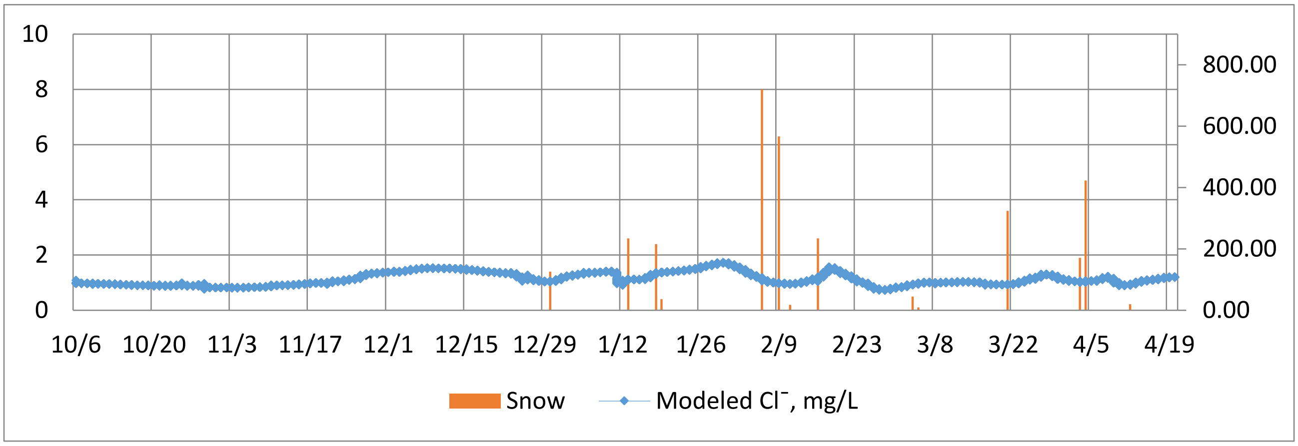


Figure 4.7b- Snowfalls and calculated chloride at site 2

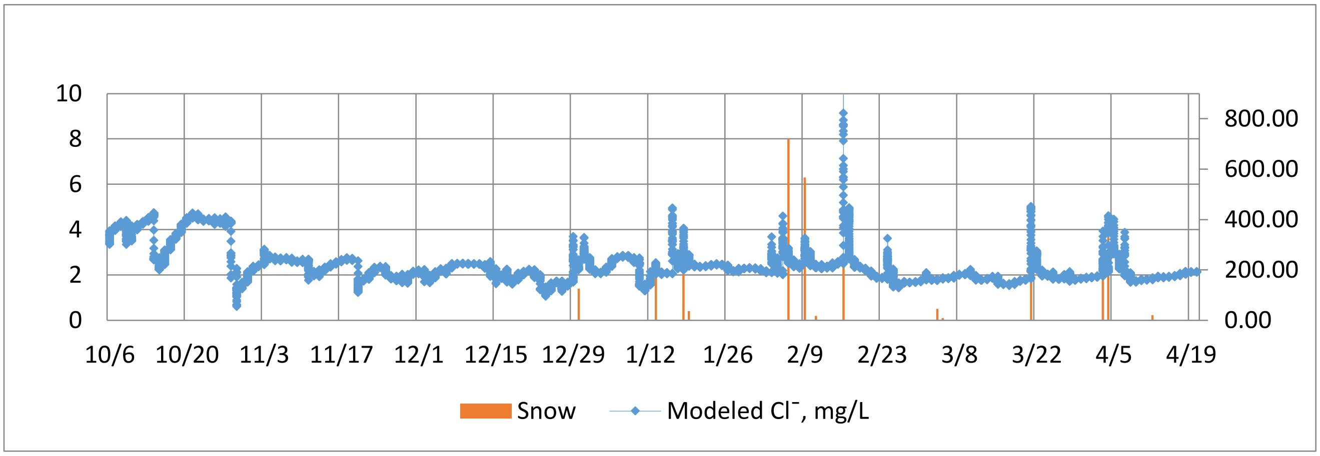


Figure 4.7c- Snowfalls and calculated chloride at site 3

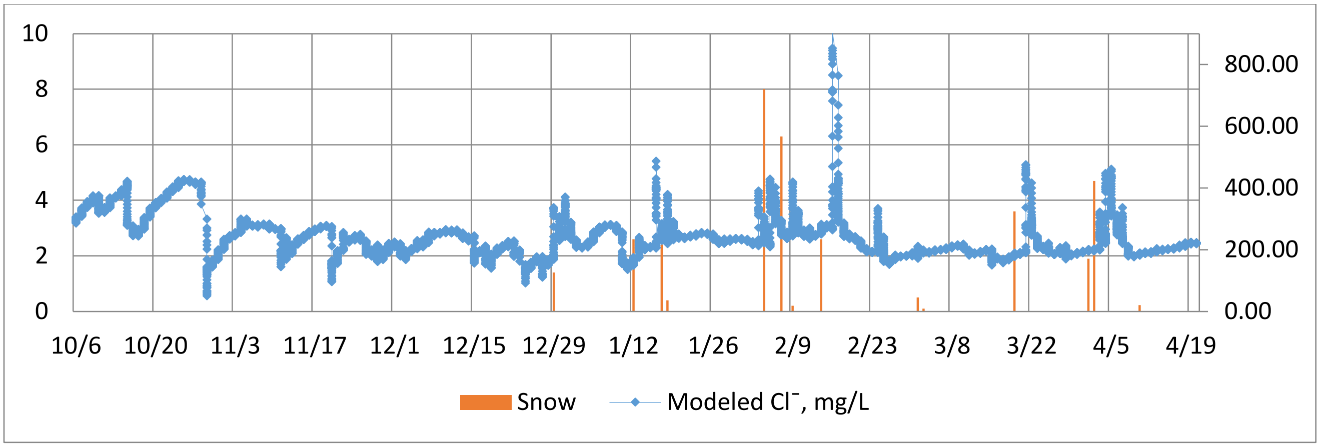


Figure 4.7d- Snowfalls and calculated chloride at site 4

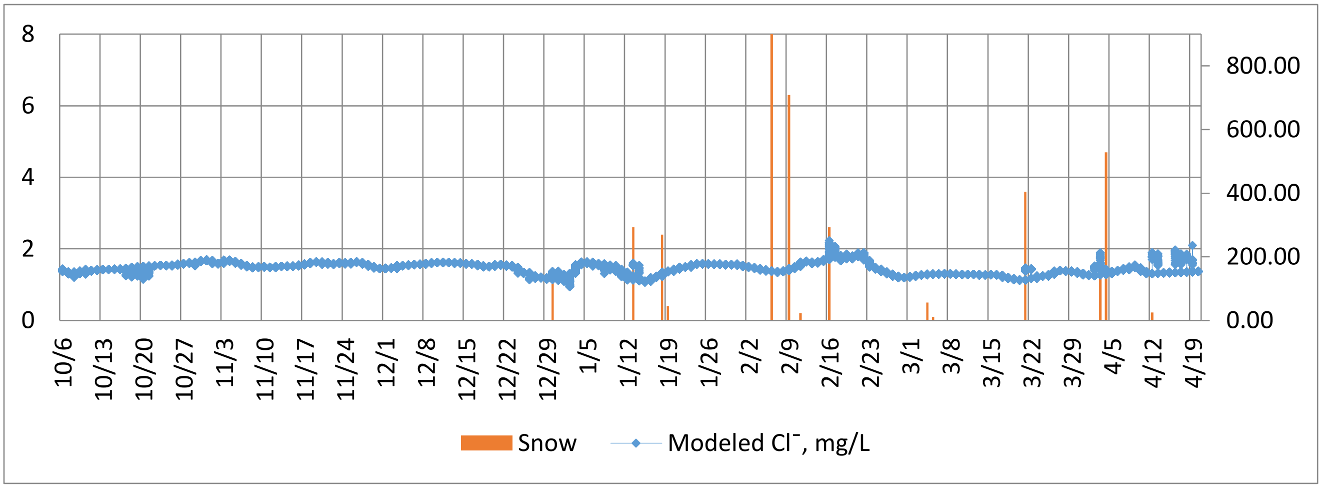


Figure 4.7e- Snowfalls and calculated chloride at site 5

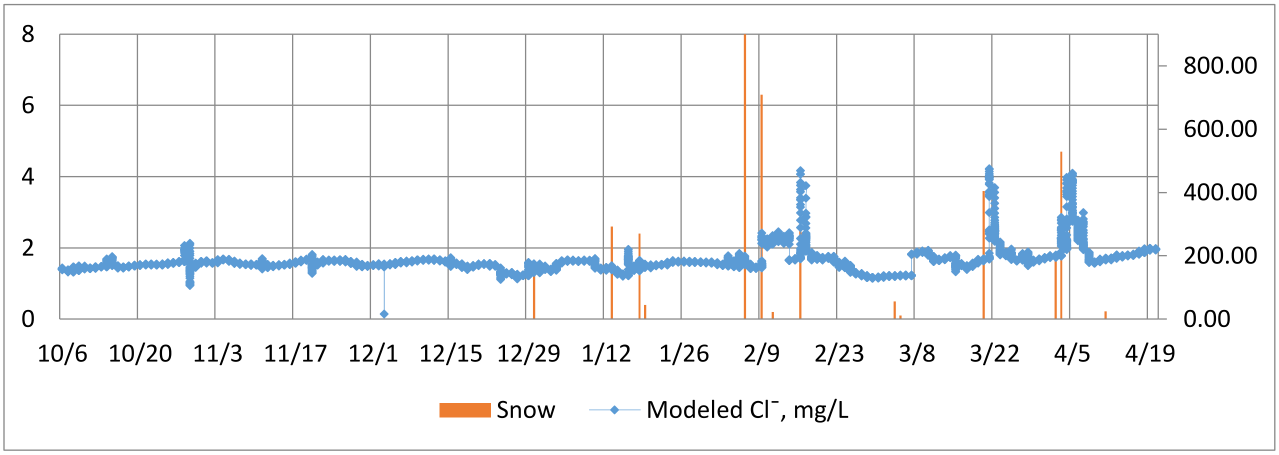


Figure 4.7f- Snowfalls and calculated chloride at site 6

4.1.1.4. Quality Control of laboratory analysis

Twenty water samples analyzed by USEPA laboratory and at WPI were compared for quality control and quality assurance purposes. The result showed that chloride concentrations from the WPI and EPA laboratory matched within a 93.25% confidence that the results are close to a 1:1 line. The water samples collected for the laboratory analysis were collected side-by-side.

Table 4.6. WPI and EPA chloride concentrations comparison

#	Date	Site	WPI	EPA
			Cl^-, mg/L	
1	10/26/15	1	76.8	83
2		2	104	100
3		3	422	390
4		4	417	320
5	11/3/15	1	91	94
6		2	80	78
7		3	260	270
8		4	257	270
9	12/3/16	1	87	86
10		2	129	140
11		3	190	180
12		4	184	200
13	3/7/2016	1	75	79
14		2	97	97
15		3	250	190
16		4	206	220
17	4/20/2016	1	75	81
18		2	119	120
19		3	209	230
20		4	324	250

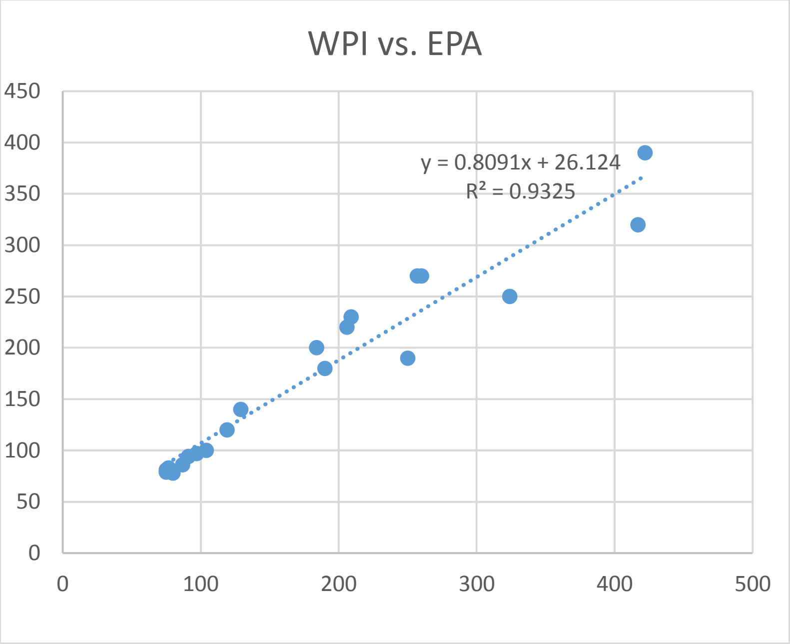


Figure 4.8. Linear regression analysis for chloride by EPA and WPI labs

4.2.2. Inorganic constituents

The laboratory analysis were performed for metals, anions, total suspended solids (TSS), dissolved oxygen (DO), pH. The mean, maximum, minimum and average concentrations found in River Meadow Brook during this study are presented along with basic information on regulatory requirements in Table 4.7. The full dataset is attached as Appendix D. The full list of constituents is as follows:

Na, K, Cl, TSS, DO are presented in ppm. Whereas, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Pb concentrations are indicated in ppb. Ppm refers to as parts per million and is equal to mg/l, and ppb stands for part per billion and is equal to µg/l.

Cr, Co, and Pb were not statistically analyzed due to very low concentrations. A negative sign indicates in front of the concentration indicate that is was below the detection limits. Therefore, it was concluded that any trends associated with these constituents are not accurate.

Table 4.7. Mean, min and max dissolved concentrations of water quality parameters in River Meadow Brook

Constituent	Units	average	min	max	Regulatory requirements.
Cl	mg/l	164.0	27.1	1228.6	230(2)
Na	mg/l	93.0	26.4	251.6	20
K	mg/l	4.7	2.5	9.4	
Al	µg/l	46.9	1.1	235.2	87
V	µg/l	1.6	0.4	2.9	
Cr	µg/l	0.3	0.04	2.5	120
Mn	µg/l	101.9	0.5	524.8	No Criteria
Fe	µg/l	203.0	17.4	466.8	1000
Co	µg/l	0.4	0.1	1.2	No Criteria
Ni	µg/l	5.8	2.2	27.7	56
Cu	µg/l	9.4	1.5	39.1	6.5(2)
Zn	µg/l	11.0	0.7	73.9	120
As	µg/l	1.9	0.7	5.7	150
Cd	µg/l	0.1	0.01	0.9	0.66(2)
Pb	µg/l	0.2	0.02	0.8	2.5
TSS	mg/l	2.7	0.2	8.3	30.00
pH		6.6	6.4	6.9	6.5-8.3
DO	mg/l	9.4	7.9	10.3	>5(1)
Sulfate	mg/l	14.9	7.0	28.8	250(4)
nitrate	mg/l	2.9	0.8	6.3	320(5)
Conductivity	µS/cm	651.7	167.5	4536.8	N/A
Temp	°C	6.0	0.1	17.6	

(1) USEPA Ambient Water Quality Standard
(2) MasDEP
(3) USEPA Maximum Contaminant Level Goal
(4) USEPA for Ambient Water Quality Standard for total Nitrogen

4.2.2.1. Relationship between impervious surface and inorganics

A SAS computer procedure, CORR (The Pearson Correlation Analysis), was used to determine the relationship between impervious surface and water quality parameters along River Meadow Brook. For the Pearson Correlation analysis, average concentrations of pollutants for each site were used (Table 4.7). The outcome was the Pearson correlation coefficient r- and P-values. The P-value is the parameter that measures a linear relationship between two variables (water quality parameters). The P-values that are less than <0.05 indicated that the relationship are statistically significant. The Pearson Correlation coefficients measured the strength and direction of a linear relationship between two variables. Table 4.8 represents the final results of the Pearson correlation analysis. Yellow highlighted cells indicate the presence of a statistically significant relationship. As described in chapter 2, the percent of impervious coverage increases from upstream to downstream in River Meadow Brook: -6.14% at site 1, -7.45% at site 2, -18% at site 3, -23.7%. at site 4.

Table 4.8. The Pearson correlation analysis

Na	0.96875
Na	0.0313
Cl	0.96874
Cl	0.0314
Mg	0.94012
Mg	0.0599
K	0.95861
K	0.0414
Al	-0.70523
Al	0.2948
V51	0.98874
V51	0.0113
Mn	0.8365
Mn	0.1635
Fe	0.9271
Fe	0.0729
Ni	0.99951
Ni	0.0005
Cu	0.87122
Cu	0.1322
Zn	0.66256
Zn	0.3374
As	0.96773
As	0.0323
Cd	-0.9375
Cd	0.0652
TSS	0.9909
TSS	0.0091
pH	0.9877
pH	0.0123
DO	-0.90991
DO	0.0901
Sulfate	0.93103
Sulfate	0.069
Nitrate	-0.29607
Nitrate	0.7039

Based on the Pearson Correlation Analysis, Al, Mn, Mg, Fe, Cu, Zn, Cd, DO, sulfate and nitrate did not have significant correlation (P>0.05). On the other hand, Cl, Na, K, V, Ni, As, TSS were significantly correlated. TSS and Ni had the most significant degrees of correlation (r=0.9909, P=0.0091) and (r=0.99951, P=0.0005), respectively. These results support previously conducted studies that TSS and Ni increase with higher percentage of impervious coverage (Metasaranta et al. 2005*)*. It was not a surprise to see a strong Na/Cl and impervious surface relationship because these are the two primary components of road salt. Na and imperviousness were correlated r=0.96875 P=0.0313; chloride r=0.96874 and P=0.0314. As the percent impervious coverage increased from upstream to downstream, pH decreased (r=0.9877 P=0.0123). Cd indicated a significant negative correlation with impervious surface (r=0.97495 P=0.0252). A negative correlation for Al and DO indicated that the concentrations of Al and dissolved oxygen increases in the opposite direction, from downstream to upstream. This result might be due to a high groundwater concentration, and the water increased dilution downstream. K (r=0.95861, P=0.0414) showed strong correlation with impervious surface. A study by Solomon and Natusch (1977) study supports the notion K can come from roads. They concluded that K, Cr, Na, Cu, Ni, Pb, Cd and several other metals were part of large particles deposited onto the roadway.

4.2.2.2. ANOVA Analysis

The Student-Newman-Keuls test was run to determine the variation in water quality parameters from site to site. Figures showing the more significant variations are included in this section.

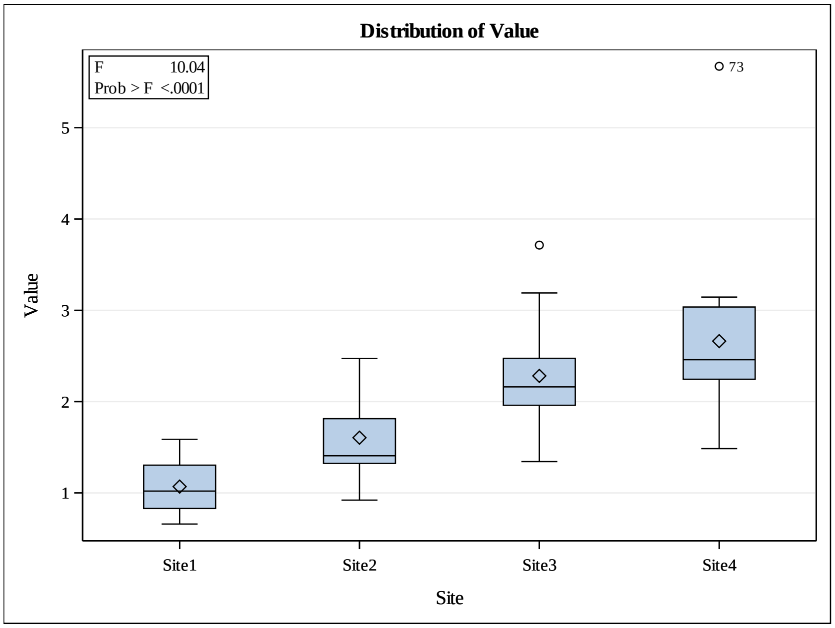
4.1.2.1. ANOVA analysis

The ANOVA analysis with the Student-Newman-Keuls test was run to identify sample means that were different from each other. The results also helped to identify trends of various inorganics along River Meadow Brook.

- *Arsenic (As)*

The mean concentrations of arsenic along River Meadow Brook were significantly different among the four sites (P<0.001) (Figure 4.9). Site 1 and 2 had the lowest concentrations of arsenic and Sites 3 and

4 had the highest concentrations of arsenic. A possible principal source of arsenic upstream of at Site 3and 4 could be fossil fuel combustion products. The mean concentration of arsenic was 1.92 µg/l, the maximum concentration was 5.67 µg/l and the minimum concentration was 0.66 µg/l..

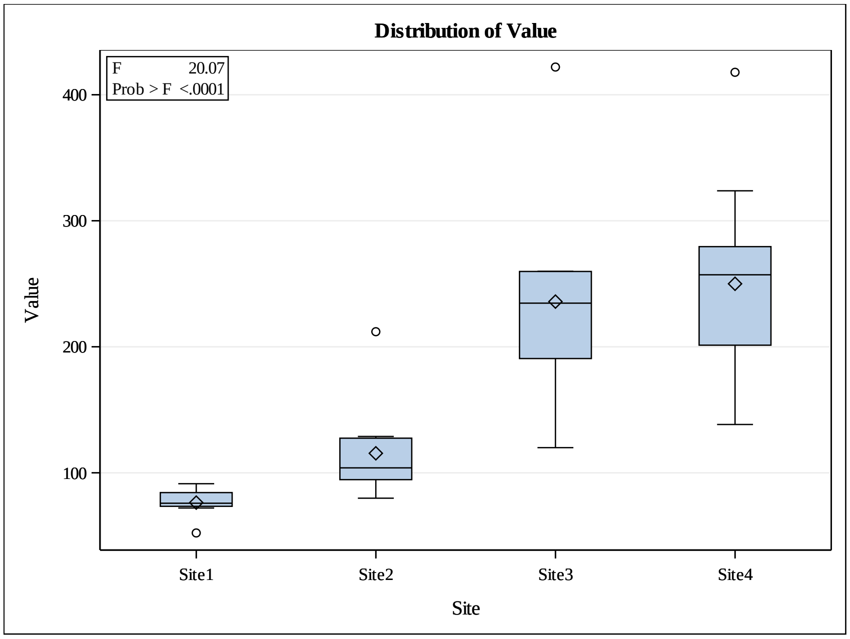


Means with the same letter are not significantly different.			
SNK Grouping	Mean	N	Site
A	2.6626	14	Site4
A			
A	2.2816	10	Site3
B	1.6048	11	Site2
B			
B	1.0691	8	Site1

Figure 4.9. ANOVA analysis for arsenic

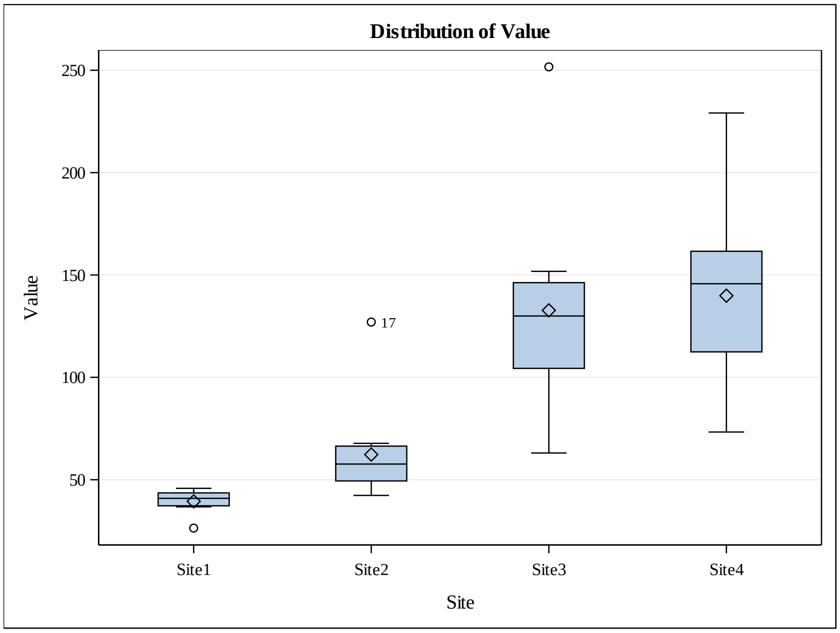
- *Chloride (Cl) and Sodium (Na)*

ANOVA analysis showed that the concentrations of sodium and chloride were significantly different at Site 3 and Site 4 compared to the concentrations of sodium and chloride at Site 1 and Site 2.(P<0.0001 for sodium and chloride) (See Figure 4.10 and Figure 4.11). The elevated concentrations of sodium and chloride at Sites 3 and 4 were due to the application of road salt in the winter time and contaminated groundwater contribution during low- flow periods. The mean concentration of sodium during the study period was 167.74 mg/l and the mean concentration for chloride was 93.87 mg/l.



Means with the same letter are not significantly different.			
SNK Grouping	Mean	N	Site
A	250.02	11	Site4
A			
A	235.88	10	Site3
B	115.52	11	Site2
B			
B	76.39	8	Site1

Figure 4.10. ANOVA analysis for chloride

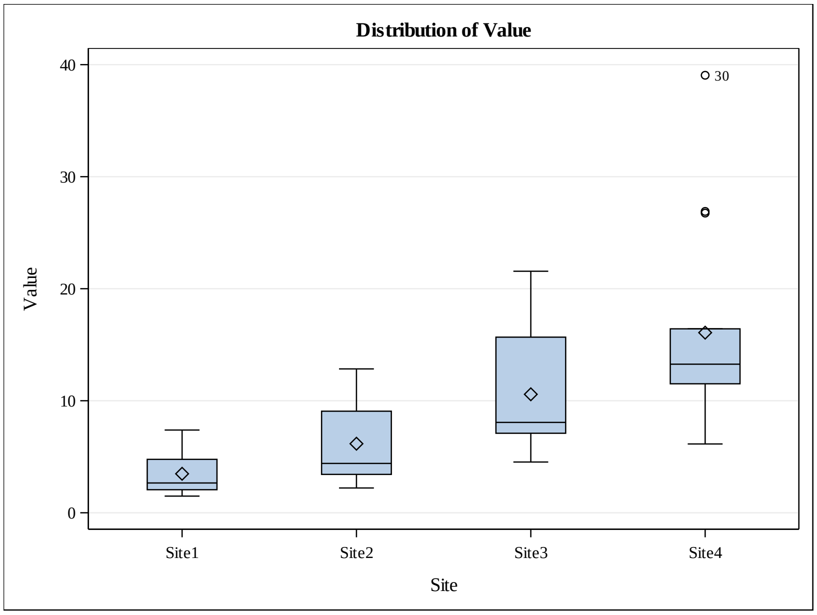


Means with the same letter are not significantly different.			
SNK Grouping	Mean	N	Site
A	139.89	13	Site4
A			
A	132.73	10	Site3
B	62.30	11	Site2
B			
B	39.45	8	Site1

Figure 4.11. ANOVA analysis for sodium

- *Copper (Cu)*

ANOVA analysis showed that the concentrations of copper also increased from Site 1 to Site 4. The mean concentration of copper at Site 4 had the highest value compared to the average concentrations of copper at Site 3, 2 and 1 (r=8.95 and P=0.0001) (Figure 4.12). It may indicate that there is an input of copper between Sites 3 and 4. Taking into the account that the principle source of copper in urban water runoff is vehicle parts and industrial waste, the ANOVA analysis make sense.



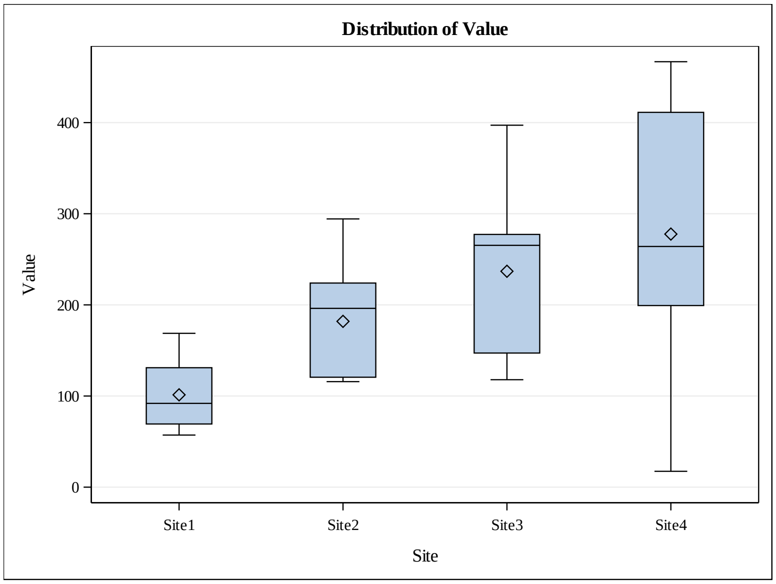
Means with the same letter are not significantly different.

SNK Grouping		Mean	N	Site
	A	16.077	14	Site4
	B	10.576	10	Site3
	B			
C	B	6.164	11	Site2
C				
C		3.481	8	Site1

Figure 4.12. ANOVA analysis for copper

- *Iron (Fe)*

Iron is a trace element required by both plants and animals. Primary sources of iron in urban runoff are auto body rust, steel highway structures and engine parts (Tiefenthaler at el.(2001))l. Based on the ANOVA test, the mean concentrations of iron along River Meadow Brook were statistically different (r=6.71 and P=0.0009) (Figure 4.13). The mean concentration of iron at Site 1 was 101.31 µg/l and 277.67 µg/l at Site 4. The overall trend was that the concentrations of iron increases as River Meadow Brook flows from upstream to downstream.

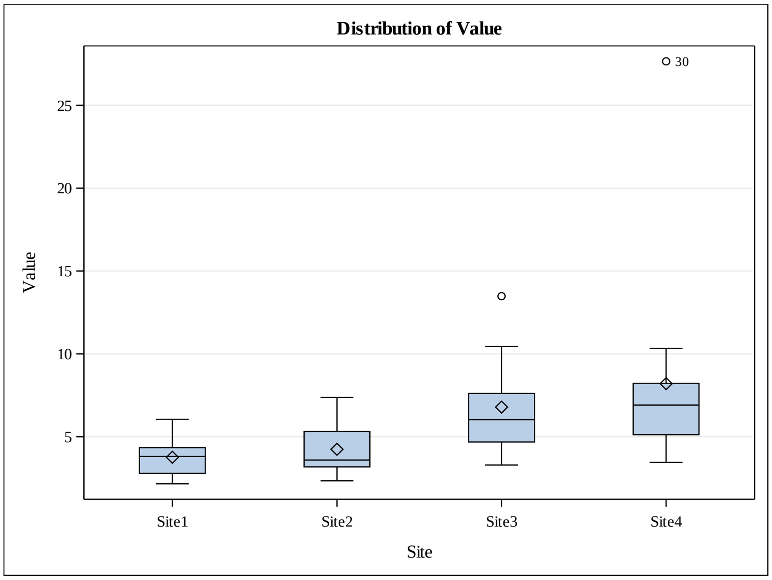


Means with the same letter are not significantly different.				
SNK Grouping		Mean	N	Site
	A	277.67	14	Site4
	A			
	A	236.87	10	Site3
	A			
B	A	181.92	11	Site2
B				
B		101.31	8	Site1

Figure 4.13. ANOVA analysis for Iron

- *Nickel (Ni)*

The primary source of nickel in urban stormwater runoff are diesel fuel and gasoline, lubricating oil, metal plating, brake lining wear and asphalt paving. Even though, there is a major transportation corridor at Site 3 and Site 4, the ANOVA analysis did not show any significant differences in concentrations of nickel along River Meadow Brook (r=3.40 and P=0.0272) (Figure 4.14). Nevertheless, the overall trend was that the mean concentrations of nickel increased from Site 1 (3.7 µg/l) to Site 4 (8.2 µg/l), so there was an increase as would be expected.

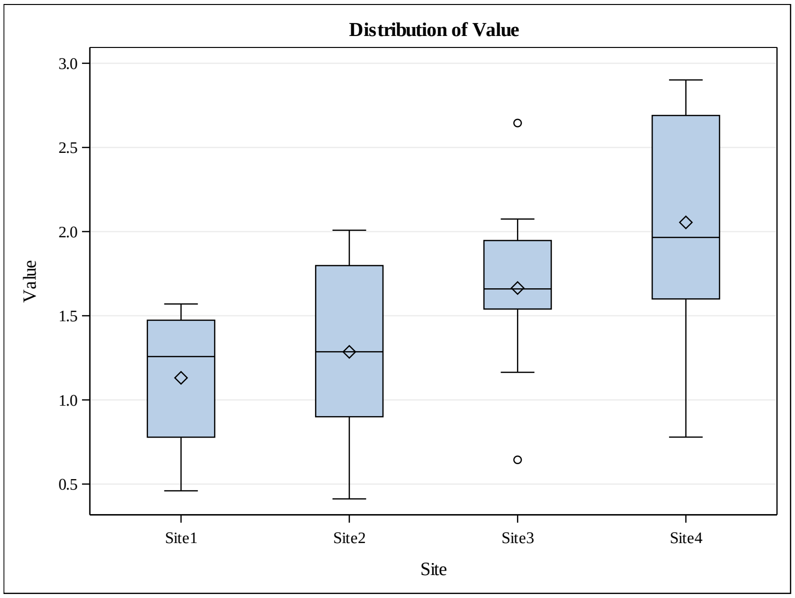


Means with the same letter are not significantly different.			
SNK Grouping	Mean	N	Site
A	8.201	14	Site4
A			
A	6.785	10	Site3
A			
A	4.248	11	Site2
A			
A	3.761	8	Site1

Figure 4.14. ANOVA analysis for nickel

- Vanadium (V)

The ANOVA analysis indicated that the mean concentration of vanadium at Site 1(1.1 µg/l) was statistically different from Site 4 (2.1 µg/l) (F=6.28 and P=0.0014) (Figure 4.15). The overall trend for vanadium was that the concentrations increased from Site 1 to Site 4.



Means with the same letter are not significantly different.				
SNK Grouping		**Mean**	**N**	**Site**
	A	2.0547	14	Site4
	A			
B	A	1.6648	10	Site3
B				
B		1.2855	11	Site2
B				
B		1.1311	8	Site1

Figure 4.15. ANOVA Analysis for vanadium

4.2.2.3. Inorganics by Season

To analyze inorganics by season, samples collected from October 6 through December 21were associated with the fall season. Samples collected from December 22nd through March 19th were winter samples, and from March 20 through April 20 were considered to be spring samples. The average concentrations of significantly correlated constituents with impervious surface were analyzed by season and presented in Figures 4.9 through 4.10.

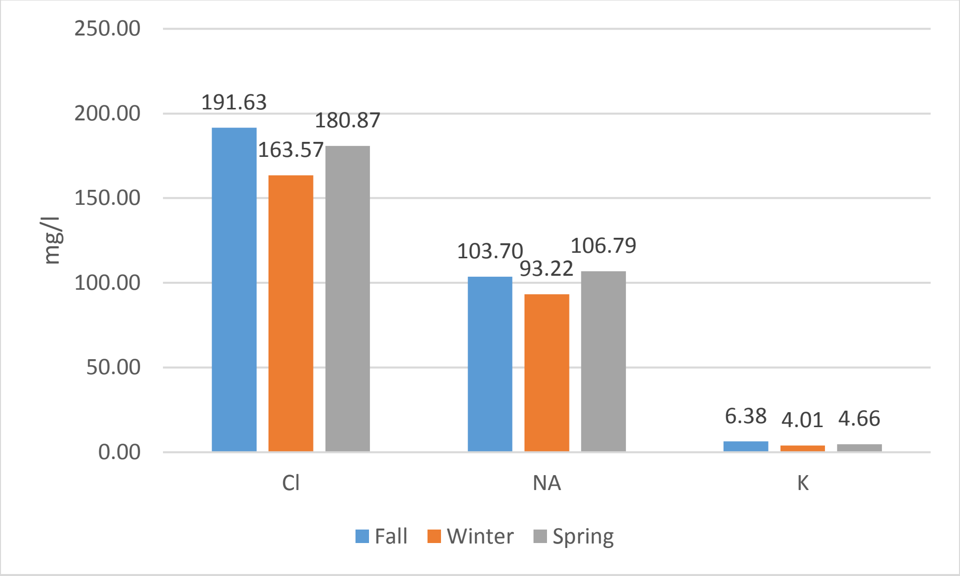


Figure 4.16. Concentrations of Na and Cl by season

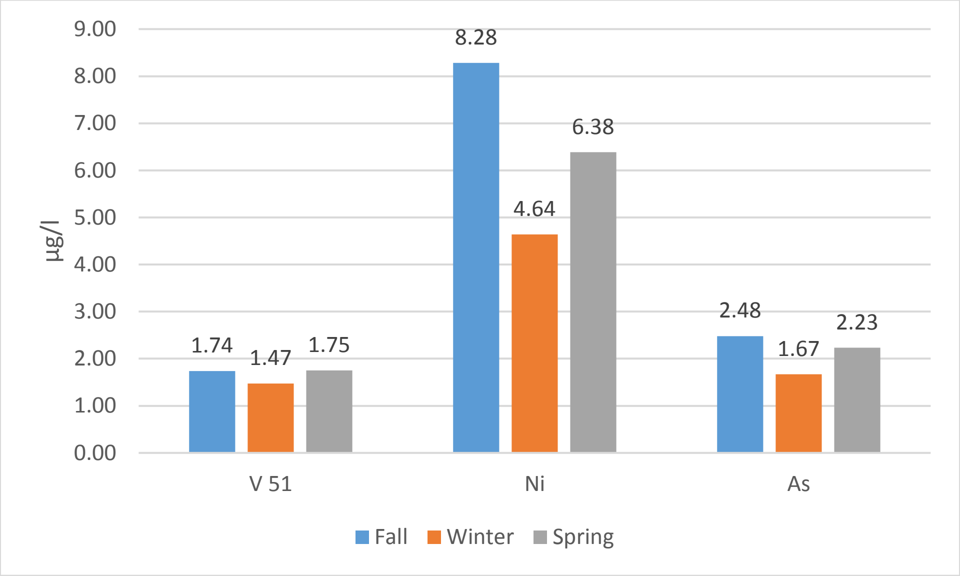


Figure 4.17. Concentrations of V, Ni and As by season

Most of the constituents show trends in which concentrations were high in the fall, lowest in the winter and trending back up in the spring. These trends might be due to much of the snowmelt occurred in the spring washing-off pollutants to the stream and low-flow period in the fall.

At River Meadow Brook, chloride concentrations were higher in the fall compared to the winter by approximately 15%. This might be due to low-flow condition, and groundwater contribution containing high concentrations of chloride. In the winter, average concentrations of chloride along River

Meadow Brook were 167.5 mg/l, it is lower than in the spring (180.87 mg/l). Approximately 25 inches of snow had fallen in the winter compare to 8.2 inches in the spring. Every snowfall was assumed to be associated with road salt application. Even though there were only 8.2 inches of snow in the spring, an abundant snowmelt that happened in the spring had possibly carried pollutants to the stream. Therefore, higher concentrations of chloride in the spring make sense. Concentrations of sodium showed a similar trend with lowest concentrations in the winter, and close concentrations in the fall and spring (104 and 107 mg/l respectively).

Higher concentrations of Cr and Cd were observed in the spring. Then the concentrations had significantly decreased in the winter, and increased again in the spring. Similar trend was noted in Gomez-Alvarez et al. (2014) where the average concentration of Cd, Cr and Cu were lower in the dry season. Concentrations of copper reaches maxima in the spring, and relatively variant at winter and fall. Concentration of vanadium were not significantly different from season to season.

As, Ni, As showed lowest concentration in the winter. Higher concentrations of these trace metals in the fall can be explained by a possible wash-off of pollutants that accumulated on impervious surface during the extended-dry period (summer). In the winter, concentrations went down possibly due to high flows and dilution. Finally, with more precipitations occurred in the spring, the concentrations went back up again.

4.3. Pollutant loads

Average pollutant loads for Na, Cl, K, Ni, V and As for the four catchment areas were calculated based on flow measurements taken from January through June. For example, at site 1 the mean concentration of Na over three sampling dates was equal to 26.4 mg/l. The mean discharge was equal to 0.8 ft^3/sec. To calculate mean daily load, a conversion factor described below was applied. Mean discharge, the concentration and the conversion factor were multiplied to obtain daily pollutant load. Detailed calculations of pollutant loads are shown in Appendix D, and the summary is presented in Table 4.10.

$$\text{Daily load} = mg/l*ft^3/sec * 28.32\ l/ft^3 * 8640\ sec/day * 1kg/10^6mg$$

Where the pollutant concentration is in mg/l, the discharge in ft^3/sec and a conversion factor is used to obtain the final units of kg/day or gram/day

f- conversion factor

c- pollutant concentration, mg/l

d- discharge, ft^3/sec

Table 4.9. Summary daily pollutant loads

	Units	Site 1	Site 2	Site 3	Site 4
Cl	kg/day	13	500	1586	2978
Na	kg/day	7	170	890	1731
K	kg/day	0.6	18	36	70
V	gram/day	0.2	6	12	25
Ni	gram/day	0.6	18	47	99
As	gram/day	0.2	7	16	33

From the chart, it is noticeable that chloride contributes the highest daily loads between 13 kg/day at site 1 to 2978 kg/day at site 4. Contribution of sodium ranged between 7 kg/day at site 1 to 1731 kg/day at site 4. Sodium contributed to 7kg/day at site 1 and 1731 kg/day at site 4. These high loadings can be explained, as discussed earlier, by the application of road salt in the winter and groundwater contribution during the low-flow period. The chronic water quality standard for chloride is 230 mg/l based on 4-day average concentrations, acute 860 mg/l based on 1-hour average. As per MassDEP, a recommended concentration of sodium does not exceed 20 mg/l. The minimum sodium concentration during the study was 26.4 mg/l at site 1, and the highest was 251.6 mg/l. The average concentration was 93.8 mg/l. Therefore, the concentrations of Na exceeded water quality standards. Exceedances and violations of chloride were described in the “Chloride” section.

Arsenic daily loads ranged between 0.2 gram/day to 25 gram/day as River Meadow Brook flows from headwaters to site 4 in Lowell, MA. During this study, the mean arsenic concentrations found in River Meadow Brook were 1.92 µg/l with the highest 5.67 µg/l (site 4) and lowest 0.66 µg/l (site 1).

According to the National Recommended Aquatic Life Criteria table, arsenic chronic concentration does not exceed 150 µg/l, and acute 340 µg/l. The principal natural sources of arsenic are fossil fuel combustion products, and atmospheric deposition from mining operations. There are no mining activities present near River Meadow Brook. Therefore, concentrations of arsenic increases from upstream to downstream because of the high automobile activities at upstream sites.

Daily loadings of nickel ranged between 0.6 gram/day at site 1 to 99 gram/day at site 4. Primary sources of nickel from road runoff are diesel fuel and gasoline, lubricating oil, metal plating, brake lining wear and asphalt paving. The average Ni concentration among the 5 sites was 5.8 µg/l. Chronic ambient water standard for Ni is based on hardness. For this study a 50 mg/l hardness was assumed. Therefore, the criteria is 56 µg/l and as 24-hour averages, the concentration should not exceed 1100 µg/l.

Daily loading for vanadium were different among four sites. At site 1, V contributed 0.2 gram/day and 25 gram/day at site 4. Vanadium is not on the list of the ambient water quality criteria. As per the background chapter of this paper, vanadium was associated with impervious surface based on previous studies. V mean concentrations found in River Meadow Brook was 1.6 µg/l.

Daily potassium loadings ranged from 0.6 kg/day to 70 kg/day. The average potassium concentration found in River Meadow Brook was 4.7 mg/l, minimum 2.5 mg/l and maximum 9.4 mg/l.

Water quality parameters from River Meadow Brook study were compared to a Campo et al. (2003) study to get a better understanding of the health of the stream. Five rivers with different level of urban disturbance were monitored during 1998-2000 for different parameters. Stillwater River represented a non-urban and undisturbed area with pristine water. Ipswich and Neposet Rivers are located in moderately urbanized areas, and Saugus and Aberjona Rivers were located in an intensely disturbed areas. River Meadow Brook was checked against the average concentrations found in the rivers (Table 4.13). Comparison of the water quality parameters showed that River Meadow Brook exceeded the average Cl, Na, K concentrations among 5 rivers. Ipswich and Aberjona that are moderately and intensely urbanized Rivers exceeded the average concentrations of Fe and Mn.

Table 4.10 Comparison River Meadow Brook with New England Rivers

River		River Meadow Brook	Stillwater	Ipswich	Neponset	Aberjona	Saugus
Drainage area, mi^2		24	32	45	35	25	23
Urbanization level			Minimum	Moderate	Moderate	Moderate	High
	Units						
Na	mg/l	93.0	10.70	31.00	26.00	58.10	54.40
Cl	mg/l	164.0	18.30	56.10	47.40	108.00	103.00
K	mg/l	4.7	1.25	2.34	1.77	3.37	2.57
Mn	µg/l	101.9	43.30	114.00	101.00	201.00	97.40
Fe	µg/l	203.0	140.00	320.00	260.00	140.00	200.00
TSS	mg/l	2.7	4.00	4.00	6.00	7.00	4.00

5. Conclusion

The goal of this project was to assess the effects of urbanization on water quality on the River Meadow Brook, a stream that flows a rural area in Chelmsford, MA to highly urbanized area with multiple roads and highway intersections in Lowell, MA. Between October 2015 and April 2016, River Meadow Brook was monitored as part of a project with two phases: a DEP study focusing on specific conductance and chloride and a second study to assess the relationship between impervious area and chloride and other inorganic constituents.

During the first phase of the project, there were two main objectives: to monitor conductivity continuously at 4 sites located in River Meadow Brook and 2 sites in the Concord River, and to re-validate a chloride assessment tool developed by MassDEP. Using the monitoring conductivity data and chloride analysis, the DEP model was used to convert the continuous conductivity data into chloride concentrations distributions for the 7-month period. Calculated chloride concentrations were used to identify chloride violations at six sites along River Meadow Brook. At two sites, chloride concentrations exceeded the chronic ambient water quality standard for 22 days and 49 days respectively. The maximum chloride concentration observed in River Meadow Brook was 1228 mg/l at site located downstream of major highway interchanges and high contributing impervious area (Site 3) and the lowest chloride concentration found to be 27.08 mg/l at the site with the lowest impervious area (Site 1) The lowest concentration was found by previous investigations for several New England Rivers with similar drainage basin areas (i.e. less than 50 mi^2). Conductivity data collected in the Concord River upstream and downstream of the confluence of with River Meadow Brook indicated that the brook may have direct impacts on the chloride concentrations in the main stem of the Concord River, since high concentrations were observed at the downstream station when high concentrations were observed in River Meadow. The maximum concentration observed at site 5, which is located upstream of the confluence with River Meadow Brook, was 250.9 mg/l. In addition, the maximum chloride concentration at Site 6, which is downstream of the confluence with River Meadow Brook, was 468.8 mg/l. Results also indicate that chloride spikes and violations occurred primarily during the winter and, typically coincided with snowfalls (when road salt application is commonly used to maintain safety on roads in Massachusetts) Therefore, in streams, located in the close vicinity to roads such as River Meadow Brook, chloride concentrations that exceed ambient water quality standards may be considered to be a common occurrence.

For the second phase of the study, the stations installed for phase 1 were also used to investigate the impact of urbanization on the water quality of River Meadow Brook. Forty-seven grab samples were collected from the four stations and were analyzed for Al, As, Cd, Co, Cr, Fe, K, Na, Mg, Ni, Pb, V, Zn, TSS, DO, pH, sulfate and nitrate to achieve that goal. The Person's Correlation Analysis was used to determine the relationship between impervious surface and water quality parameters. The ANOVA analysis with the Student-Newman-Keuls test was performed to determine whether the mean values of water quality parameters were significantly different from site to site. The result from the Pearson's Correlation Analysis showed that the concentrations of Cl, Na, K, V, Ni, Cu, As, TSS increased along with the percent of impervious coverage. Dissolved oxygen and Al showed a negative correlation with impervious surface, although there were likely due to the stream conditions or, in case of Al, associated with the high concentrations of Al in groundwater due weathering of granitic rock. The result from the ANOVA test showed that the concentrations of As, Cl, Na and V are significantly lower at downstream sites (Site 1 and 2) compared to upstream sites (Site 3 and 4). The ANOVA result indicated that the concentrations of As, Cl, Na and V in River Meadow Brook located downstream of major highway intersection and high impervious area (Site 3 and Site 4) may have a direct negative on the brook.

River Meadow Brook was compared to five other streams in New England with a similar drainage basin characteristics. The comparison showed that River Meadow Brook contained the highest concentrations of Na, Cl and K among the streams. These high concentrations are likely a result of the use of road salt and heavy traffic volumes associated with the major highway interchanges in the region.

The overall trend for the key constituents (Na, Cl, K, V, Ni, As, TSS and pH) was that pollutant load increased significantly as the stream flows from less developed areas into more urbanized areas associated with roads and urban activities. In addition, there are increases in concentrations as well as increases in load.

Seasonal changes were found to play a role in pollutant concentrations in River Meadow Brook. The lowest concentrations of the key components were found to be lower in the winter, and higher in the fall and spring. This trend suggests that snowmelt washes off a significant portion of pollutants to River Meadow Brook, especially at the sites located near highways and roads.

6. Recommendations.

This study is intended to serve as a basis for additional steps to protect River Meadow Brook and other surface streams in Massachusetts. As indicated previously, the sampling sites on River Meadow Brook that were located near highways and roads had multiple chronic and acute violations of sodium and chloride. It is highly likely that these concentrations were due to the application of road salt in the winter. Given these results, there is a basis for adding River Meadow Brook to the 303d list as chloride impaired.

The high concentrations of sodium and chloride in the fall, particularly during low-flow periods, suggests that groundwater entering River Meadow Brook is affected by the high concentrations of Na, Cl and other constituents. A Total Maximum Daily Loads (TMDL) analysis would help to develop approaches to reduce impact from road salt. In addition, to gain a better understanding of the variations Na, Cl, metals and other constituents throughout the year, additional studies are recommended. Water quality monitoring of the stream over a long period of time would provide additional information of seasonal changes and dry/wet periods. Several of the trace metals tested showed that the relationship between the percent of impervious coverage and increase in concentrations as the stream flows from upstream to downstream. This result indicates that the trace metals associated with vehicles and impervious surface increase as the stream flows through a more urbanized area.

In summary, this research provides a basis for assessing the impacts of urbanization on River Meadow Brook. A more detailed review of these relationship, and consideration total and dissolved loads of constituents in other streams, would provide a valuable follow-up to develop a full understanding of the impacts of urbanization on streams in New England.

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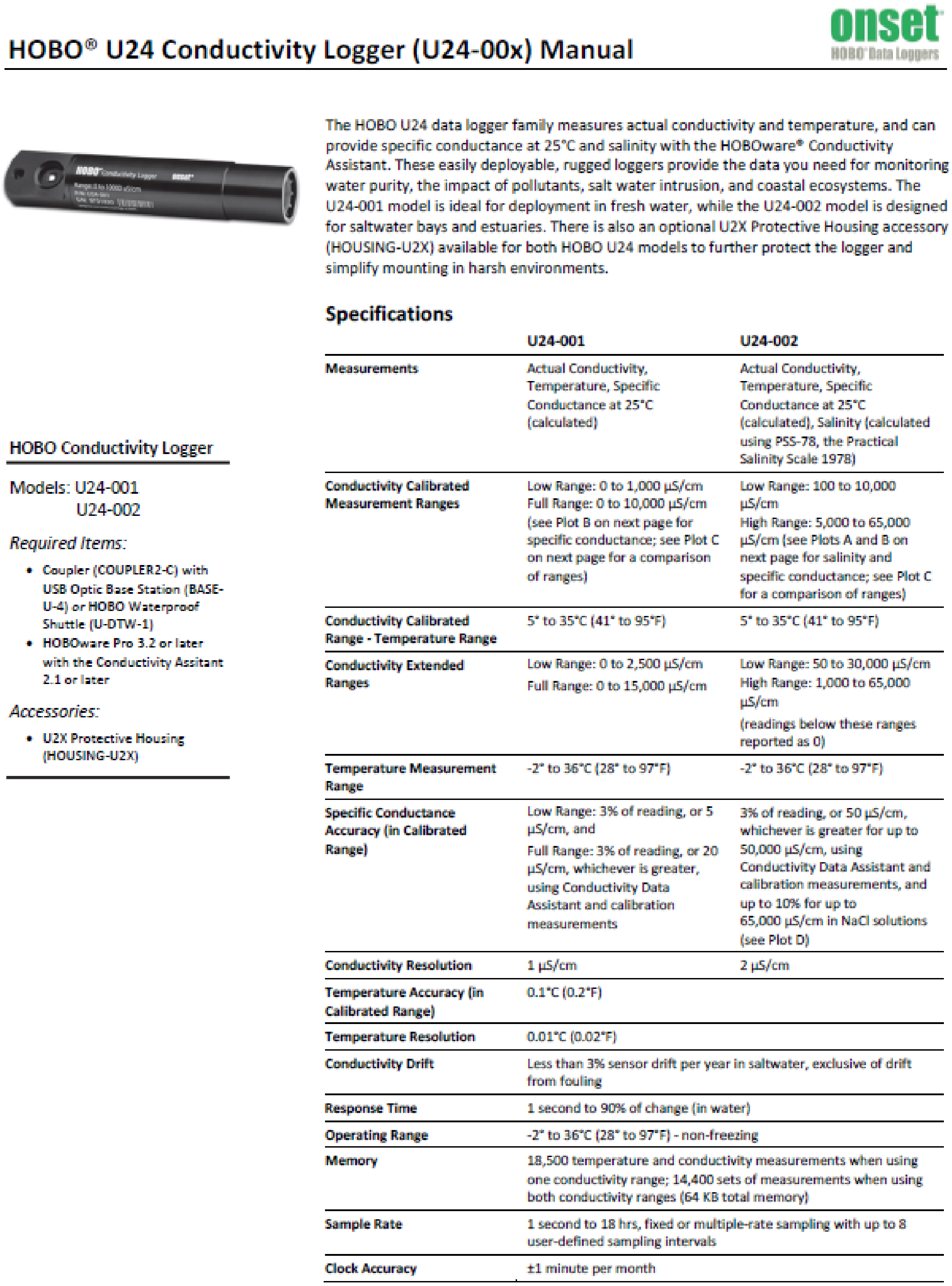
Appendix A. HOBO Conductivity logger Manual



HOBO® U24 Conductivity Logger (U24-00x) Manual

onset
HOBO® Data Loggers

The HOBO U24 data logger family measures actual conductivity and temperature, and can provide specific conductance at 25°C and salinity with the HOBOware® Conductivity Assistant. These easily deployable, rugged loggers provide the data you need for monitoring water purity, the impact of pollutants, salt water intrusion, and coastal ecosystems. The U24-001 model is ideal for deployment in fresh water, while the U24-002 model is designed for saltwater bays and estuaries. There is also an optional U2X Protective Housing accessory (HOUSING-U2X) available for both HOBO U24 models to further protect the logger and simplify mounting in harsh environments.

HOBO Conductivity Logger

Models: U24-001
U24-002

Required Items:

- Coupler (COUPLER2-C) with USB Optic Base Station (BASE-U-4) or HOBO Waterproof Shuttle (U-DTW-1)
- HOBOware Pro 3.2 or later with the Conductivity Assitant 2.1 or later

Accessories:

- U2X Protective Housing (HOUSING-U2X)

Specifications

	U24-001	U24-002
Measurements	Actual Conductivity, Temperature, Specific Conductance at 25°C (calculated)	Actual Conductivity, Temperature, Specific Conductance at 25°C (calculated), Salinity (calculated using PSS-78, the Practical Salinity Scale 1978)
Conductivity Calibrated Measurement Ranges	Low Range: 0 to 1,000 µS/cm Full Range: 0 to 10,000 µS/cm (see Plot B on next page for specific conductance; see Plot C on next page for a comparison of ranges)	Low Range: 100 to 10,000 µS/cm High Range: 5,000 to 65,000 µS/cm (see Plots A and B on next page for salinity and specific conductance; see Plot C for a comparison of ranges)
Conductivity Calibrated Range - Temperature Range	5° to 35°C (41° to 95°F)	5° to 35°C (41° to 95°F)
Conductivity Extended Ranges	Low Range: 0 to 2,500 µS/cm Full Range: 0 to 15,000 µS/cm	Low Range: 50 to 30,000 µS/cm High Range: 1,000 to 65,000 µS/cm (readings below these ranges reported as 0)
Temperature Measurement Range	-2° to 36°C (28° to 97°F)	-2° to 36°C (28° to 97°F)
Specific Conductance Accuracy (in Calibrated Range)	Low Range: 3% of reading, or 5 µS/cm, and Full Range: 3% of reading, or 20 µS/cm, whichever is greater, using Conductivity Data Assistant and calibration measurements	3% of reading, or 50 µS/cm, whichever is greater for up to 50,000 µS/cm, using Conductivity Data Assistant and calibration measurements, and up to 10% for up to 65,000 µS/cm in NaCl solutions (see Plot D)
Conductivity Resolution	1 µS/cm	2 µS/cm
Temperature Accuracy (in Calibrated Range)	0.1°C (0.2°F)	
Temperature Resolution	0.01°C (0.02°F)	
Conductivity Drift	Less than 3% sensor drift per year in saltwater, exclusive of drift from fouling	
Response Time	1 second to 90% of change (in water)	
Operating Range	-2° to 36°C (28° to 97°F) - non-freezing	
Memory	18,500 temperature and conductivity measurements when using one conductivity range; 14,400 sets of measurements when using both conductivity ranges (64 KB total memory)	
Sample Rate	1 second to 18 hrs, fixed or multiple-rate sampling with up to 8 user-defined sampling intervals	
Clock Accuracy	±1 minute per month	

Appendix B. Area-velocity flow calculations

January 11th, 2016

Table 4.8a. 01/01/16 flow calculation for site 1

Zone	Distance across stream, (in)	Width, ΔW (in)	Depth, D (in)	Mean velocity, v (ft/sec)	Mean velocity, v(in/sec)	Area, ΔW*D (in^2)	Discharge, inches^3/sec
A	0.0	0.8	0.0	0.0	0.0	0.0	0.0
B	1.5	5.5	6.0	2.5	30.0	33.0	990.0
C	11.0	7.9	6.5	2.5	30.0	51.2	1535.6
D	17.3	6.5	7.0	1.6	19.2	45.5	873.6
E	24.0	3.4	0.0	0.0	0.0	0.0	0.0
						Total Q:	3399.2
							1.96714

Total Q: 3399.2 in^3/sec

1.96714 **cfs**

Table 4.8b. 01/01/16 flow calculation for site 2

Zone	Distance across stream, (in)	Width, ΔW (in)	Width, ΔW (ft)	Depth, D (ft)	Mean velocity, v (ft/sec)	Area, ΔW*D (ft^2)	Discharge, ft^3/sec
A	0.0	14.5	1.2	0.0	0.0	0.0	0.0
B	29.0	26.0	2.2	1.0	1.0	2.1	2.1
C	52.0	24.5	2.0	1.9	1.3	3.9	5.0
D	78.0	33.0	2.8	3.1	1.2	8.4	10.1
E	118.0	36.5	3.0	3.1	1.2	9.5	11.4
F	151.0	28.5	2.4	3.8	0.6	9.0	5.4
G	175.0	22.5	1.9	2.6	0.4	4.8	1.9
H	196.0	27.5	2.3	1.7	0.3	3.9	1.2
I	230.0	17.0	1.4	0.0	0.0	0.0	0.0
						Total Q:	**37.1398**

ft^3/sec

Table 4.8c. 01/01/16 flow calculation for site 3

Zone	Distance across stream, (in)	Width, ΔW (in)	Width, ΔW (ft)	Depth, D (ft)	Mean velocity, v (ft/sec)	Area, ΔW*D (ft^2)	Discharge, ft^3/sec
A	0.0	4.8	0.4	0.0	0.0	0.0	0.0
B	9.6	31.0	2.6	1.8	1.0	4.7	4.7
C	62.0	65.7	5.5	2.2	1.3	12.2	15.9
D	141.0	77.0	6.4	2.0	1.2	13.0	15.6
E	216.0	76.0	6.3	2.1	1.2	13.4	16.0
F	293.0	77.0	6.4	2.1	0.6	13.3	8.0
G	370.0	64.0	5.3	1.9	0.4	9.9	4.0
H	421.0	29.5	2.5	2.7	0.3	6.7	2.0
I	429.0	4.0	0.3	0.0	0.0	0.0	0.0
						Total Q:	**66.20** **ft^3/sec**

Table 4.8d. 01/01/16 flow calculation for site

Zone	Distance across stream, (in)	Width, ΔW (in)	Width, ΔW (ft)	Depth, D (ft)	Mean velocity, v (ft/sec)	Area, ΔW*D (in^2)	Discharge, inches^3/sec
A	0.0	Blockage					
A'	30.0						
B	36.0	33.5	2.8	2.3	1.3	6.4	8.4
C	97.0	69.0	5.8	2.3	2.0	13.4	26.8
D	174.0	53.5	4.5	2.6	1.4	11.6	16.3
D'	204.0	Concrete footing					
E'	252.0						
E	273.0	39.0	3.3	2.5	1.8	8.2	14.7
F	330.0	64.5	5.4	1.9	1.9	10.4	19.7
G	402.0	50.5	4.2	1.8	1.4	7.7	10.8
H	431.0	14.5	1.2	0.0	0.0	0.0	0.0
			27.04			Total Q:	**96.76** **ft^3/sec**

April 1st, 2016

Table 4.8e. 04/01/16 flow calculation for site

Zone	Distance across stream, ft	Width, ft	depth, ft	Mean velocity, ft/sec	Area, ft^2	Discharge, cfs	
0	0	2.5	0.000	0.000	0.000	0.000	
1	5	5	1.042	1.300	5.208	6.771	
2	10	5	1.000	1.000	5.000	5.000	
3	15	5	1.125	0.950	5.625	5.344	
4	20	5	1.083	1.000	5.417	5.417	
5	25	5	1.333	1.300	6.667	8.667	
6	30	3.5	1.417	1.000	4.958	4.958	
7	32	1	0.000	0.000	0.000	0.000	
						36.156	**ft^3/sec**

Table 4.8f. 04/01/16 flow calculation for site 2

Zone	Distance across stream, ft	Width, ft	depth, ft	Mean velocity, ft/sec	Area, ft^2	Discharge, cfs	
0	1	2	0.693	0.600	1.387	0.832	
1	5	3.5	2.683	0.550	9.392	5.165	
2	8	3.5	3.663	0.325	12.822	4.167	
3	12	3	2.123	0.200	6.370	1.274	
4	14	5	1.733	0.150	8.667	1.300	
5	22	4.5	0.693	1.300	3.120	4.056	
6	23	0.5	0.000	0.000	0.000	0.000	
						16.794	**ft^3/sec**

Table 4.8g. 04/01/16 flow calculation for site 3

Zone	Distance across stream, ft	Width, ft	depth, ft	Mean velocity, ft/sec	Area, ft^2	Discharge, cfs	
0	0.417	0.25	0.167	1.000	0.042	0.042	
1	0.917	0.54	0.167	2.000	0.090	0.181	
2	1.500	0.29	0.375	1.600	0.109	0.175	
						0.397	**ft^3/sec**

April 11th 2016

Table 4.8h. 04/11/16 flow calculation for site 4

Location	Width, ft	ΔW, ft	Velocity (V), ft/s	depth to bottom, ft	depth to water, ft	water depth (D), ft	Area, ΔW*D (ft^2)	Discharge, ft^3/sec
	0.0	0.5		Blockage			0.0	0.0
0	1.0	1.5	0.4	10.0	6.7	3.3	5.0	2.0
1	3.0	3.6	0.6	9.0	6.0	3.0	10.5	6.3
2	8.1	5.8	0.7	9.3	6.0	3.3	19.0	13.3
3	14.5	4.5	0.3	9.6	6.0	3.6	15.9	4.8
	17.0			Concrete				
	21.0							
4	22.8	3.3	0.3	8.7	6.0	2.7	8.9	2.7
5	27.5	5.4	0.6	8.9	5.5	3.4	18.5	11.1
6	33.5	4.2	0.4	8.8	6.0	2.8	11.8	4.7
7	35.9	1.2	0.0			0.0	0.0	0.0
							Total Q:	**44.90** **ft^3/sec**

Appendix C. Laboratory Analysis

		Date	Cl	NA	K	Ca	Al	V 51	Cr-1 52	Mn 55	Fe-1 57	Co	Ni	Cu	Zn	As	Cd	Pb	TSS	pH	DO	Sulfate	nitrate
			ppm	ppm			ppb												mg/l		mg'l		
Site1	F	10/23/15	76.80	36.76	5.39	11.94	10.10	0.46	0.25	0.49	57.15	0.11	3.59	1.49	0.74	0.78	0.03	0.03					1.50
	F	11/3/15	91.39	45.79	5.72	14.57	28.17	1.51	0.97	3.87	72.54	0.65	6.05	7.39	3.85	1.59	0.47	0.35				26.41	2.44
	F	12/3/15	86.98	40.73	3.57	11.43	108.80	1.44	0.29	3.61	149.56	0.11	4.25	2.32	2.42	1.40	0.02	0.23	0.71	6.94		28.81	4.43
	W	1/11/16	52.32	26.38	2.48	4.95	235.22	1.57	0.21	54.55	168.77	0.16	2.16	6.03	5.20	0.88	n/d	0.30	2.37			13.83	2.74
	W	2/24/16	81.72	42.66	2.81	10.56	105.32	0.71	0.23	24.55	71.93	0.17	2.32	1.79	3.86	0.66	0.02	0.19	0.51	6.69	10.27	16.41	0.79
	W	3/7/16	75.00	44.46	3.61	10.21	97.96	1.35	0.21	10.27	66.69	0.12	4.03	3.50	4.26	1.06	0.02	0.09				13.40	
	S	4/1/16	72.11	37.77	2.70	8.11	111.95	0.84	0.23	0.95	112.55	0.10	3.25	2.65	3.02	0.98	0.02	0.09		6.58	10.15	10.40	3.37
	S	4/20/16	74.80	41.06	2.78	11.99	92.51	1.17	0.25	10.98	111.30	0.16	4.43	2.67	23.98	1.21	0.03	0.12				9.27	6.20
average			76.39	39.45	3.63	10.47	98.75	1.13	0.33	13.66	101.31	0.20	3.76	3.48	5.92	1.07	0.09	0.18	1.20	6.74	10.21	16.93	3.07
min			52.32	26.38	2.48	4.95	10.10	0.46	0.21	0.49	57.15	0.10	2.16	1.49	0.74	0.66	0.02	0.03	0.51	6.58	10.15	9.27	0.79
max			91.39	45.79	5.72	14.57	235.22	1.57	0.97	54.55	168.77	0.65	6.05	7.39	23.98	1.59	0.47	0.35	2.37	6.94	10.27	28.81	6.20
Site2	F	10/23/16	103.96	46.05	5.92	9.07	5.17	0.57	0.16	91.06	233.92	0.15	5.31	3.43	1.39	1.81	0.02	0.05				6.95	6.31
	F	11/3/16	79.90	42.32	5.97	8.19	8.13	1.80	1.11	29.16	120.61	1.19	5.63	8.22	3.15	2.35	0.94	0.75					1.40
	F	12/3/16	128.88	67.76	4.99	9.39	10.81	1.98	0.08	26.24	139.30	0.06	2.98	4.40	1.15	1.64	0.01	0.11	2.07	6.86		9.14	2.84
	W	1/9/16	127.53	66.42	3.76	8.73	47.98	1.44	0.14	51.94	221.37	n/d	3.24	11.34	1.84	1.38	n/d	0.02				11.98	1.59
	W	1/11/16	113.65	58.56	3.42	8.77	58.24	1.48	0.04	93.32	294.31	0.06	3.18	9.07	4.05	1.32	n/d	0.05	1.76			15.64	1.90
	W	2/24/16	94.62	49.40	2.92	8.87	61.79	0.41	0.14	56.80	115.79	0.17	2.34	2.21	3.04	0.92	0.01	0.10	0.24	6.41	9.79	13.33	1.93
	W	3/5/16	91.80	51.03	3.23	8.19	45.40	1.02	0.15	22.29	117.39	0.11	3.46	3.42	2.76	1.34	0.01	0.09				11.68	1.40
	W	3/7/16	97.12	54.72	3.49	8.26	44.11	1.29	0.14	28.00	138.92	0.12	3.60	3.66	2.60	1.41	0.01	0.08				12.17	
	W	3/8/16	212.01	127.00	5.01	16.11	20.28	2.01	0.12	149.15	199.36	0.47	7.37	12.84	8.59	2.47	0.03	0.10				12.54	2.50
		4/1/16	102.57	57.66	3.40	8.91	49.58	0.90	2.52	19.69	223.96	0.16	5.14	5.40	73.88	1.31	0.02	0.10		6.69	9.55	7.31	
		4/20/16	118.70	64.33	3.69	12.03	41.90	1.24	0.14	61.54	196.16	0.17	4.47	3.83	19.59	1.71	0.01	0.12				11.10	3.83
average			115.52	62.30	4.16	9.68	35.76	1.29	0.43	57.20	181.92	0.27	4.25	6.16	11.10	1.60	0.12	0.14	1.35	6.65	9.67	11.18	2.63
min			79.90	42.32	2.92	8.19	5.17	0.41	0.04	19.69	115.79	0.06	2.34	2.21	1.15	0.92	0.01	0.02	0.24	6.41	9.55	6.95	1.40
max			212.01	127.00	5.97	16.11	61.79	2.01	2.52	149.15	294.31	1.19	7.37	12.84	73.88	2.47	0.94	0.75	2.07	6.86	9.79	15.64	6.31
Site3	F	10/23/16	422.00	251.64	9.36	27.97	7.95	1.54	0.36	524.83	277.29	0.86	13.48	15.68	60.83	3.71	0.23	0.15				19.23	4.32
	F	11/3/16	259.90	144.78	7.91	18.91	13.83	1.65	0.25	403.63	397.12	0.97	10.44	21.56	10.09	3.19	0.04	0.13				20.34	1.46
	F	12/3/16	190.70	89.40	5.05	12.79	22.16	2.65	0.18	110.66	216.75	0.34	4.69	4.53	9.21	2.18	0.11	0.19	1.68	6.67		18.09	2.62
	W	1/8/16	254.14	136.48	5.19	17.77	25.16	1.69	n/d	219.80	256.51	0.59	6.11	7.57	8.80	2.18	n/d	0.10					4.26
	W	1/11/16	120.02	63.06	3.20	7.26	80.16	1.67	0.15	147.34	274.08	0.46	3.30	11.29	9.75	1.34	n/d	0.35	6.60			13.12	3.07
	W	2/24/16	259.80	151.77	3.61	13.36	39.10	0.64	0.18	107.64	117.91	0.44	4.19	5.43	10.12	1.57	0.07	0.14	2.76	6.51	9.75	16.53	1.85
	W	3/5/16	174.07	104.38	4.26	13.02	27.30	1.63	0.13	80.65	128.94	0.33	5.95	7.10	5.86	1.96	0.03	0.10				14.62	2.85
	W	3/7/16	250.65	146.26	6.07	18.80	26.00	1.95	0.13	103.01	147.15	0.40	6.57	7.90	6.17	2.15	0.03	0.09				23.31	
	S	4/1/16	218.66	123.46	4.93	16.37	21.07	1.16	0.13	109.22	275.11	0.35	5.52	16.47	4.77	2.06	0.02	0.14		6.53	7.99	12.36	
	S	4/20/16	208.90	116.09	4.57	20.02	23.28	2.07	0.14	153.18	277.86	0.52	7.61	8.23	20.51	2.47	0.02	0.14				11.30	4.11
duplicate 3	S	4/20/16	206.11	111.22	4.31	18.20	22.15	2.39	0.15	154.49	279.48	0.53	8.02	9.82	21.13	2.66	0.03	0.13				15.16	4.00
average			233.18	130.78	5.31	16.77	28.01	1.73	0.18	192.22	240.74	0.53	6.90	10.51	15.20	2.32	0.06	0.15	3.68	6.57	8.87	16.40	3.17
min			120.02	63.06	3.20	7.26	7.95	0.64	0.13	80.65	117.91	0.33	3.30	4.53	4.77	1.34	0.02	0.09	1.68	6.51	7.99	11.30	1.46
max			422.00	251.64	9.36	27.97	80.16	2.65	0.36	524.83	397.12	0.97	13.48	21.56	60.83	3.71	0.23	0.35	6.60	6.67	9.75	23.31	4.32
Site4	F	10/23/16	417.84	229.12	9.31	30.86	1.07	2.81	0.16	27.78	17.38	0.33	27.65	39.05	9.34	5.67	0.05	0.04				17.81	3.82
	F	11/3/16	257.16	145.72	8.26	4.52	9.33	1.58	0.20	262.91	466.81	0.51	10.34	26.75	10.44	3.04	0.02	0.70				16.66	1.35
	F	12/3/16	184.08	104.39	5.17	13.67	16.94	2.90	0.23	150.41	321.20	0.32	5.01	7.10	9.29	2.41	0.02	0.29	2.78	6.60		14.33	2.26
	W	1/8/16	279.50	151.36	5.73	17.83	13.84	2.22	n/d	287.01	424.24	0.65	6.71	15.88	8.82	2.45	n/d	0.10					2.47
	W	1/11/16	138.38	73.31	3.27	7.52	59.89	1.83	0.09	183.36	303.95	0.50	3.45	12.56	7.93	1.49	n/d	0.29	8.28			11.20	2.46
	W	2/24/16	278.47	161.58	3.92	15.26	32.78	0.78	0.17	170.40	128.37	0.59	4.75	6.14	11.25	1.84	0.05	0.20	2.90	6.60	9.93	15.42	1.40
	W	3/5/16	201.30	119.18	5.00	14.48	25.57	1.84	0.13	123.81	185.62	0.42	6.65	10.28	7.17	2.25	0.03	0.11				14.11	2.59
	W	3/7/16	205.82	123.98	4.76	15.95	22.45	2.08	0.12	151.67	232.81	0.56	7.12	11.51	7.23	2.47	0.02	0.11				15.76	
	W	3/16/16		112.44	4.48	13.26	39.03	1.86	0.24	60.50	256.86	0.27	6.31	11.67	9.32	2.25	0.03	0.16					
	S	3/20/16	203.17	101.70	3.80	11.74	33.50	1.60	0.19	178.50	462.80	0.60	7.78	26.90	10.30	2.70	0.04	0.16				13.77	1.83
	S	3/22/16		182.76	9.21	16.06	31.40	2.10	0.20	200.30	435.60	0.65	7.70	35.30	10.50	3.20	0.04	0.16					
	S	4/1/16	260.67	147.84	5.78	19.88	26.47	1.21	0.15	77.19	199.27	0.27	5.12	16.42	4.72	1.83	0.02	0.15		6.56	7.94	16.79	
	S	4/11/16	200.09	164.83	5.63	21.96	34.05	2.63	0.19	90.33	271.29	0.30	7.25	13.41	24.81	2.69	0.02	0.15					
	S	4/17/16					13.72	2.69	0.15	15.21	205.60	0.11	8.23	13.12	25.28	3.05	0.07	0.11					
	S	4/20/16	323.80	183.08	6.55	28.20	16.54	2.75	0.15	191.37	411.23	0.55	8.45	14.28	18.53	3.15	0.03	0.20				19.73	5.11
average			245.86	142.95	5.78	16.51	25.10	2.06	0.17	144.72	288.20	0.44	8.17	17.36	11.66	2.70	0.03	0.20	4.65	6.59	8.94	15.56	2.59
min			138.38	73.31	3.27	4.52	1.07	0.78	0.09	15.21	17.38	0.11	3.45	6.14	4.72	1.49	0.02	0.04	2.78	6.56	7.94	11.20	1.35
max			417.84	229.12	9.31	30.86	59.89	2.90	0.24	287.01	466.81	0.65	27.65	39.05	25.28	5.67	0.07	0.70	8.28	6.60	9.93	19.73	5.11
			`																				
average			167.74	93.87	4.72	13.36	46.91	1.55	0.28	101.95	203.04	0.36	5.77	9.38	10.97	1.92	0.08	0.17	2.72	6.64	9.42	15.02	2.86
min			52.32	26.38	2.48	4.52	1.07	0.41	0.04	0.49	17.38	0.06	2.16	1.49	0.74	0.66	0.01	0.02	0.24	6.41	7.94	6.95	0.79
max			422.00	251.64	9.36	30.86	235.22	2.90	2.52	524.83	466.81	1.19	27.65	39.05	73.88	5.67	0.94	0.75	8.28	6.94	10.27	28.81	6.31

Appendix D. Pollutant loads calculations

	mean conc.	d, cft/sec	f	L, gram/day
	site 1			
Cl	76.4	0.7	244.68	13083.6
Na	39.4	0.7	244.68	6756.6
K	3.6	0.7	244.68	622.2
V	1.1	0.7	244.68	0.2
Ni	3.8	0.7	244.68	0.6
As	1.1	0.7	244.68	0.2

	mean conc.	d, cft/sec	f	L, gram/day
	site 2			
Cl	115.5	17.7	244.68	500299.7
Na	62.3	17.7	244.68	269790.6
K	4.2	17.7	244.68	18030.1
V	1.3	17.7	244.68	5.6
Ni	4.2	17.7	244.68	18.4
As	1.6	17.7	244.68	7.0

	mean conc.	d, cft/sec	f	L, gram/day
	site 3			
Cl	233.2	27.80	244.68	1586095.4
Na	130.8	27.80	244.68	889546.4
K	5.3	27.80	244.68	36143.3
V	1.7	27.80	244.68	11.8
Ni	6.9	27.80	244.68	46.9
As	2.3	27.80	244.68	15.8

	mean conc.	d, cft/sec	f	L, gram/day
	Site 4b			
Cl	245.9	49.50	244.68	2977729.3
Na	142.9	49.50	244.68	1731346.2
K	5.8	49.50	244.68	69959.5
V	2.1	49.50	244.68	24.9
Ni	8.2	49.50	244.68	98.9
As	2.7	49.50	244.68	32.7