

**The Effect of Chloride Ion on Heavy Metal Partitioning and
Transport in an Urban Watershed:
Patroon Creek, Albany, NY**

Abstract of

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Charles J. Begeal
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Abstract

Road deicing salt use in the United States has increased over an order of magnitude in the last 60 years with urbanization and a need to keep roads safe during winter months. This increase has caused an overall increase in the base concentration of Cl⁻ in streams near roads that receive deicing salts. Many streams in the Northeast United States are in watersheds where road deicing salt is used, and where extensive industrialization has led to the pollution of soils, sediments, and surface waters by heavy metals. This study addresses the effect that dissolved chloride has on fluvial transport and partitioning of heavy metals between the dissolved and suspended phases in one urban watershed. The study area consists of the Patroon Creek Watershed, which drains an area of 37 km² within the City of Albany, and Town of Colonie, NY. Patroon Creek flows 11 km from the Albany Pine Bush through progressively more urbanized areas into the Hudson River. Over a period of one and a half years, monthly samples were taken for both major ion and total heavy metal analysis, and an autosampler at the USGS stream gage was used to sample storm events. Chloride was found to have no significant effect on total heavy metal concentrations in the watershed; however total heavy metal concentrations and suspended particulate matter shows a strong positive correlation. Increasing chloride concentration does show some effect on the partitioning of chloride complex forming heavy metals toward the dissolved phase. This implies that heavy metals are entering the stream adsorbed to suspended particulates. Once in the stream chloride causes partial desorption from particulate surfaces into the dissolved phase where they form chloride complexes and may become more bioavailable to aquatic organisms.

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1. Introduction

Over the last two centuries industrialization has led to the introduction of many contaminants into urban ecosystems. These contaminants have adverse effects on the environment when alone and may interact with one another to more negatively impact urban aquatic environments. Two common types of water contaminants found in urban areas in temperate climates are Cl^- and heavy metals (Cd, Cu, Pb, Zn, etc.) derived from both point and non-point sources. The majority of chloride in urban streams is a result of road deicing salt usage during winter months. Chloride also enters streams through leaching of contaminated soils and sediments by storm runoff and groundwater.

Heavy metals have been introduced into urban ecosystems mostly due to industrial waste, atmospheric deposition, and to a lesser extent corrosion of metals in buildings and automobiles. Leaching of contaminated soils and surface runoff, release these metals into the surrounding aquatic environments. Several studies have posed the question of how chloride and heavy metals interact with one another in road side environments and urban streams, and the potential effect of their interaction (Backstrom et al., 2004, Warren & Zimmerman, 1994, Norrstrom & Jacks, 1998, Gosz, 1977, Amrhein et al., 1992).

1.1 Use of Road De-icing Salts

Over the last 60 years the use of NaCl as a road de-icing salt has increased by more than an order of magnitude leading to various effects from both sodium and chloride (Jackson & Jobbagy, 2005). This increase has been in response to an increase in road surface area following an increase in urbanization during the mid-twentieth century, and the need to keep roads safe during winter months. In the United States in particular, salt sales for highway use have increased from 140,000 mega-grams (Mg) to over 18 million

Mg since the 1940s (Jackson & Jobbagy, 2005; Fig. 1). Four major deicing salts used are NaCl, CaCl₂, MgCl₂, and KCl, with NaCl dominating. Other de-icers include Calcium Magnesium Acetate (CMA) and other acetate compounds, and agricultural bi-products. The preferential use of NaCl as a de-icer is due to its low price and its effectiveness (Jackson & Jobbagy, 2005). Once in the environment rock salt (NaCl) dissolves congruently to Na⁺ and Cl⁻ by the following equation:



1.2 Environmental Impacts of De-Icing Salts

Sodium chloride affects the chemistry of surface water, groundwater, soils, and sediments. The effects of chloride ion and sodium ion may be considered separately.

1.2.1 Chloride Effects

Chloride levels in surface waters of the Northeastern United States have been steadily increasing due to road salt use over the last 40 years (Kaushal *et al.*, 2005). Chloride concentrations in the Mohawk River and Wappinger Creek within the Hudson River Watershed of New York now range between 30 and 50 mg/L, up from a concentration between 10 and 20 mg/L throughout the 1980's (Kaushal *et al.*, 2005). In the Gwynn's Falls Watershed of Baltimore, Maryland, streams in rural areas with low percentages of impervious surfaces have chloride concentrations ranging between 20 and 50 mg/L (Kaushal *et al.*, 2005). Godwin *et al.* (2003) showed that mean chloride levels from 1990 to 1998 were greater than three times those from 1952-1953 in the Mohawk River. They also showed that from 1990 to 1998, chloride levels increased at a daily rate of approximately 0.0027 mg/L likely due to road salt application.

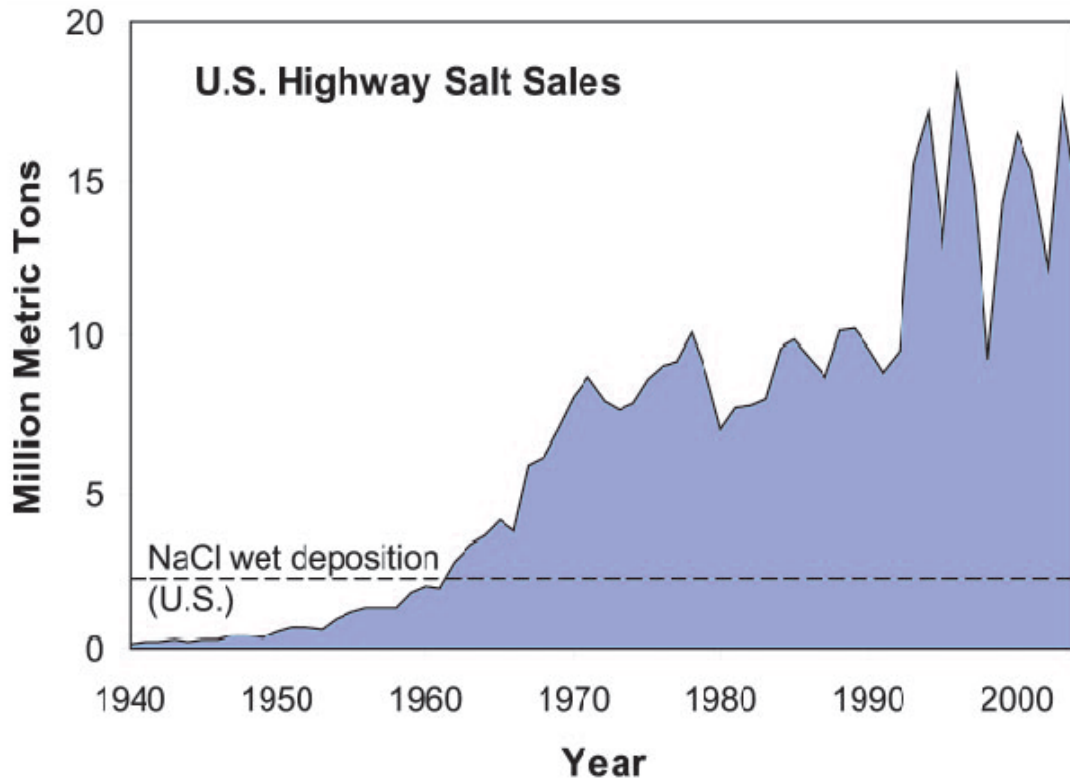


Figure 1. Sales of rock salt for highway use in the U.S. from 1940 to 2004 in millions of metric tons (Mg). The dashed line denotes estimate of the calculated annual wet deposition of Na and Cl in the U.S., derived primarily from sea salt. The amount of Na and Cl in road salt topped Na and Cl deposition for the continental U.S. some time in the early 1960s. Estimated U.S. wet deposition of NaCl is based on data from 1999-2003 using deposition isopleth maps from Illinois State Water Survey, NADP Office (2005). The product of the mean area and deposition rates for each isopleth interval was calculated by state and summed. For Na and Cl, rates of dry deposition should be smaller than rates of wet deposition. (From Jackson and Jabbogy, 2005).

Salt storage has been shown to occur in lakes due to increased sodium chloride from the use of deicing salts (Cherkauer & Ostenso, 1976). This storage of salts in lakes leads to an increase in chloride concentration in lakes' outflow year-round. This effect on downstream chloride concentrations due to the impoundment of salt contaminated water has also been noted down stream of a dam reservoir on the Don River in Toronto (Scott, 1979).

Along with an increase of chloride in surface waters, groundwater has also been shown to have increasing chloride levels (Williams et al., 1999; Foos, 2003, and Howard & Haynes, 1993). Chloride levels ranging from 116 to 1834 mg/L have been observed in springs near Cuyahoga Falls, Ohio with the highest levels in springs nearest to areas with high percentages of road surfaces (Foos, 2003). Spring chloride levels in Toronto, Canada springs positively correlate with levels of urbanization and have far greater seasonal stability than surface waters with highest chloride levels in January and February (Williams et al., 1999). Baseflow levels, mostly from groundwater recharge in streams near Toronto, Ontario, Canada showed an increase in chloride from 1988-1991 from 486 tons to 1318 tons (Howard & Haynes, 1993).

Increased levels of chloride in surface waters have adverse affects on land plants, fish, and aquatic macroinvertebrates. Above 250 mg/L Cl^- many freshwater species experience chronic toxicity (Jackson & Jobbagy, 2005). At 4500 mg/L *Physa* sp. (Pouch Snail), and *Crangonyx* sp. (an Amphipoda), tolerant species, became stressed, and non-tolerant species, *Gammarus pseudolimnaeus* (Freshwater shrimp), showed decreases in biological activity (Williams et al., 1999). Northern Monkshood have shown adverse affects with increased chloride from road salting (Smith, 1999). Sugar maples have

shown damage such as scarring due to increased road salting (NRC, 1991). A secondary drinking water standard for taste is capped for levels of chloride higher than >250 mg/L (Jackson & Jobbagy, 2005; NYSDOH, 2007).

1.2.2 Sodium Effects

Na^+ from road salt interacts with soils through cation exchange. Cation exchange capacity (CEC) is a measure of a soil's ability to hold cations by electrical attraction. It is measured by the total of exchangeable Ca^{2+} , Mg^{2+} , Na^+ , and K^+ in $\text{cmol}(+)/\text{kg}$. Cation exchange between aqueous NaCl solutions and clay minerals in soils leads to a decrease in the Na:Cl ratio and an increase in the concentration of base cations in aqueous solution, particularly Ca (Fabricius & Olofsson, 1996; Shanley, 1994, Norrstrom & Bergstedt, 2001).

Exchangeable sodium percentage (ESP) represents the percentage of the cation exchange capacity occupied by sodium ions:

$$ESP = \left\{ \frac{[\text{Na}^+]}{CEC} \right\} \times 100 \quad (2)$$

Where $[\text{Na}^+]$ is the concentration of sodium in cmol/kg and CEC is the cation exchange capacity. Sodic soils, in which colloid dispersion problems are high, have ESP values of 6-14, and strongly sodic soils have an ESP of 15 or greater. The sodium absorption ratio (SAR) of soil solutions is used to characterize salt-affected soils, and takes into account the moderation of sodium by calcium and magnesium. SAR is calculated by the following equation:

$$SAR = \frac{[\text{Na}^+]}{\sqrt{2([\text{Ca}^{2+}] + [\text{Mg}^{2+}])}} \quad (3)$$

Where $[\text{Na}^+]$, $[\text{Ca}^{2+}]$, and $[\text{Mg}^{2+}]$ are the concentrations of sodium, calcium, and magnesium in mmol/L, respectively. A major use of SAR is in understanding the permeability of soils for agriculture, as a high SAR corresponds with low permeability. Increased aqueous sodium concentrations resulting from deicing salt application may promote colloid mobility leading to the destruction of soil aggregate, and lowered hydraulic conductivity (Amrhein et al., 1992; Norrstrom & Jacks, 1998; Norrstrom & Bergstedt, 2001). Salt conditions that lead to colloid dispersion occur naturally in arid to semi-arid regions, but due to increased road salt use in humid areas such as Northern and Western Europe, and the Northeastern United States, ESP values greater than 15 and SARs from 0 to 3 may be achieved which are levels sufficient for colloid dispersion (Norrstrom & Bergstedt, 2001).

1.3 Surface Runoff Transport of Heavy Metals

Much of the heavy metal concentration released by runoff occurs during the first flush. This is defined as a large percentage of pollutant load in runoff during the initial stages of a storm event (Lee et al., 2002). They determined that its occurrence is based on the type of pollutant, catchment area, impervious surface area, and the intensity of a storm. Bertrad-Krajewski et al.(1998) define the first flush as when at least 80 percent of the pollutant mass is transported in the first 30 percent of storm volume. The most important parameters for this large influx of heavy metals during a rain storm event are the preceding dry period, rainfall duration and maximum intensity, and the maximum inflow (Gupta & Saul, 1996). In regards to heavy metal transport in a stream, it has been observed that the dissolved phase of Zn, Cd and Cu, exhibit a stronger first flush behavior, than the particulate phase (Sansalone & Buchberger, 1997; Sansalone & Glenn,

2000; Soller et al., 2003). This is likely due to dissolved metals being more easily eroded from impervious surfaces, i.e. parking lots and roads, and transported through surface water (Soller et al., 2003).

1.3 Effects of De-icing Salts on Heavy Metal Geochemistry

NaCl deicing salt can potentially affect the transport and speciation of heavy metals (e.g. Cd, Cu, Pb, Zn) in surface waters through several physico-chemical processes, including dispersion of metal-bearing colloidal particles, desorption and partitioning into the dissolved phase, and increase aqueous solubility through the formation of aqueous chloro-complexes (Amrhein et al., 1992, Warren and Zimmerman, 1994, Backstrom et al., 2004).

Transport of trace metals adsorbed to colloidal particles and suspended particulate matter is influenced by the effects of Na^+ on soils and sediments through the process of dispersion. Zn, Cu, Cd and Pb enter surface waters mostly adsorbed to suspended particulate matter (Gosz, 1977). This is due to the strong affinity of trace metals for clays, particulate organic matter and Fe-oxides, whose mobilization occurs when adsorbed interlayer Na is high (Amrhein & Strong, 1990; Amrhein et al., 1993; Norrstrom & Jacks, 1998). Trace metal-bearing colloidal particles are released directly to surface waters or to groundwater that may eventually recharge surface waters (Amrhein et al., 1993; Amrhein et al., 1992; Norrstrom & Jacks, 1998).

There are two types of surface complexes made between metals and particle surfaces. The first are outer-sphere complexes in which there is a water molecule between the metal and the particle surface. These complexes tend to be weak and easily broken by increases in ionic strength, and are formed by alkali, and alkaline earth metals.

Inner-sphere complexes characterize the second type of bonding between metals and particle surfaces. In these complexes there is no water molecule between the metal and the bonding surface, so the metal is bonded directly to anions on the mineral surface. Transition metals form this type of complex. These bonds are not easily broken by increases in ionic strength and require that pH be decreased below the point of zero charge (pzc). The pzc is the pH in which the mineral surface has a neutral charge (Sparks, 2003). Thus with decreases in pH, heavy metals are released into the dissolved phase from their surface complexes.

Desorption of Cu, Cd, Zn and Pb into the dissolved phase has been shown to occur with increased chloride concentration in both stream and estuarine waters (Valenta et al., 1986; Gowlimowski et al., 1990; Warren & Zimmerman, 1994; Thouvenin et al., 1997). The extent of sorption is measured by the distribution coefficient (K_d).

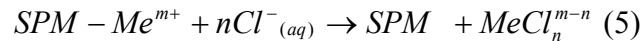
$$K_d = \frac{c_p}{c_s} \quad (4)$$

Where c_p is the concentration of trace metal in the particulate phase and c_s is the concentration of trace metal in solution, or dissolved phase.

Chloride-induced desorption is seen in decreased partition coefficients of trace metals, Cd in particular, in sediments toward the sea (Valenta et al., 1986; Gowlimowski et al., 1990).

Metal chloride complexation is a mechanism by which desorption and subsequent partitioning of trace metals into the dissolved phase may change in surface waters (Backstrom et al., 2004; Doner, 1978; Backstrom et al., 2003). This may be initiated by chloride-induced desorption of trace metals (Warren & Zimmerman, 1994).

This interaction is characterized by the reaction



where $SPM-Me^{m+}$ is a particulate with a metal cation adsorbed to its surface, and $Cl^{-}_{(aq)}$ is chloride in solution. Chlorocomplexes have been observed to be particularly strong for Cd, Hg, Pb and Zn (Hahne and Krootje, 1973). Equilibrium constants (K_{eq}) are given in Table 1. From Table 1 it can be seen by positive $\log K_{eq}$ values that at 25°C Cd, Cu, Pb and Zn will favor complexation over remaining as a dissolved free cation when in the presence of chloride. Speciation modeling using PHREEQ-C-2, where metal organic complexes and high ionic strength from NaCl were considered, has shown that at chloride concentrations ranging from 41 to 779 mg/L, Cd, Pb, and Zn increased in dissolved concentrations, as well as chloride complexation (Backstrom et al., 2004). What was observed is that as the chloride concentration increased, complexation with the given metals was more likely to occur. This increase in percentage of metal in chloride complexes presumably occurs in winter months when deicing salt use is most prevalent (Backstrom et al., 2003).

Table 1. List of Equilibrium Constants (K_{eq}) for Chloride Complexation Reactions. Data from Drever, 1997.

Chloride-complex Reaction	Log K_{eq} at 25°C
$Cd^{2+} + Cl^{-} = CdCl^{+}$	1.98
$Cu^{2+} + Cl^{-} = CuCl^{+}$	0.43
$Cu^{2+} + 2Cl^{-} = CuCl_2$	0.16
$Pb^{2+} + Cl^{-} = PbCl^{+}$	1.60
$Pb^{2+} + 2Cl^{-} = PbCl_2$	1.80
$Zn^{2+} + Cl^{-} = ZnCl^{+}$	0.43

1.4 Study Objectives

The goal of this study is to examine the effects of NaCl road deicing salts on heavy metal speciation and transport in urban surface water at the watershed scale. This differs from bench-top studies in which experiments are done in the laboratory, or roadside studies that observe the effects of NaCl moving through the soil at given depths and distances from the road. Unlike these studies, this study examines many locations along the stream and its tributaries in an attempt to characterize the transport of NaCl and its effect on heavy metals throughout the watershed due to the use of deicing salts. This study addresses the relation between chloride concentration and total heavy metal concentration, as well as the relation between chloride concentration and the partitioning of heavy metals between the dissolved and particulate phases. Temporal and spatial variations of heavy metals within Patroon Creek are examined in order to understand distribution and potential point and non-point sources of the heavy metals. The main objectives are to answer the following questions:

1. How are metals distributed among dissolved, particulate, and colloidal phases in Patroon Creek?
2. What is the effect of chloride on the partitioning of heavy metals between the particulate and dissolved phase?
3. What is the effect of road salt on the aqueous transport of heavy metals?

2. Study Area

2.1 Site Description

2.1.1 Watershed Characteristics

The Patroon Creek Watershed (37 km²) includes portions of the city of Albany and the towns of Colonie and Guilderland, New York, and is drained by Patroon Creek. Patroon Creek flows in a generally WNW to ESE direction for 11 km, from the Pine Bush Natural Area, at an elevation of 91 m, to the Hudson River in downtown Albany, at sea level (0m; Figure 2). For most of its length the creek is immediately adjacent to Interstate 90 and Amtrak/Conrail railroad tracks. Patroon Creek drains a watershed that is dominated by urban and suburban land use.

Two major tributaries contribute to Patroon Creek, an unnamed tributary noted as the “North Branch” in this paper and Sand Creek, both of which drain from the WNW direction (Figure 2). The North Branch of Patroon Creek drains an area dominated by industrial and commercial land use, with few natural areas. Sand Creek drains a mostly residential area with some natural areas.

There are also two reservoirs along the creek. Six Mile Reservoir, or Rensselaer Lake, is located 9.6 km (6 miles) upstream from the mouth near the head waters. Three Mile Reservoir, or the Patroon Reservoir, is located 4.8 km (3 miles) upstream from the mouth adjacent to the westbound lanes of Interstate 90, between exits 5 and 4 (Figure 2).

The creek bed is composed mainly of fine silt to sand, with little rocky material or vegetation. The banks of Patroon Creeks are mostly steep from erosion. Approximately one-third of the creek’s length has been moved from its natural position into man-made

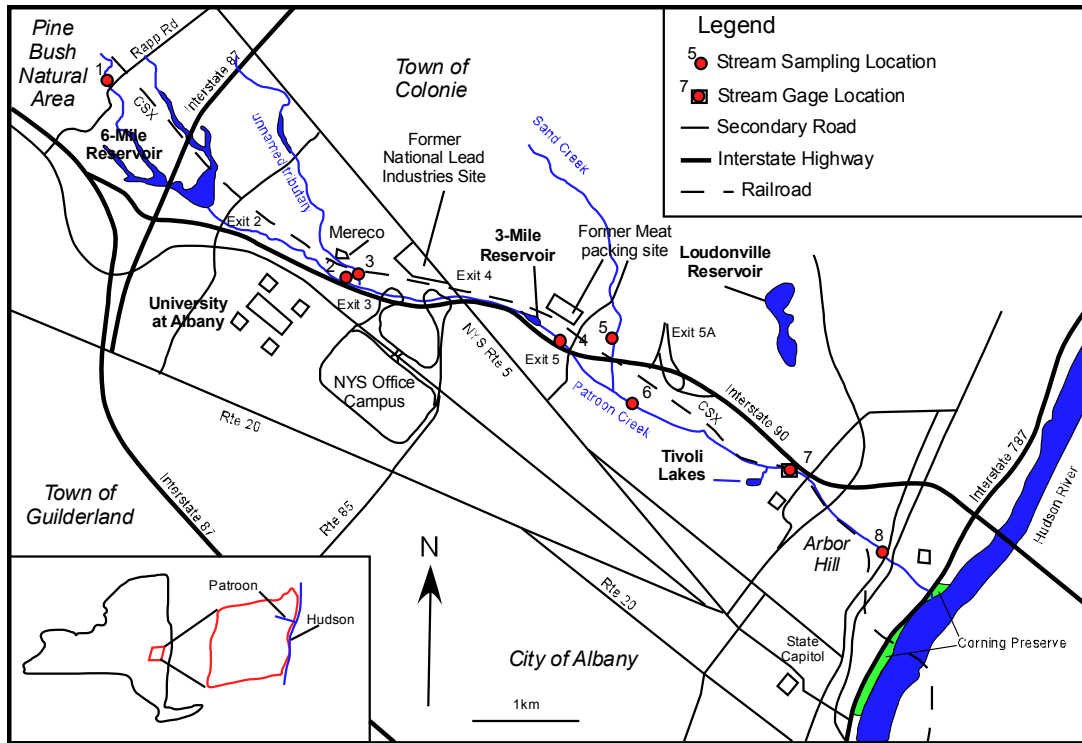


Figure 2. Map of Patroon Creek, Albany, NY. Site Code 1, 2, 3, 4, 5, 6, 7, & 8 represent Rapp Rd., Main Branch, North Branch, Tobin Plant, Sand Creek, Cement Plant, Gage, and Erie Blvd, respectively.

channels and underground culverts during the construction of I-90; some of which were being altered during the course of this study.

2.1.2 Geology and Soils

The underlying bedrock consists of Ordovician shale from the Schenectady Formation. Three types of glacial sediments, Wisconsinian in age, make up the surficial geology of the watershed. Dunes of wind-reworked lake sediments, and well-sorted, stratified, non-calcareous fine to medium sands occur around the headwaters in the Pine Bush Natural Area. These are well drained, permeable deposits of varying thickness, from 1-10 m (Cadwell et al., 1986). The stream then cuts through underlying lacustrine clays and silts, that are mostly calcareous and vary in thickness, upwards of 100 m and lacustrine sand deposits of near-shore origin from Glacial Lake Albany, that are well sorted, stratified, generally quartz sand, and vary in thickness from 2-20 m. At the mouth of the creek, it cuts through Ordovician bedrock and recent Hudson River flood plain deposits (Cadwell et al., 1986).

Much of the soil around Patroon Creek is classified as Man-made fill, which are nearly level to steep sloping areas where impervious surfaces cover greater than 85% of the land (USEPA, 2003). This includes areas of miscellaneous fill, with few areas that have retained natural soil characteristics after disturbance.

2.1.3 Hydrology

The USGS stream gage near Tivoli St. in downtown Albany is located at 42 40'17"N, 73 43'22" W. A gage has been present at this site from early 1979 to 1981, and 2002 to the present. Annual Peak Stream Flow is shown in Appendix I. Mean monthly

discharge, temperature, and specific conductivity for the study period are shown in Table 2.

Table 2. Mean Monthly Discharge, Temperature, and Specific Conductivity of Patroon Creek, Albany, NY at the USGS Stream Gage (Site 7) during the study period.

Month	Mean Monthly discharge (m ³ /s)	Mean Monthly Temperature (°C)	Mean Monthly specific Conductance (µS/cm @ 25°C)
10/2004	0.664	13.07	881.55
11/2004	0.798	7.81	947.72
12/2004	0.891	3.96	1017.30
01/2005	0.919	2.29	1282.97
02/2005	0.692	2.69	1348.80
03/2005	0.944	3.76	1497.59
04/2005	0.968	10.44	1166.95
05/2005	0.789	13.56	1055.95
06/2005	0.694	19.63	1194.92
07/2005	0.981	21.41	891.18
08/2005	0.580	21.47	1080.35
09/2005	0.526	19.48	1010.12
10/2005	1.313	13.24	881.55
11/2005	0.985	8.44	1032.84
12/2005	0.785	3.92	1471.01
01/2006	1.061	4.08	1506.75
02/2006	0.898	4.15	1246.70
03/2006	0.52		

2.1.4 Land Use History

Patroon Creek is one of only two remaining above-ground creeks in the City of Albany. It had been used by sawmills from as early as the 1600's and was one of the city's public drinking water sources up until 1920. Since the late 1800's, underground culverts have made up approximately 30% of the stream's length. The stream was straightened and channelized significantly for the construction of Interstate 90 in the mid 1960's, and now flows between Amtrak/Conrail tracks and I-90 for much of its course.

The stream flows through three natural preserves. The Albany Pine Bush Preserve is a 300 hectare protected area including 223 hectares of pine barrens surrounding Six Mile Reservoir. Tivoli Preserve is 33 hectares of wetlands, ponds, forests and fields, and

serves as a habitat to over 50 species of birds. At its mouth, Patroon Creek flows through the Corning Preserve, 200 hectares of bike paths, picnic areas, walking trails, and boat launches, where it flows into the Hudson River.

Impermeable surfaces make up 32-38% of Patroon Creek Watershed’s surface area (Audette, 2004). These surfaces include highways, streets, building rooftops and parking lots. These and other land uses and their percentages of the watershed are presented in Table 3.

Table 3. Percentage of different types of impervious surfaces within the 37 km² Patroon Creek Watershed. Ranges are given in some cases because of uncertainty (data from Audette, 2004)

Categories	Area km ²	% of Watershed
Parking Lots	4.09	11
Highways/Interstates	0.87	2
Two and Four Lane Roads	2.60	7
Rooftops	3.89-6.11	13-19
Total Impervious Surfaces	11.45-13.67	32-38

2.2 Heavy Metal Contamination in the Patroon Creek Watershed

Patroon Creek has pollution typical of an urban stream. It has been contaminated since the late nineteenth century by urban runoff, surficial erosion, heavy metals and other chemicals from industry, sewage and illegal dumping. Stream sediments are contaminated with heavy metals including mercury, lead, cadmium, and depleted uranium (Arnason and Fletcher, 2003; 2004). Based on benthic micro invertebrate indices, Patroon Creek has been classified as moderately to severely impacted (Audette, 2004, Bode et al., 1993). Sewage leakages from known and unknown sources have led to contamination by coliform bacteria. By New York State Department of Environmental

Conservation fresh surface water classification, Patroon Creek is listed as a Class C water body (NYSDEC, 2006). This means that the stream may be used for fishing, but not as a drinking source or for swimming. Based on these factors, the creek is also listed as one of the ten most impacted streams in New York (Bode et al., 1993, NYDEC, 2004).

Two well-documented point sources of heavy metal contamination lie within the Patroon Creek Watershed. The Mercury Refining Inc (Mereco) site is on the EPA National Priorities List (Figure 2). Mereco is responsible for mercury contamination of 3-Mile reservoir sediment downstream from the site (Arnason and Fletcher, 2003; CDM, 2003). This site is located on 0.26 ha adjacent to the North Branch of Patroon Creek, and served as a storage and processing site for Hg-bearing wastes since 1955 (Arnason and Fletcher, 2003).

The National Lead Industries (NLI) site is located approximately 1 km upstream of Three Mile Reservoir (Figure 2). This is a FUSRAP (Formerly Utilized Sites Remedial Action Plan) site. NLI is responsible for lead, cadmium, and depleted uranium in creek sediments, and uranium release to the atmosphere from 1958 to 1984 (Arnason and Fletcher, 2003).

In addition to these point sources, other poorly documented sites exist. The closed Tobin First Prize Meat packing plant, the former West Albany Railroad Shops, and an operating cement storage area, all lie within the Patroon Creek Watershed. The creek also flows through Tivoli Preserve near where the State-operated ANSWERS (Albany, NY Solid Waste to Energy Recovery System) incineration plant operated from 1984 to 1994, releasing air pollutants such as ash and other by-products which may have contaminated the surrounding soils

(Times Union, www.timesunion.com/communities/ahej).

There are many sources of non-point pollution within the watershed. Automobile wear from framing and tires, sewage leakage, and possible landfill leachate from the Albany Landfill located near Site 1 (Fig. 2) are just some examples.

3. Study Methods

3.05 Sampling Design

Sampling was set up to allow a comparison of the partitioning of heavy metals during high and low chloride levels, throughout the year on a watershed scale. Many locations within the watershed were sampled in order to understand the effects of chloride on total concentrations of heavy metals throughout the study area. Sampling was conducted at the USGS Stream Gage during storm events to catch chloride contaminated runoff to study the partitioning of metals at this location as a representation of the entire watershed.

3.1 Field Methods

Water samples were measured for major ion concentrations, total heavy metal concentration, and for heavy metal partitioning measurements. Major ion samples were collected biweekly to monthly at seven sites (1-4; 6-8; Fig. 2) from November, 2004 to March, 2006, with an eighth site added (5; Fig. 2) in March, 2005. Total heavy metal samples were collected from December, 2004 to March, 2006 at three sites (1, 3, 7; Fig. 2) with two sites (2, 7; Fig. 2) added in March 2005. The sampling period spanned two winters and one spring, summer, and fall season. Major ion and total heavy metal samples were collected by grab method into D.I.-washed, 250 mL, and acid-washed 125 mL high-density polyethylene bottles, respectively. Samples were stored in a refrigerator in the dark at 4 °C within 3 hours of collection. Heavy metal water samples were acidified with HNO₃ in the laboratory within 3 hours of collection. Specific conductance (µS/cm) and temperature (°C) were measured at each sampling site using a YSI 30 specific conductivity meter. Dissolved oxygen (mg/L) and temperature were also taken

at each site using a YSI 550DO dissolved oxygen meter, calibrated prior to each measurement.

Grab samples for heavy metal partitioning measurements were taken manually during storm events at the USGS Stream Gage Site 01359133 (site 7; Fig. 2) from March, 2005 to October, 2005 with 6 storm events sampled. These samples were collected in 1 L acid-washed, Nalgene high-density polyethylene bottles. Dissolved oxygen, specific conductivity, and temperature measurements were recorded during each sampling event.

From October 25, 2005 to March 13, 2006 samples at the gage were taken using an ISCO (#) automatic water sampler. The auto-sampler took water samples with every 15 cm increase in stream stage height over 0.3 m. 0.3 m of stage height was determined to be representative of base flow conditions in the stream, and a stage above this marked a storm event. After the peak discharge of a storm event, the autosampler would cease sampling when the stage height decreased more than 5 cm from the peak discharge. Samples were stored within the auto-sampler for up to 3 weeks, and then placed in a refrigerator in the dark at 4 °C. Evaporation was assumed to be minimal. Specific conductance, gage height, and temperature readings were recorded from the USGS 01359133 Patroon Creek at Northern Blvd. at Albany, NY website.

<http://waterdata.usgs.gov/ny/nwis/uv?01359133>).

Hourly and daily precipitation amounts and air temperature were collected from the National Oceanic and Atmospheric Administration (NOAA) National Climate Data Center in Ashville, NC for the Albany International Airport (Appendix II).

3.2 Laboratory Methods

3.2.1 Base Ion Water Analysis

Grab samples, and autosampler samples were analyzed for pH with an Orion 420A+ pH meter and for alkalinity by titration with 1.6 N H₂SO₄ to a pH=4.5 endpoint in the laboratory using a Hach Digital Titrator micro burette. Alkalinity is expressed as mg/L as CaCO₃.

For each base ion sample a 20 mL aliquot was passed through a 0.45 μm Millipore filter. Filtered samples were then diluted by adding 0.5 mL of sample to 4.5 mL of 18.3 MΩ deionized water. Diluted samples were then analyzed by Ion Chromatography using a Dionex ICS-90 for base cations (Li, Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺), and a Dionex DX-120 for base anions (F⁻, Cl⁻, NO₃⁻, SO₄²⁻, and PO₄³⁻).

3.2.2 Heavy Metal Water Analysis

Grab samples for total heavy metal concentrations, were acidified to 1% HNO₃, and then stored under refrigeration for up to 3 weeks prior to analysis. 10 mL aliquots were then taken of each sample, and 0.1 mL of an internal drift standard, containing 1ppm Be, Sc, Ga, Y, In, Pr, Re, Bi, and Th, was added to each.

Storm event samples from the autosampler were analyzed for the partitioning of heavy metals between the dissolved and particulate phases. This was done by shaking each sample to form a roughly homogeneous mixture, and then taking a 50 mL aliquot from each sample for bulk heavy metal analysis. Each aliquot was then prepared as for grab samples. The remaining sample was weighed to the nearest tenth of a gram, and filtered through a 0.45 μm Millipore filter into an acid-cleaned 1000 mL flask, using a vacuum pump. The filtered water sample was then weighed, and an aliquot of 50 mL

was acidified to 1% HNO₃. The water sample was then prepared and analyzed for heavy metals as described above. The sediment portion was prepared as described below.

All water samples were analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) using a Perkin Elmer/Sciex Elan 6100 DRC. The samples were analyzed for elemental masses ⁹Be, ¹¹B, ⁵⁹Co, ⁶⁵Cu, ⁶⁶Zn, ⁷¹Ga, ⁷⁵As, ⁸²Se, ⁸⁵Rb, ⁸⁶Sr, ⁸⁹Y, ⁹⁸Mo, ¹¹²Cd, ¹¹⁵In, ¹³³Cs, ¹³⁷Ba, ¹⁴¹Pr, ¹⁸⁴W, ¹⁸⁷Re, ²⁰⁸Pb, ²⁰⁹Bi, and ²³⁸U. Be, Ga, Y, In, Pr, Re, and Bi were internal standard elements. Mass interference corrections were made in Cd and As analyses for Sn and Se, respectively. ²⁷Al, ⁵⁴Fe, and ⁵⁵Mn, with ⁷¹Ga as the internal standard, were analyzed by dynamic reaction cell (DRC). Analysis details are presented in Appendix III.

3.2.3 Heavy Metal Suspended Sediment Analysis

The sediment remaining after filtration of storm event samples was dried, and weighed. Samples from March, 2005 to October, 2005 that contained at least 0.1g of sample excluding the filter paper were digested by low-pressure HF digestion. 0.1 g of each sample was first weighed into a Teflon Savillex 13 mL screw-top beaker. Then 2 mL of HF, 1 mL HNO₃, and 0.1 mL of an internal standard, containing 10 ppb Rh, In, Re, and Bi, were added. Each beaker was capped, clamped into retainers and heated in an oven at 120 °C overnight. Samples were then evaporated to dryness, 3 mL of HF was added, capped and clamped into retainers, and heated at 120 °C overnight. They were again evaporated to dryness, 2 mL of HNO₃ was added, and they were evaporated to dryness a third time. Then 2.1 mL of high-purity HNO₃ and 13 mL of D.I. water were added, and they were clamped into retainers and heated overnight at 80 °C. A 0.5 mL

aliquot of this solution was then transferred into a 13 mL plastic autosampler test tube, 12 mL of D.I. was then added. Samples were then capped and shaken.

Samples from October, 2005 to March, 2006 that contained at least 0.1 g of sample, as well as Sand Creek 03/28/05 and Gage 10/12/05 were digested for leachable trace ions by EPA Method 3050B. Samples were weighed to 0.1 g and transferred to 50 mL polyethylene Digitubes®. 0.5 mL of D.I. water and high-purity HNO₃ were added to each sample. Samples were then placed on a hot block and heated to 95 °C for 10-15 minutes. Samples were then cooled in a water bath. 0.5 mL of high-purity HNO₃ was then added to each sample. Samples were then heated at 95 °C for 30 minutes. These last two steps were repeated once to remove brown fumes. Samples were then heated for 2 hours at 95 °C, then cooled in a water bath. 0.2 mL of D.I. water and 0.3 mL of 30% H₂O₂ were then added to each sample. Samples were then placed on the hot block, covered, and heated until effervescence ceased. 0.7 mL of 30% H₂O₂ was then added to each sample. Samples were then heated for 2 hours at 95 °C, and then cooled in a water bath. All samples were then diluted to 50 mL. 1 mL of each sample and an internal standard containing 10 ppb of Rh, In, Re, and Bi were transferred to individual 13 mL autosampler tubes and diluted to 10 mL.

All samples were then analyzed by ICP-MS. The analysis method for these samples analyzed the following elemental masses, ⁵⁹Co, ⁶⁴Cu, ⁶⁴Zn, ⁷⁵As, ⁸²Se, ⁹⁸Mo, ¹⁰³Rh, ¹¹⁴Cd, ¹¹⁵In, ¹⁸⁴W, ²⁰⁸Pb, ²⁰⁹Bi, and ²³⁸U. Details of the ICP-MS analysis are in Appendix III. Interference corrections made were Ni for Zn, Kr for Se, Ru for Mo, Sn for Cd, and Os for W.

3.3 Factor Analysis

Factor analysis was used to identify covariance in the dataset and organize the multiple variables of the Storm Event samples using the software package SYSTAT[®]. Factor analysis is a statistical process of taking multiple variables and defining them by a small number of independent factors. In factor analysis relationships among variables cannot be pre-assumed (Drever, 2002). All variables are analyzed independently from one another.

3.4 Quality Assurance

Concentrations of base and trace ions were only reported if accurate, precise, and above minimum reporting levels for the analytical method used. To check for accuracy standards were analyzed with known ionic concentrations (Appendix IV). These consisted of a 5 anion standard and a 6 cation standard from the Dionex corporation, and a 5 ion standard created in the laboratory for Ion Chromatography, a trace ion standard for ICP-MS, and San Joaquin soil standard (SRM 2709) for sediment trace ion analysis. Ion Chromatography analyses also contained a sample fortified with standard solutions (LFM) to measure analyte recovery. A sample containing 4.0 mL deionized water, 0.5 mL sample and 0.5 mL 5 ion standard solution was used to determine this recovery by the following equation:

$$\% \text{Recovery} = 100x \frac{[LFM] - [sample]}{[standard]} \quad (6)$$

where [LFM] represents the measured concentration of the ion in the laboratory fortified sample matrix, [sample] represents the concentration of the ion in the unfortified sample, and [standard] is the concentration of the ion in the standard solution (Appendix IV).

The precision of the analytical method was determined by duplicate sample analysis and reported as the percent relative standard deviation (%RSD):

$$\%RSD = 100\left(\frac{\sigma}{x}\right) \quad (7)$$

σ represents the standard deviation of the sample and its duplicate and x represents the mean ionic concentration of the sample and its duplicate (Appendix IV).

Minimum detection limit (MDL) was set as the sum of the mean and 3 standard deviations of the ionic concentrations in 18.3 M Ω -cm deionized water laboratory blanks as reported by all analytical methods. The minimal reportable limit (MRL) was set as the sum of the mean and 10 standard deviations of the ionic concentrations in the analysis blanks (Appendix IV). Samples that were below the MDL were included in analyses as a concentration of half of the minimum detection limit for the given element.

4. Results

4.1 Hydrology

Monthly mean stream discharge data are presented in Appendix x. When comparing discharge data from the study period and the two previous years, it is noted that discharge during the study period, except for August and September, 2005 is higher than previous years. Minimum and maximum discharge for the study period was 0.2492 m³/s between 9/24-9/25/05, and 17.526 m³/s on 6/29/05, respectively. Hydrographs for the study period are shown in Appendix V.

A storm hydrograph for Patroon Creek for November 29-30, 2005 from USGS stream gage data is shown in Figure 3. The initiation of the storm near the end of November 29 is noted by a sharp increase in discharge. After a rapid peak, stream discharge decreases more gradually for the duration of the storm event. Precipitation is also shown in Figure 3. It increases very rapidly at the same time as discharge, but peak discharge occurs approximately 4 hours after peak precipitation. This relationship shows that in urban streams discharge increases very rapidly at the onset of a storm event, due mostly to the high percentage of impervious surfaces.

Patroon Creek has periods containing plateau-like features in its hydrographs. These are most notable in Figure 4A. Two of these discharge plateaus occur from July 21 through 24, and July 28 through 31. These features are indicative of water releases from Six Mile Reservoir, and are noted by a sharp increase in discharge to a plateau that ends hours later as abruptly as it began.

Specific conductance is greatly affected by discharge, with its response differing between summer and winter storm events. Figure 4A shows the typical summer relation

between discharge and conductivity during July 2005. Conductance decreases with increased discharge because of the dilution of baseflow with rain water entering the stream during summer storm events. All increases in discharge also correspond with rain events. These rain events lead to decreased specific conductance while discharge increases. This inverse relation between discharge and specific conductance is further demonstrated in Figure 4B. During periods of reservoir release, specific conductance abruptly decreases to a trough and then abruptly increases hours later.

The relationship of these two variables is more complex during winter storm events (Figure 5 & 6). The effects of road deicing salt use during winter months can be seen in an increase in conductance with increased discharge in both figures. This increased conductance is not always proportional to increases in stream discharge however. For some storm events there is little increase in discharge, but a large increase in conductivity. This is likely due to there being less melt water under the icy conditions in which road salt is applied, so small quantities of water contain a large concentration of NaCl.

The differences between this cause-and-effect relationship during a high snowfall and low snowfall winter are contrasted in Figures 5 and 6. Figure 5 shows this relationship during February 2005, in which higher snowfall conditions and more road salt application can be implied by the increase in conductance during the majority of increased discharge events, and snowfall events, when there is little or no increase in discharge. An example of increased conductance with little change in discharge occurs between February 4 and 7 (Figure 5). Cyclical increasing and decreasing of conductance during this period coincides with increasing and decreasing discharge likely due to the

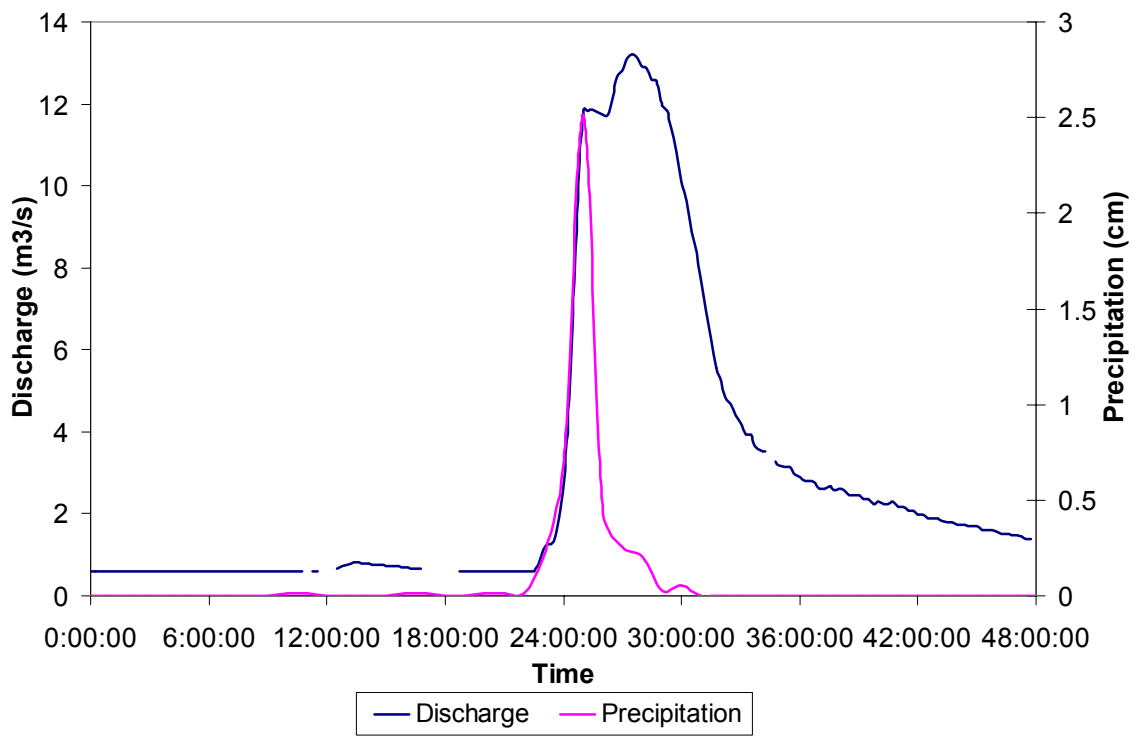


Figure 3. Discharge and Precipitation for November 29-30, 2005 from the Patroon Creek USGS Stream Gage. Recordings begin on November 29, 2005 at 0:00 hrs.

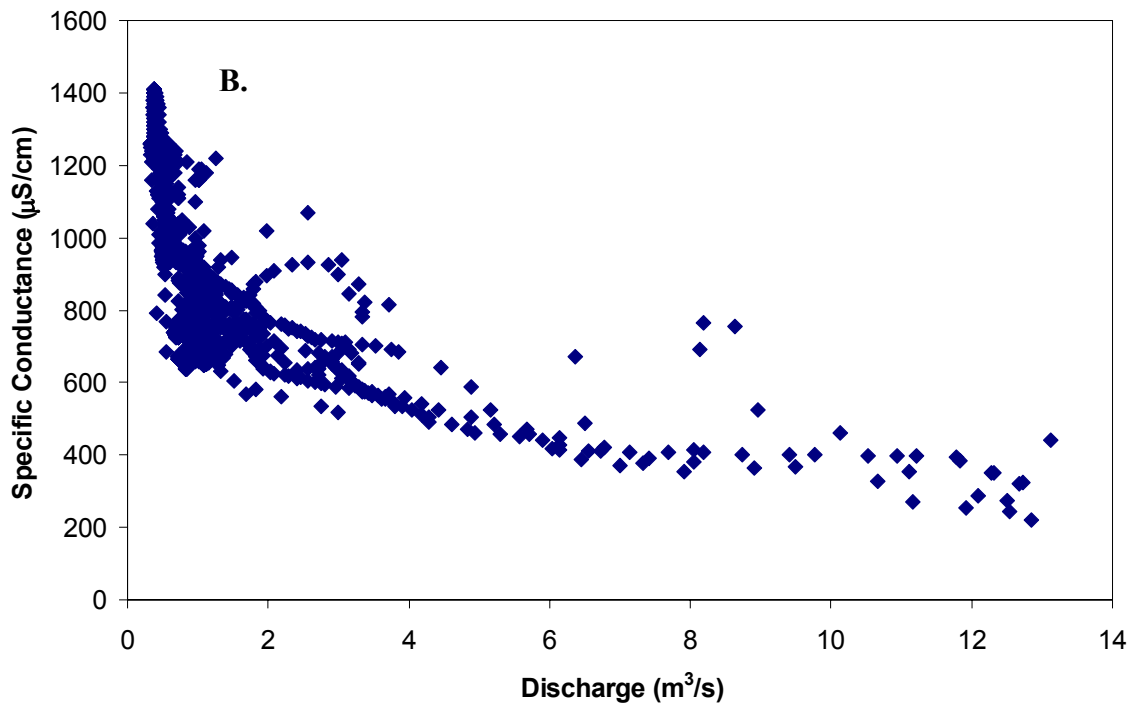
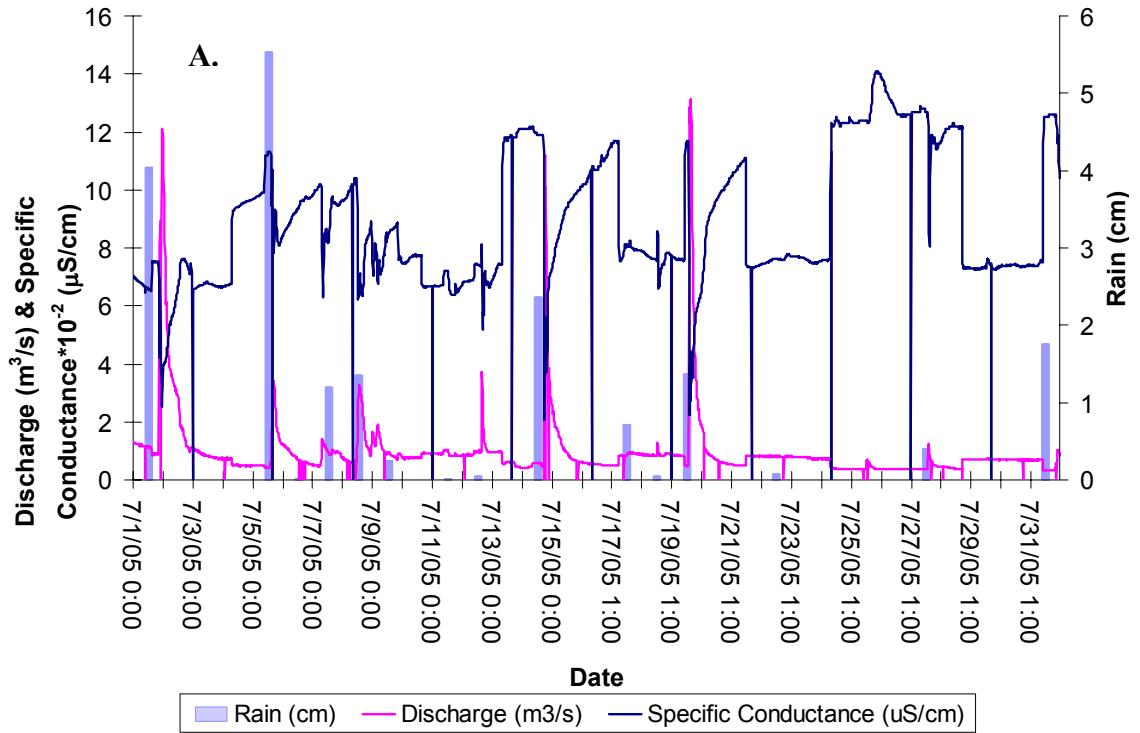


Figure 4. July 2005 Hydrology Data from the Patroon Creek USGS Stream Gage.

diurnal melting of the snow pack. Decreased snow pack suggests that this increased conductance with respect to little increase in discharge is likely from the entrance of high concentrations of road salt in the snow melt.

Also on February 16 through 17, 2005 there was a rain storm event in which the conductivity and discharge both increase suggesting increased chloride concentration in the stream (Fig. 5). This likely represents a freezing rain event in which icy conditions would lead to the use of road salt and its washing into the stream, raising stream specific conductance. Alternatively, melting of the snow pack would send chloride contaminated melt water into the stream. A freezing rain event is more likely as there was no record of snowfall and no change in the snow pack depth.

Figure 6 is representative of January 2006 which was a lower snow period than February 2005, in which road salt was not as often applied. This can be inferred due to the apparent significant decreases in conductivity with increased discharge. This period is representative of the period in which metal partitioning data were collected suggesting a bias in metal partitioning results toward low snow and ice conditions, when less NaCl is applied to road surfaces. Red arrows in Figure 6 indicate storm events in which samples were collected. More samples were collected for partitioning analysis during storm events with larger discharge values. A sequence of conductivity changes to notice is between January 14 and 18. On January 14, specific conductance decreases with increased discharge which corresponds less than 1cm of rain. Also late in the day on January 14 snow is recorded suggesting that the preceding rain was likely sleet, both of which would have led to the application of road deicing salt. This snow continues through to January 15 and snow melt is recorded almost immediately after due to a drop

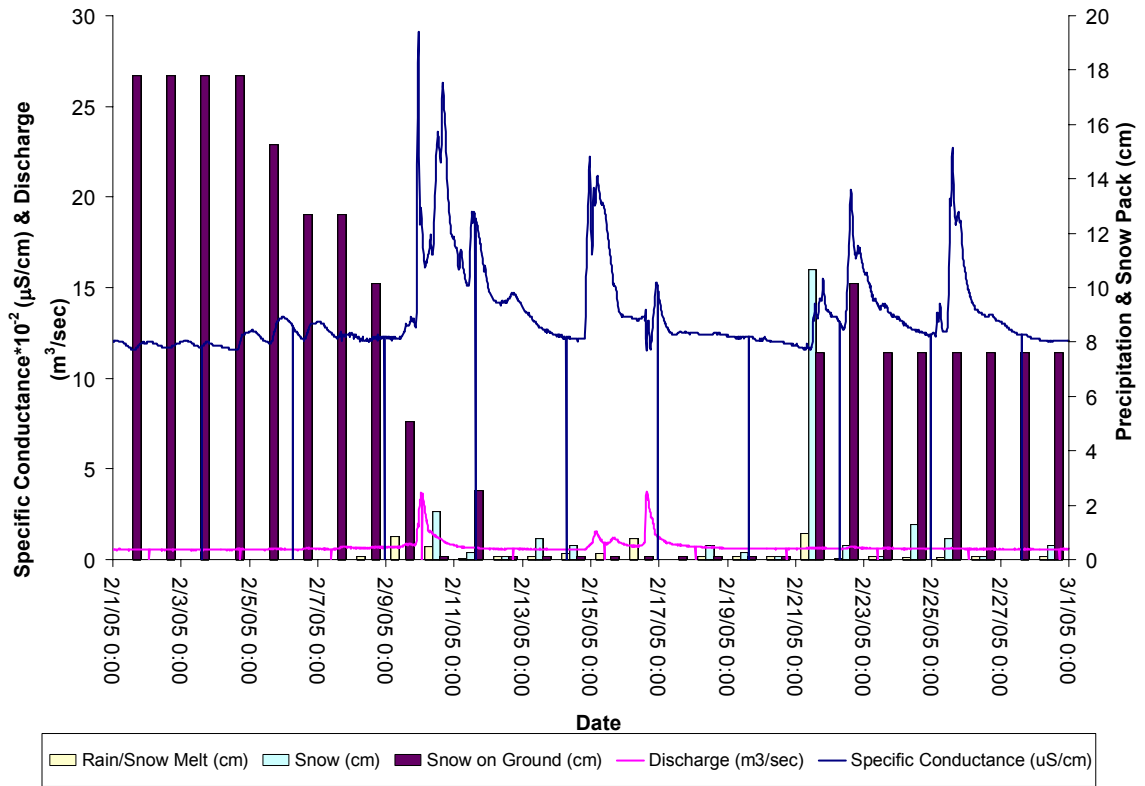


Figure 5. February 2006 Hydrology Data from the Patroon Creek USGS Stream Gage.

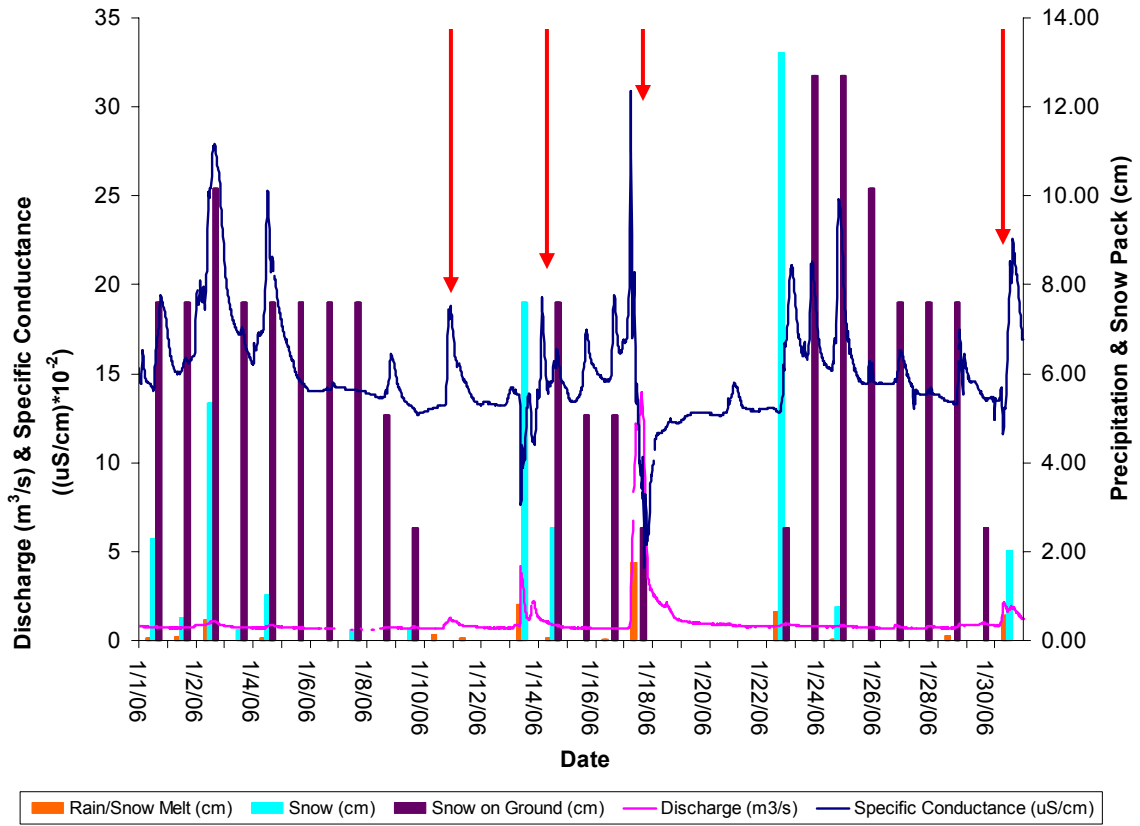


Figure 6. January 2006 Hydrology Data at the USGS Stream Gage. Red arrows note storm events that were sampled for Trace Metal Partitioning Data.

in snow pack depth. With this snowmelt is a corresponding periodic increase in specific conductance and little to no change in stream discharge. This event was not sampled for analysis by the auto-sampler into January 14 when specific conductance was at its highest because of its low discharge. An increase in conductance however does correspond with an increase in discharge as well as a large decrease in snow cover, due to a rain storm washing salt containing snowmelt into Patroon Creek on January 18, 2006. Conductance is observed decreasing later in the storm event, likely due to more dilute runoff later in the storm event. The early stages of this storm were sampled for analysis due to its high discharge values. The changes in the relationship between discharge and specific conductance are a unique tool in recognizing the likely presence of chloride in streams from a hydrograph.

The data from Patroon Creek have been divided into two major groups, those collected by grab sampling during baseflow, and those collected by grab sampling and the auto-sampler during storm events.

4.2 Baseflow Chemistry

The concentrations of major ions (Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-}) in Patroon Creek have been described in detail by Erickson, 2004. Erickson, 2004, found that the water of Patroon Creek is calcium bicarbonate-type water near the headwaters and becomes more sodium chloride enriched further downstream. Increased chloride and sodium input was shown to be due to deicing salt application. Sodium and chloride-type water is derived from road runoff during winter months and contaminated groundwater and surface water during summer months (Erickson, 2004). Here major ions will be summarized with particular influence on the characteristics of sodium and chloride.

4.2.1 Major Ions

4.2.1.1 Mean Concentrations

Average anion and cation concentrations are shown, with standard deviations, in Tables 4 and 5, respectively.

Figure 7 shows that the water during this study is dominantly a sodium chloride-type water. Erickson 2004 data is represented by the red ovals, and is less saline overall than data presented during this study period. This may be due to the bias toward winter conditions because of sampling during two winters but only one spring, summer, and fall.

Table 4. Statistical summary of anion concentrations in Patroon Creek at all sampling sites from October 12, 2004 to March 14, 2006.

	Fluoride (meq/L)	Chloride (meq/L)	Nitrate (meq/L)	Sulfate (meq/L)	Bicarbonate* (meq/L)
Minimum	n.d	1.5	n.d.	0.17	1.1
1st quartile	n.d.	4.9	n.d.	0.65	2.8
Mean	n.d.	6.4	0.04	0.75	3.2
Median	n.d.	6.0	n.d.	0.75	3.1
3rd quartile	n.d.	7.2	0.07	0.87	3.6
Maximum	.02	23	0.62	1.1	5.3
Std. Deviation	0.0	2.7	0.08	0.17	0.76
n	180	180	180	180	180

*Bicarbonate concentrations are calculate values. Phosphate values were below the MDL

Table 5. Statistical summary of cation concentrations at all sampling sites from October 12, 2004 to March 14, 2006.

	Sodium (meq/L)	Ammonium (meq/L)	Potassium (meq/L)	Magnesium (meq/L)	Calcium (meq/L)
Minimum	1.7	n.d.	0.02	n.d	0.79
1st quartile	4.5	n.d.	0.07	1.2	3.7
Mean	6.4	0.04	0.09	1.6	4.2
Median	6.0	n.d.	0.09	1.4	4.5
3rd quartile	7.3	0.07	0.10	1.5	5.0
Maximum	24	0.49	0.28	6.4	7.6
Std. Deviation	2.7	0.06	0.03	1.2	1.4
N	180	180	180	180	180

4.2.1.2 Temporal and Spatial Variation of Sodium and Chloride

Figure 8 shows that as in Erickson (2004) there is a linear correlation between chloride and sodium, likely due to the use of halite as a deicing salt. Because of this correlation, chloride concentrations will be used as a representative of sodium concentrations also. The correlation however gives a slope of only 0.9847, < 1 , which may be due to Na^+ exchange with other cations (Ca^{2+} , Mg^{2+} , K^+). Spatial variation of chloride ion concentration in Patroon Creek indicates that Site 3 (North Br) has the highest chloride concentrations (Appendix VI). The concentration of chloride at all other sites shows some variation, with Site 1 having the lowest because it is the least urbanized, while concentrations at North Branch, which is in proximity to many paved surfaces, are close to twice these values. Temporal variation of chloride concentration shows that concentrations are highest in the winter and early spring (Appendix VI). There is also an increase to near winter levels in chloride concentration during the summer when deicing salts are not applied. This may be related to salt storage in soils, sediments, or groundwater that contribute the majority of water to the stream during summer drought conditions. This may also be related to storage of NaCl in the waters of the three reservoirs in the Patroon Creek Watershed, which are continuously released. These variations are very similar to those shown by Erickson, 2004.

4.2.2 Trace Ions

4.2.2.1 Average Concentrations

Table 6 shows the average total concentrations, with standard deviation, of all trace metals studied.

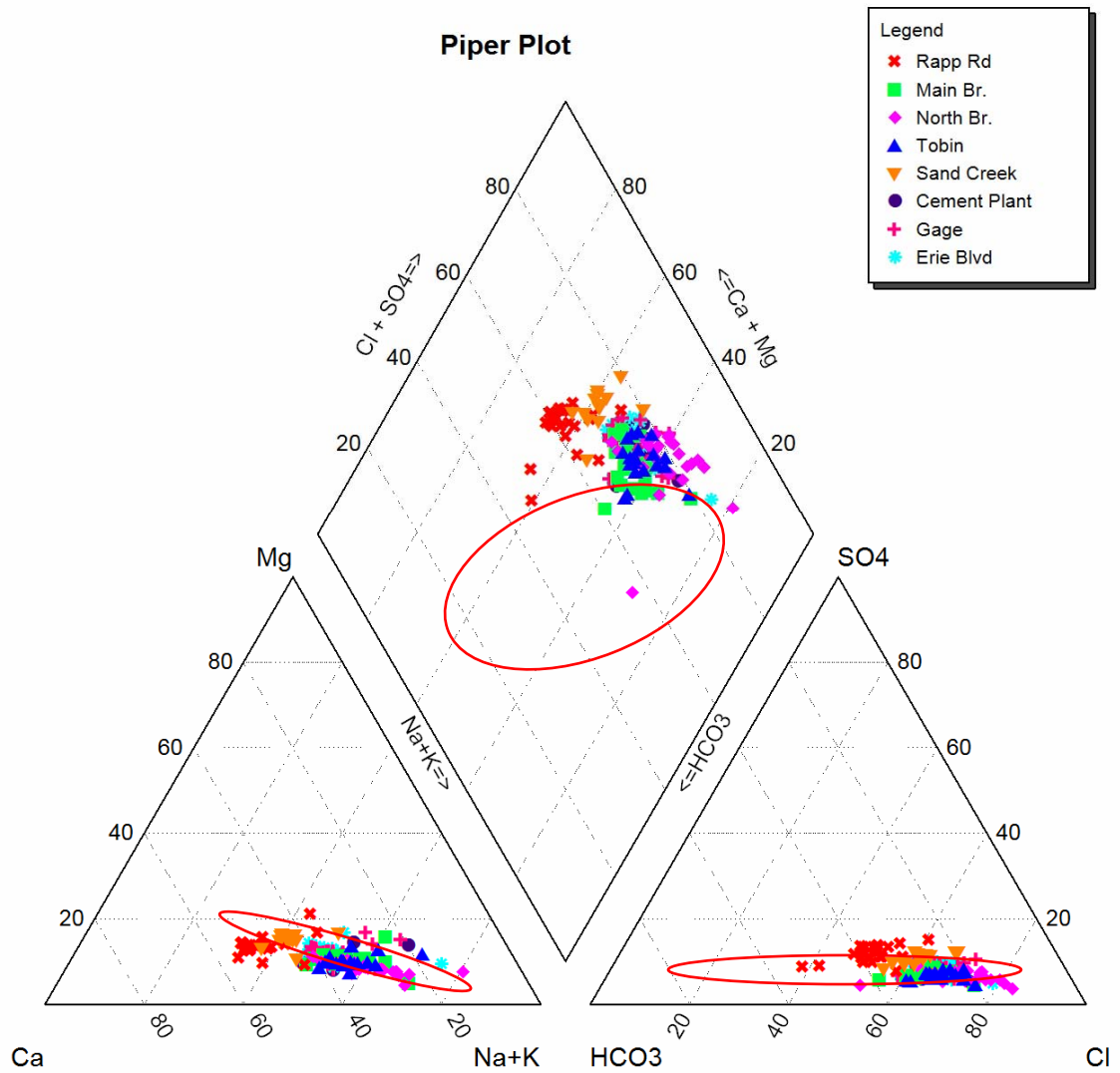


Figure 7. Piper Diagram illustrating spatial differences in surface water ionic chemistry for Patroon Creek. Red ovals represent the data range presented in Erickson, 2004. n=180

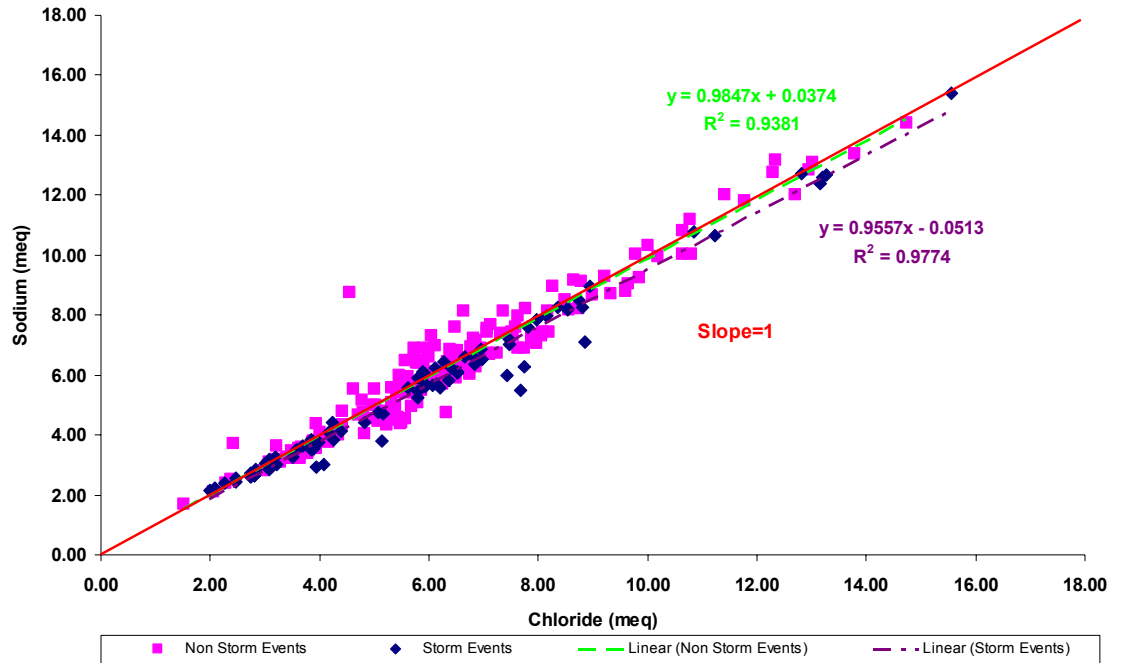


Figure 8. Relationship between the chloride and sodium ion concentrations in Patroon Creek in milliequivalents (meq) in both non-storm event and storm event samples. n=180

4.2.2.2 Temporal and Spatial Variation of Total Trace Metals in Patroon Creek

Zn, Cu, Cd, Pb, As, and Al showed no appreciable trends with respect to site along the creek. U continuously increased in mean concentration from Site 2 (Main Br) and downstream with the largest increase from Site 3 (North Branch) to Site 5 (Sand Creek) (Appendix VI). National Lead Industries, which is responsible for Uranium pollution is located between these two sites. Iron is initially high at Site 1 at the headwaters of Patroon Creek and then drops significantly by Site 2 remaining relatively constant downstream (Appendix VI).

Concentrations of Zn, Pb, Cd, Cu, U, Fe and Al show little to no seasonal variation in Patroon Creek (Appendix VI). Arsenic in Patroon Creek increases from April-July, then decreases into October (Appendix VI).

Table 6. Statistical summary of total trace ion concentrations in µg/L in Patroon Creek at all sampling sites during the study period.

	Minimum	1 st quartile	Mean	Median	3 rd quartile	Maximum	Std. Deviation	n
B	10.0	24.0	29.0	29.0	34.0	55.0	8.00	113
Al	9.90	51.0	330	120	240	5.07 x 10 ³	740	113
Mn	110	310	430	410	550	845	150	113
Fe	390	770	1.90x10 ³	1.01x10 ³	2.50x10 ³	1.17 x 10 ⁴	2.00 x 10 ³	113
Co	0.140	0.270	0.440	0.340	0.460	2.60	0.360	113
Cu	0.360	1.50	5.00	3.00	5.50	63.0	7.50	113
Zn	1.70	3.80	9.60	5.40	8.80	29.0	13.0	113
As	0.580	0.86	1.2	1.00	1.30	3.50	0.530	113
Se	n.d.	n.d.	0.81	0.730	0.930	9.30	0.850	113
Rb	0.517	1.07	1.23	1.21	1.34	2.37	0.263	113
Sr	61.3	271	293	301	328	488	76.1	113
Mo	0.200	0.460	2.30	0.560	0.760	101	10.0	113
Cd	0.006	0.013	0.036	0.018	0.036	0.260	0.049	113
Cs	0.004	0.0088	0.140	0.011	0.018	13.0	1.20	113
Ba	28.0	53.0	64.0	59.0	75.0	120	17.0	113
W	n.d.	0.028	0.980	0.100	3.00	3.10	1.40	113
Pb	0.051	0.600	2.60	1.00	2.20	26.0	4.60	113
U	0.110	0.350	0.540	0.480	0.650	2.40	0.290	113

4.2.2.3 Total Heavy Metal Concentration Correlations with Chloride and Particulates

The concentration of trace ions also has been shown to correlate with increased concentrations of suspended particulates (Gosz, 1977). Total Cd, Cu, Pb, and Zn concentrations showed a weak negative correlation with Cl concentration during this study, whereas U and As showed no correlation with Cl (Appendix VI). The correlation between Fe and Al which were used to represent particulates, and the trace ions focused on, are not significant during baseflow (Appendix VI).

4.3 Storm Event Chemistry

4.3.1 Major Ions

4.3.1.1 Average Concentrations

Average concentrations of anions and cations during storm events are given in Tables 7 and 8, respectively.

Figure 8 shows a good correlation between Na and Cl, due to the application of halite as a deicing agent, in storm event samples. As with baseflow the correlation is not a 1:1 ratio, which is likely due to cation exchange of Na for other base cations (Ca, Mg, K).

Table 7. Statistical summary of anion concentrations for storm events in Patroon Creek from August, 2005 to February, 2006.

	Fluoride (meq/L)	Chloride (meq/L)	Nitrate (meq/L)	Phosphate (meq/L)	Sulfate (meq/L)	Bicarbonate (meq/L)
Minimum	n.d.	2.00	n.d.	n.d.	0.230	n.d.
1st quartile	n.d.	3.90	0.056	n.d.	0.410	1.70
Mean	0.0019	6.20	0.094	0.002	0.650	2.20
Median	n.d.	5.90	0.081	n.d.	0.640	2.30
3rd quartile	0.0046	7.50	0.130	n.d.	0.780	2.80
Maximum	0.011	28.0	0.280	0.150	2.30	3.90
Std. Deviation	0.0029	3.70	0.060	0.018	0.340	0.810
N	76	76	76	76	76	76

Table 8. Statistical summary of cation concentrations for storm events in Patroon Creek from August, 2005 to February, 2006.

	Sodium (meq/L)	Ammonium (meq/L)	Potassium (meq/L)	Magnesium (meq/L)	Calcium (meq/L)
Minimum	2.14	n.d.	0.0543	0.0137	2.16
1st quartile	3.51	n.d.	0.0731	0.612	2.74
Mean	5.83	0.0425	0.104	0.944	3.69
Median	5.64	0.0173	0.0895	0.965	3.75
3rd quartile	6.89	0.0684	0.107	1.32	4.56
Maximum	20.0	0.257	0.804	1.53	6.28
Std. Deviation	3.09	0.0550	0.0804	0.369	1.07
N	76	76	76	76	76

4.3.2 Trace Ions

4.3.2.1 Average Total and Dissolved Concentrations

Statistical distribution of filtered, unfiltered, and sediment concentrations of trace metal, and semimetal concentrations for storm event samples are shown in Tables 9, 10, and 11, respectively. All heavy metal concentrations that were below the MDL were included in the statistical analyses as half of the minimum detection limit, and this concentration was included in subsequent analyses.

Table 9. Statistical summary dissolved trace ion concentrations (ppb) in Patroon Creek during storm events from August, 2005 to February, 2006. n=76

	Minimum	1st quartile	Mean	Median	3rd quartile	Maximum	Std. Deviation	n
B	7.60	18.0	23.0	23.0	27.0	40.0	7.30	76
Al	3.20	11.0	25.0	17.0	26.0	160	26.0	76
Mn	n.d.	0.310	1.30	0.470	0.660	56.0	6.50	76
Fe	n.d.	8.40	16.0	12.0	17.0	130	18.0	76
Co	0.0590	0.0920	0.140	0.140	0.170	0.380	0.061	76
Cu	0.100	2.00	3.00	2.50	3.20	15.0	2.10	76
Zn	n.d.	n.d.	6.80	2.80	4.70	160	23.0	76
As	0.240	0.410	0.560	0.480	0.570	4.10	0.430	76
Se	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	76
Rb	0.730	1.00	1.30	1.30	1.40	6.20	0.670	76
Sr	120	160	230	230	290	350	71.0	76
Mo	0.350	0.550	1.00	0.680	0.830	22.0	2.50	76
Cd	n.d.	0.0100	0.0180	0.0130	0.0180	0.210	0.0240	76
Cs	0.000420	0.0100	0.0440	0.0220	0.0620	0.410	0.0610	76
Ba	22.0	29.0	42.0	41.0	52.0	69.0	13.0	76
W	0.0150	0.0390	0.110	0.0650	0.130	1.10	0.150	76
Pb	0.0300	0.0860	1.30	0.110	0.160	86.0	9.80	76
U	0.0250	0.450	0.640	0.630	0.830	1.60	0.270	76

4.3.2.2 Transport Mechanisms of Heavy Metals into Patroon Creek

Factor analysis of total trace metal concentrations, chloride, suspended particulates, and discharge values in storm event samples showed that three factors defined more than 80% of the variance of the data (Fig 9). Factor 1 is likely defined by sediment release into the

stream environment based on its strong correlation with SPM, and explains the variance of total Co, Cd, Cs, Cu, As, Pb, Zn, Fe, and Al. Factor 2 is likely defined by

Table 10. Statistical summary of total trace ion (ppb) in Patroon Creek during storm events from August, 2005 to February, 2006. n=76

	Minimum	1st quartile	Mean	Median	3rd quartile	Maximum	Std. Deviation
B	7.8	18	23	22	27	38	7.0
Al	22	150	690	380	860	4600	900
Mn	n.d.	230	380	320	460	1300	280
Fe	140	1300	3500	2400	4800	12000	3000
Co	0.15	0.45	1.4	0.84	1.6	10	1.9
Cu	1.1	3.6	11	6.5	12	110	15
Zn	1.9	11	41	25	52	190	44
As	0.33	0.98	1.8	1.4	2.0	14	1.7
Se	n.d.	n.d.	n.d.	n.d.	n.d.	1.4	0.28
Rb	1.0	1.3	1.6	1.5	1.8	5.3	0.64
Sr	66	140	210	220	280	330	72
Mo	0.11	0.35	0.83	0.51	0.68	22	2.5
Cd	0.0063	0.027	0.098	0.064	0.11	0.63	0.11
Cs	n.d.	n.d.	n.d.	n.d.	n.d.	0.25	0.048
Ba	30	47	59	57	67	120	19
W	0.017	0.034	0.080	0.053	0.12	0.27	0.062
Pb	0.18	2.0	19	6.1	17	310	42
U	0.40	0.56	0.75	0.73	0.90	2.1	0.27

Table 11. Statistical summary of concentration of trace ions in particulates (ppm) in Patroon Creek during storm events from August, 2005 to February, 2006. n=15

	Minimum	1st quartile	Mean	Median	3rd quartile	Maximum	Std. Deviation
Co	3.0	7.5	8.0	8.1	8.9	11	2.1
Cu	36	72	85	90	98	120	23
Zn	160	380	450	410	500	950	180
As	8.6	15	18	19	20	31	5.0
Se	0.056	0.96	1.1	1.1	1.3	1.8	0.40
Mo	0.39	0.82	0.96	0.90	1.1	1.4	0.27
Cd	0.14	0.65	0.78	0.88	0.96	1.2	0.30
W	0.084	0.17	0.25	0.26	0.31	0.43	0.10
Pb	8.8	56	100	68	170	300	83
U	0.31	0.40	0.56	0.51	0.60	1.4	0.27

Factor Loadings Plot Total Metal Concentrations

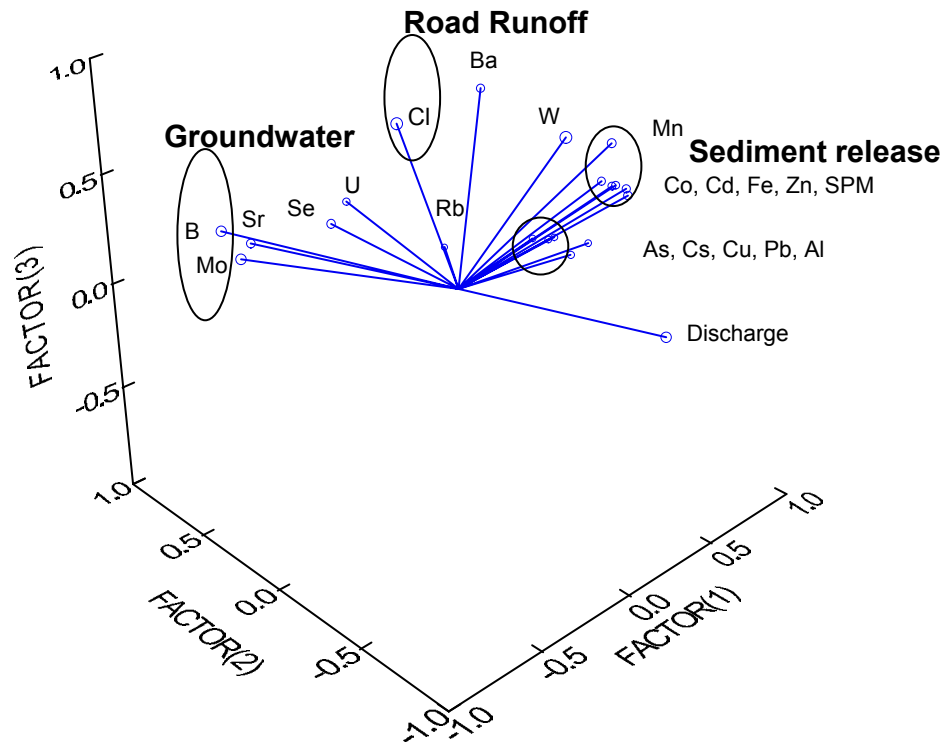


Figure 9. Factor Analysis distribution of Total Heavy Metal Concentrations, Cl, SPM, and discharge.

groundwater transport as it has a strong negative correlation with discharge, and explains the variance of U, Se, Sr, B, and Mo. Therefore when discharge is low these metals are high, and low under high discharge values. These trace ions form soluble oxides that are already in solution. Factor 3 is likely defined by road runoff into Patroon Creek, as it correlates strongly with Cl likely from road salt application and Tungsten from tire wear (Backstrom et al., 2004).

Factor analysis of winter and summer storm event samples are shown in Figure 10. During winter storm events, the majority of variance is defined by three factors. Factor 1 is likely controlled by discharge (Fig. 10A). In Table 12 factor loadings along with Figure 10 show that discharge controls the concentrations of heavy metals such as Zn, Cd, Cu, and Pb in Patroon Creek during winter months. Factor 2 which is likely groundwater controls the concentrations of base ions Ca, Mg, K, and heavy metals like U and Ba. Factors 1 and 2 are interdependent in that when discharge increases, the elements that it controls increase, and those controlled by groundwater decrease. The opposite is true for when discharge decreases. Factor 3 during winter months is controlled by road salt contaminated runoff transporting Na and Cl into the stream, as well as W from tire wear. These same three factors control elemental concentrations during summer storm events (Fig. 10B). Na and Cl, however, are controlled by discharge and groundwater fluxes, not road runoff.

Figure 11 shows a strong correlation between Suspended Particulate Matter and Total Zn, Cu, Cd, and Pb concentrations. This is consistent with factor analysis showing that these metals are likely transported by sediments. U has a negative correlation with discharge, likely due to U being transported to the stream by groundwater (Appendix

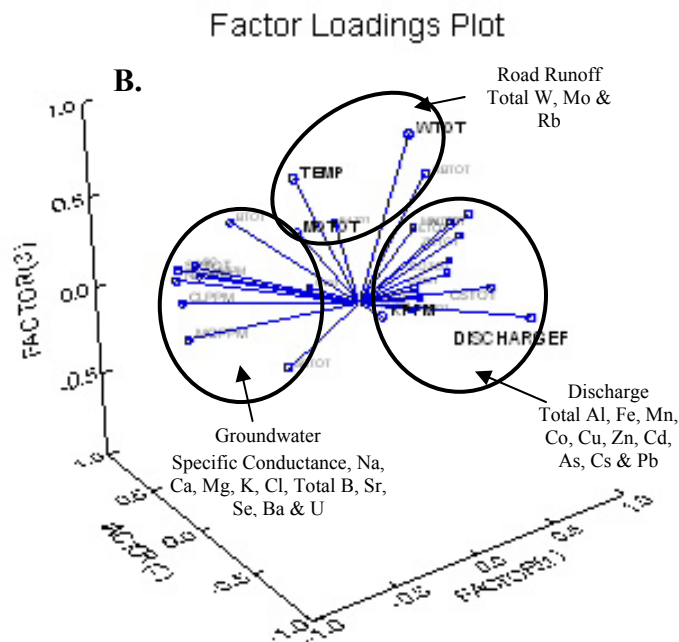
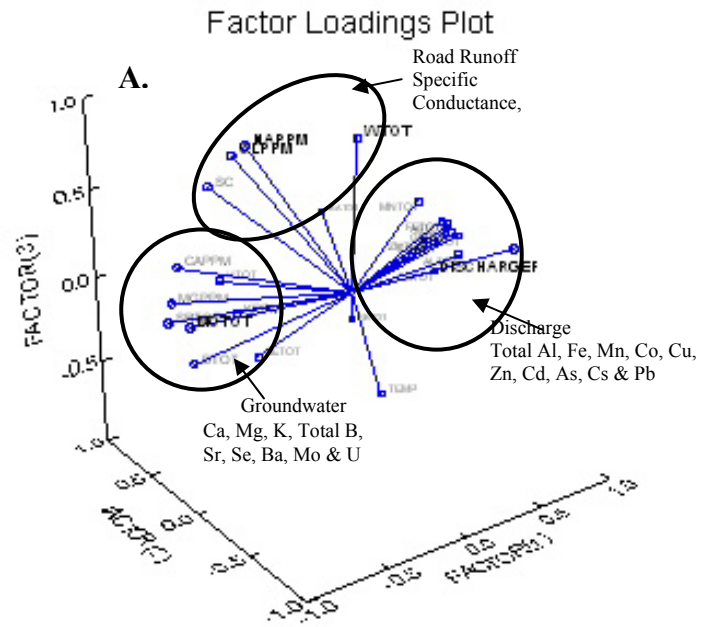


Figure 10. Factor Analysis Plots for Storm Event Samples during the Winter seasons of 2004-2005 and 2005-2006 (A), and the Summer of 2005 (B).

Table 12. Factor loadings for Storm Event Samples separated between Winter and Summer Storm Events. Major Ions are in ppm. Trace Metals are total concentrations in ppb.

	Factor 1		Factor 2		Factor 3	
	Winter	Summer	Winter	Summer	Winter	Summer
Discharge (ft³/s)	0.664	0.562	-0.523	-0.688	0.265	0.021
Temperature (°C)	0.345	-0.231	0.191	0.247	-0.771	0.654
Specific Conductance (µS)	-0.501	-0.511	0.607	0.784	0.527	0.077
Na	-0.390	-0.655	0.405	0.730	0.783	0.045
Mg	-0.738	-0.639	0.628	0.664	-0.090	-0.272
Cl	-0.453	-0.672	0.438	0.652	0.732	-0.052
K	-0.525	0.008	0.306	-0.188	-0.087	-0.005
Ca	-0.665	-0.489	0.683	0.781	0.080	0.016
Al	0.936	0.895	0.237	0.210	-0.069	0.241
B	-0.664	-0.273	0.545	0.802	-0.439	0.268
Mn	0.806	0.619	0.454	0.344	0.222	0.182
Fe	0.895	0.900	0.350	0.363	0.111	0.150
Co	0.875	0.900	0.386	0.384	-0.021	-0.160
Cu	0.948	0.765	0.259	0.455	0.038	-0.305
Zn	0.816	0.896	0.402	0.275	0.001	0.098
As	0.896	0.754	0.293	0.493	0.113	-0.259
Se	-0.231	-0.168	0.583	0.422	-0.529	-0.478
Rb	0.420	0.677	0.585	0.325	-0.471	0.485
Sr	-0.836	-0.726	0.499	0.585	-0.133	0.169
Mo	-0.807	-0.251	0.318	0.184	-0.098	0.386
Cd	0.914	0.865	0.321	0.323	0.050	-0.057
Cs	0.793	0.807	0.273	-0.098	-0.151	-0.072
Ba	0.409	0.432	0.867	0.834	0.128	0.110
W	0.148	0.332	0.158	0.028	0.788	0.840
Pb	0.912	0.690	0.273	0.437	0.060	-0.361
U	-0.320	0.242	0.837	0.815	-0.129	-0.236

VI). As discharge increases, the groundwater input to the stream is diluted and so U decreases (Appendix VI). U then has higher concentrations when discharge decreases and groundwater input to the stream is higher.

4.3.2.3 Variations in SPM, chloride, and metals during Storm Events

The concentration of metals in dissolved and particulate phases were measured as functions of time during three storm events; November 30, 2005, January 14, 2006 and January 18, 2006. Temporal variations in discharge, suspended particulate matter (SPM)

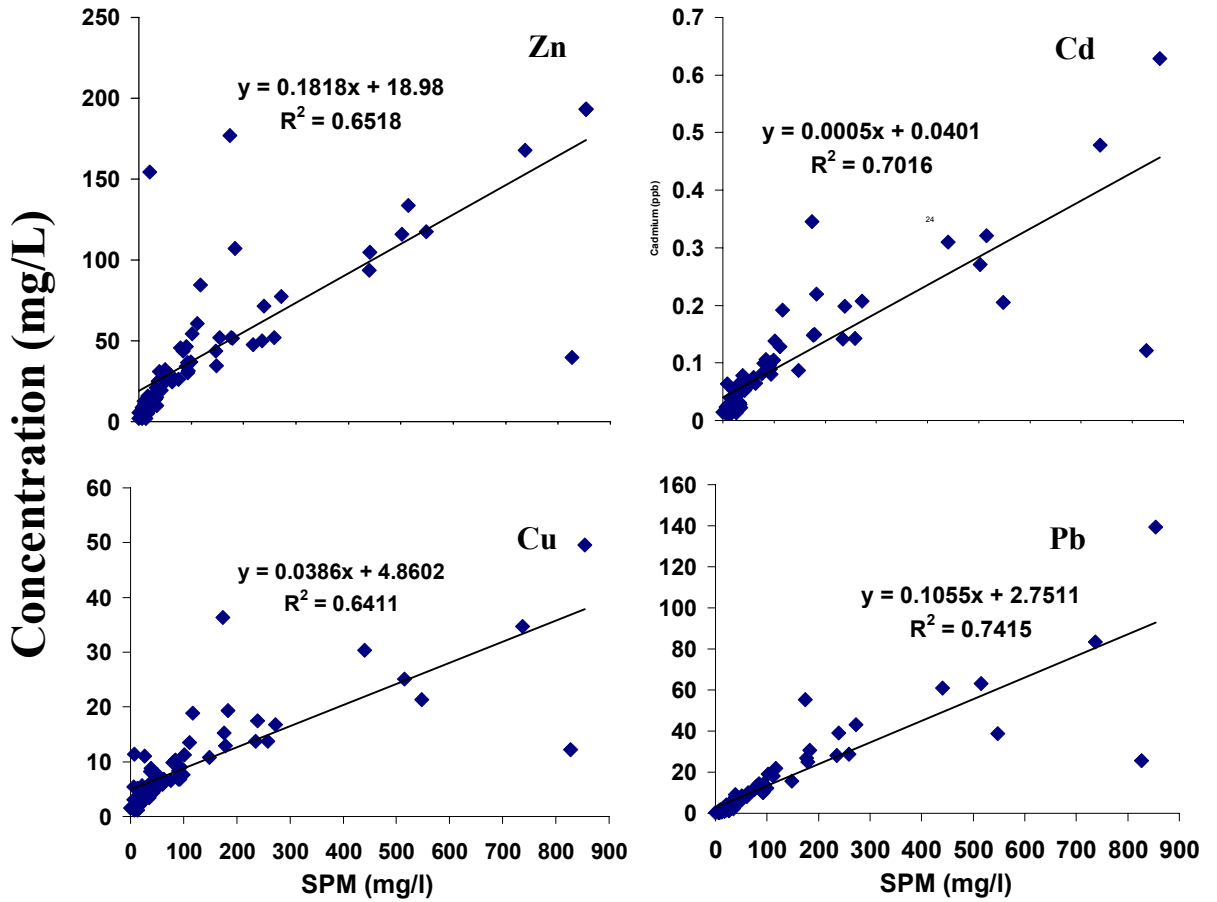


Figure 10. Total Concentrations of Zinc, Cadmium, Copper, and Lead as a function of Suspended Particulate Matter fluxes for storm event samples from the Patroon Creek Gage site from August, 2005 through February 2006, n=77.

chloride, and dissolved and suspended metal concentrations (Zn, Cu, Cd, and Pb) were analyzed for each event (Fig. 12-14). A brief description of each storm is also provided.

In the November 30, 2005 storm event rain increases rapidly for the first 3 hours of the storm, followed by a rapid decrease for the next hour and slowly decreases until it ends for the next 6 hours (Fig 12A). Precipitation varies inversely with chloride, likely due to the dilution of chloride in stream water with increased precipitation. The increase in chloride within the 1 AM hour occurs almost simultaneously with a decrease in precipitation. Discharge increased rapidly within the first 3 hours, and the onset of precipitation, plateaued for ~4 hours, and then decreased gradually through the next 7 hours. pH is relatively constant through the storm with a small decrease coincident with the maximum discharge value (Fig 12A). SPM, which also represents particulate Cd, Cu, Pb and Zn concentration, also increased rapidly in the first hour, peaked around 1:30 am, and then decreased continuously for the remainder of the storm (Figure 12A). This mirrors precipitation during the storm event. In contrast chloride concentration decreased rapidly within the two hours, reached a minimum at 1:30 am when SPM was at its peak, and then increased during the third hour (Fig 12C). This was followed by a gradual decrease and then a second increase beginning around 6:30 am and continuing for the remainder of the storm. This trend is inversely related to precipitation, likely due to the dilution of chloride in stream water with increased precipitation. The increase in chloride within the 1 am hour occurs almost simultaneously with a decrease in rainfall. Discharge increased rapidly within the first 3 hours, and the onset of precipitation, plateaued for ~4 hours, and then decreased gradually through the next 7 hours. Total concentrations of Cd, Cu, Pb, and Zn mirror the trend of SPM throughout this storm event, suggesting its

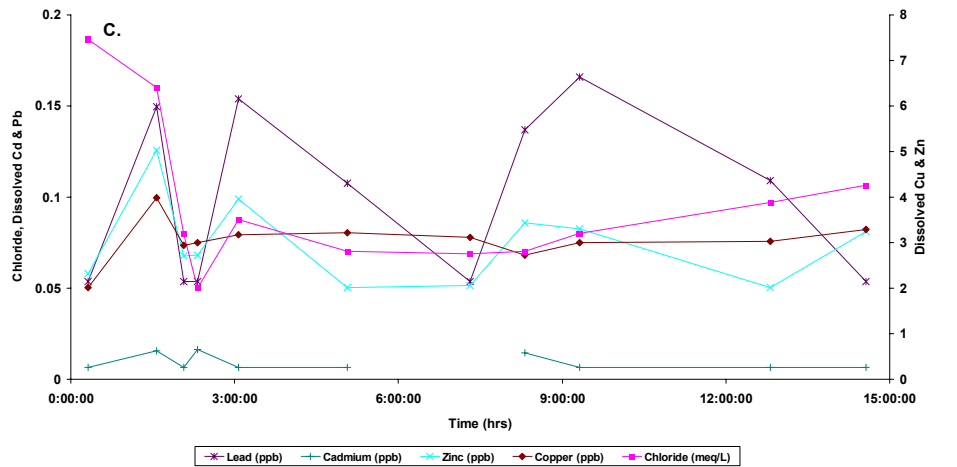
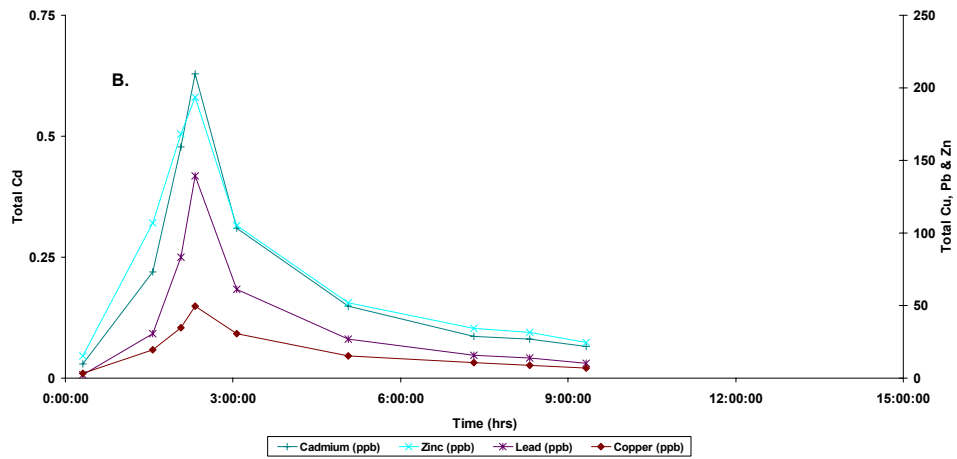
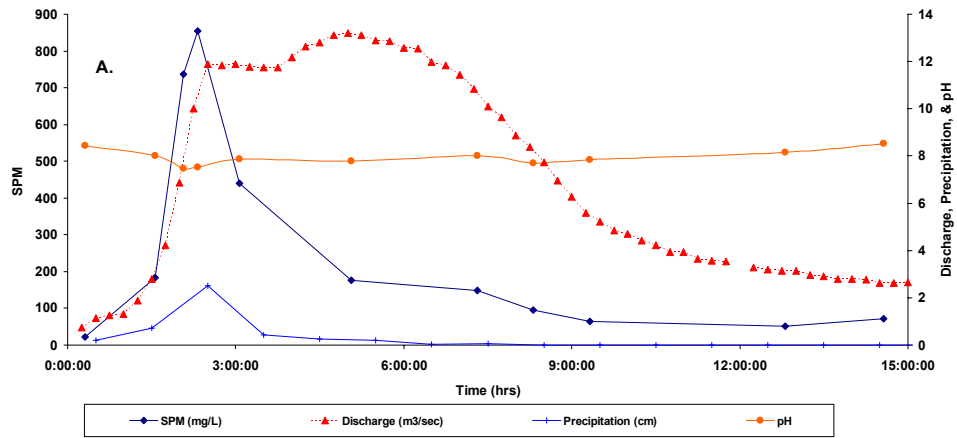


Figure 12. November 29-30, 2005 Storm Event starting at 22:30. High of 13°C, Low of 3°C.

control on their transport through the stream (Fig 12B.). Dissolved concentrations of all metals increase rapidly for the first ~ 3 hours of the storm, followed by a rapid decrease for the next half hour (Fig 12C). Cd, Pb, and Zn, then increase for a half-hour and slowly decrease for the remainder of the event. These variants then increase slowly for 2 hours and then decrease again for the remainder of the event, with Zn increasing for the last 2 hours of the event. Cu, after the first 3 hours of the storm, showed a small increase for the remainder of the storm event with a short trough 9.5 hours into the storm (Fig 12C). The final increase in the dissolved concentrations of these metals near 6:30 am coincides well with the gradual increase in chloride concentration from this point to the end of the storm event. This correlation in the trend of chloride and the dissolved concentrations of these metals occurs throughout the event, with less significant changes seen in chloride concentration (Fig 12C). In the beginning of this event when the particulate concentrations of these metals increased, Cl and dissolved metal concentrations decreased, suggesting more of these metals in the particulate phase with decreasing Cl. The opposite trend between particulate Zn, and Cl and dissolved Zn is seen as Cl increased and decreased. This suggests that with increased chloride, more of these metals are in the dissolved phase. This should lead to a decrease in K_d with increased chloride concentration.

The storm of January 14, 2006 started with freezing rain increasing for the first half hour and with a rapid decrease until it stops one half hour later. Snowfall begins approximately 9 hours into the storm and plateaus for one hour and then stops by 11 hours into the event. Discharge increased rapidly with the initial freezing rain then peaked after 1 hour, then gradually decreased for ~6 hours and leveled off for

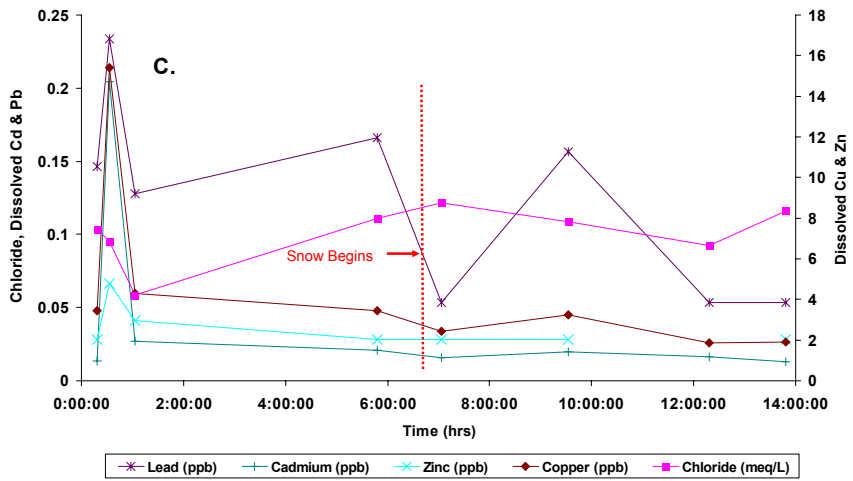
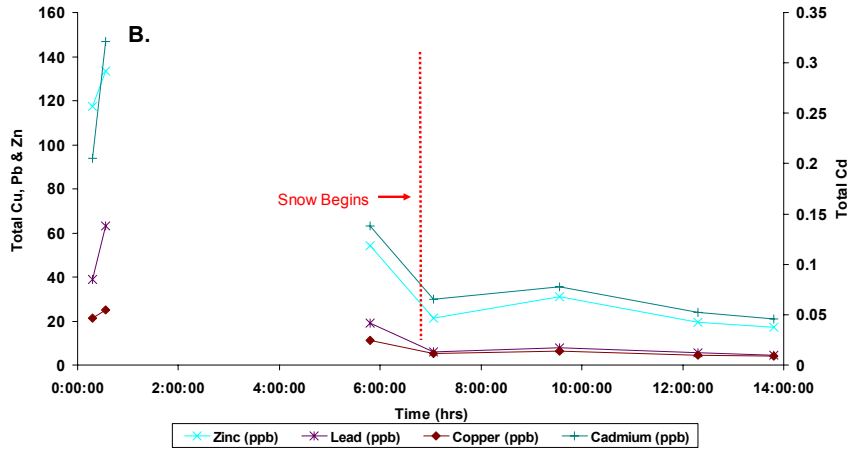
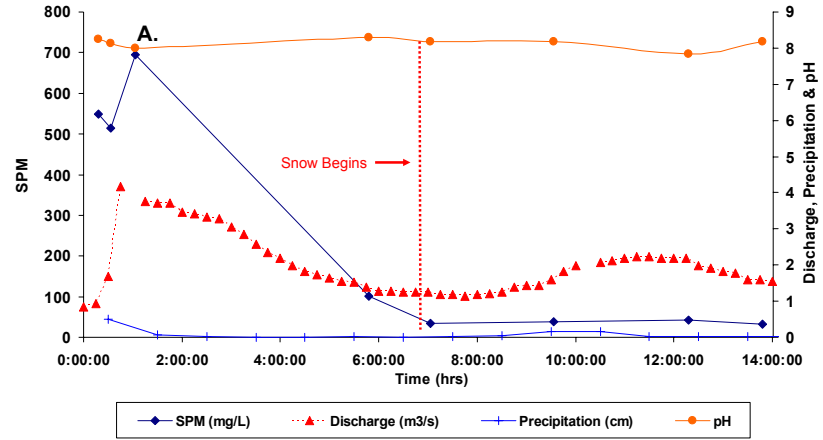


Figure 13. January 14, 2006 Rain storm event starting at 8:30 turning to snow storm by mid-afternoon. High of 13.3°C, Low of -4.4°C.

approximately 2 hours (Figure 13A). A gradual increase in discharge, triggered by snowfall, followed at approximately 17:00 for the next 2 hours, and plateaued for ~1 hour and decreased gradually for the remainder of the storm. As in the November 30, 2005 storm, pH generally follows the opposite trend as discharge (Fig 13A). Suspended particulate matter, also representing particulate concentrations of Cd, Cu, Pb, and Zn, increased initially and then decreased gradually for approximately 4 hours, and then showed a minor increase for ~7 hours, followed by a decrease for the remainder of the storm (Fig 13A.). The initial increase of SPM in this event is much more significant than the secondary peak. Unfiltered and Filtered Cd, Cu, Pb, and Zn followed approximately the same trend as SPM, increasing rapidly for the first 30 minutes, followed by a rapid decrease for approximately 30 minutes and then a decrease for the next 4 hours (Fig 13B & 13C). They increased again for only approximately 3 hours, then decreased gradually for the remainder of the storm. Filtered Pb concentrations unlike the others showed a gradual increase followed by a decrease in concentration after the rapid initial decrease (Fig 13C.). Chloride levels during the January 14, 2006 storm followed an almost exactly opposite trend as the other parameters (Fig 13A). Cl⁻ initially decreased rapidly, followed by a gradual increase for approximately the next 3 hours where it leveled off for roughly 2 hours, then decreased gradually for 2 hours and increased for the remainder of the storm. Particulate Cd, Cu, Pb and Zn are represented by SPM and have higher concentrations with decreased Cl concentration.

With the initiation of the January 18, 2006 storm event shown in Figure 14, rainfall has already plateaued, as if the autosampler did not begin collecting samples until some point after the actual initiation of rainfall. This plateau remains relatively constant

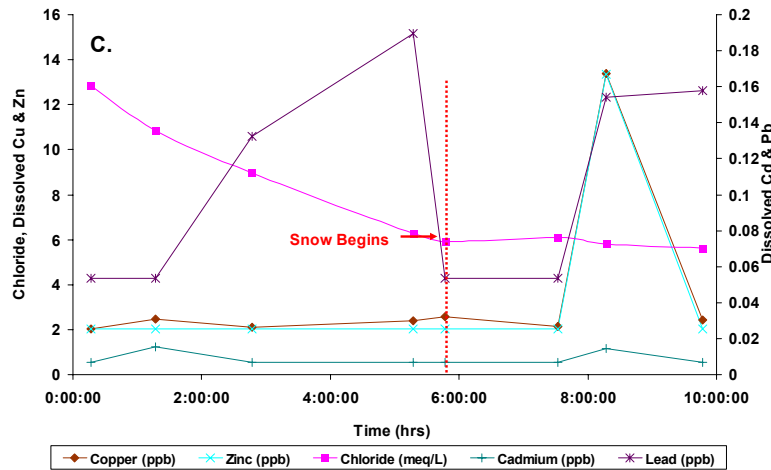
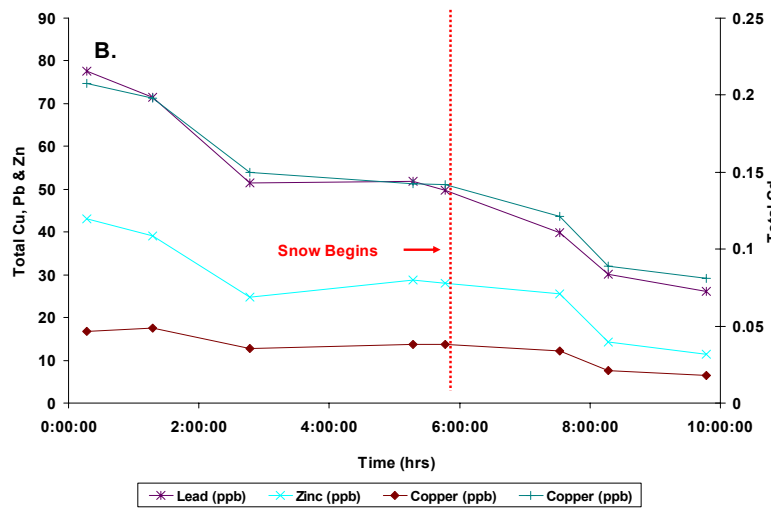
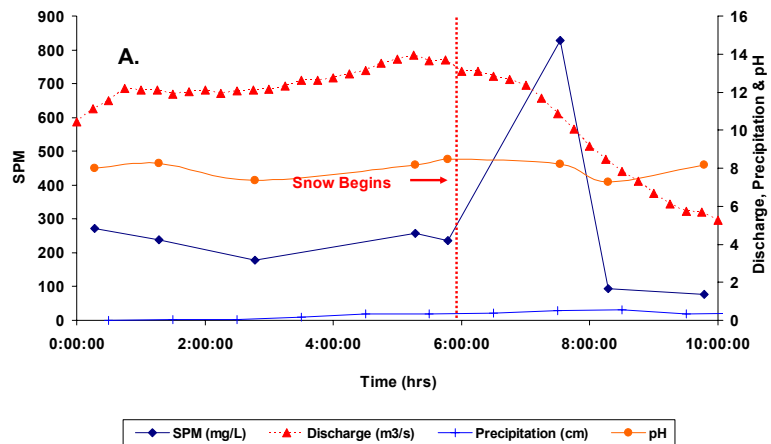


Figure 14. January 18, 2006 Torrential Rain Storm event starting at 9:30 turning to snow by mid-afternoon. High of 12.2°C, Low of 0.99°C.

for 5 hours until it dissipates as it changes to snowfall. Discharge remained relatively stable through out the storm as it gradually increased for the first 6 hours, and then decreased more rapidly for the remaining 4 hours of the event. SPM, which also represents particulate Cd, Cu, Pb and Zn concentrations, decreased gradually for the first 3 hours and then gradually increased for approximately 4 hours. It then increased rapidly for 2 hours, followed by a rapid decrease for approximately 1 hour where it leveled off for the remainder of the event (Fig 14A). Unlike during the previous storms, pH follows approximately the same trend as discharge for the first 8 hours of the storm (Fig 14A). For the final hour and a half of this storm pH increases as discharge decreases. Chloride showed a gradual decrease for the first approximately 6 hours of the storm, and then leveled off for the remaining 4 hours of recordings for the storm (Fig 14C). Undissolved concentrations of Cd, Cu, Pb and Zn followed much the same trend as SPM, however not as exaggerated (Fig 14B). The major difference occurred near 15:00 when Cd, Cu, Pb and Zn decreased as SPM increased. Dissolved Pb increased gradually for the first ~4.5 hours of the storm, then decreased rapidly for 0.5 hours where it leveled off for approximately the next 1.5 hour, increased rapidly for 0.5 hours and plateaued for ~1 hour until the end of recordings for the event (Fig 14C). The other heavy metals shown all remained relatively stable for the first 7 hours of the storm. They then increased rapidly for approximately a half-hour, and then decreased rapidly for the next hour of the storm event, coinciding with the final peak in SPM (Fig 14A & 14C).

4.3.2.4 Effect of Chloride on Dissolved Heavy Metal Concentrations

The previous diagrams show that chloride and dissolved heavy metals are closely related during the storm events. This would suggest that dissolved heavy metals have a positive correlation with chloride concentration. Overall, however, there is little correlation between these two variables (Appendix VI).

4.3.3 Partitioning of Heavy Metals between the Suspended and Dissolved Phases

Partitioning between the dissolved and particulate phases is determined by the change in K_d (4) as a function of chloride. Zn, Cu, Pb, and Cd correlations are shown in Figure 15A by their $\log K_d$ as a function of the \log of chloride concentration. K_d values of Cu and Cd show little correlation with chloride. Pb and Zn, however display a decrease in $\log K_d$ values with increased chloride. This suggests that an increase in partitioning of these metals to the dissolved phase corresponds to an increase in chloride concentration. For this figure the K_d values in which dissolved heavy metal concentrations were below the MDL have been removed. This is the way that K_d data were presented by Warren and Zimmerman, 1994.

When values below the MDL are added into the analysis, the trends of K_d values of these metals with respect to chloride concentration are significantly changed (Figure 15B). K_d values for Cd and Cu retain their trend of little response to chloride changes. Pb and Zn however lose their trends with chloride, and show the same lack of control by chloride on their K_d values.

Figures 16 through 18 represent Time-Series plots of $\log K_d$ values, \log Chloride, and pH for the each storm event presented. For the November 30, 2005 storm event K_d values for Cu, Pb and Zn increase with the initial decrease in chloride

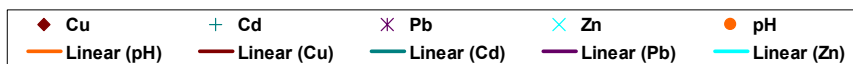
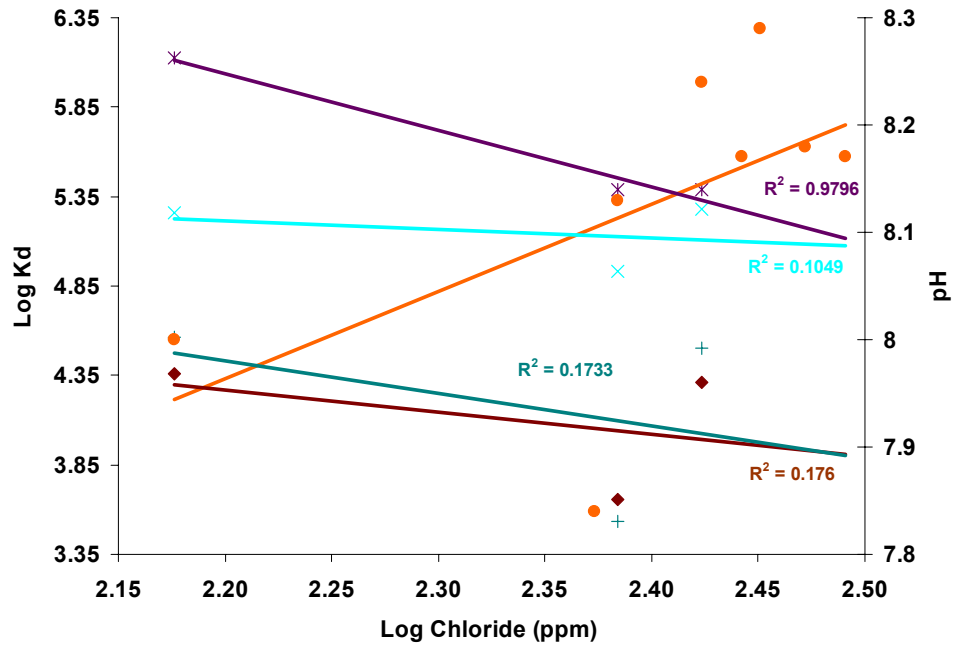
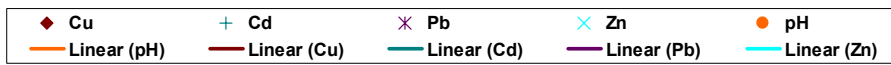
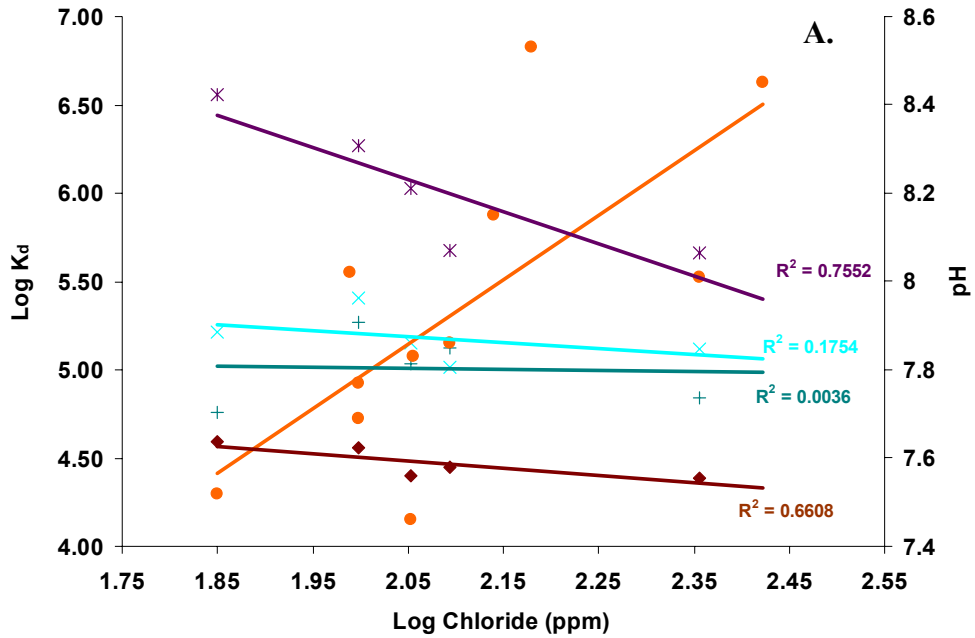


Figure 15. Log K_d values of Cd, Cu, Zn and Pb, and pH as a function of Chloride concentration. Sub-figure A. shows only values with dissolved heavy metal concentrations >MDL. Sub-figure B. has include values with dissolved heavy metal concentrations <MDL.

concentration while the K_d Cd decreases with chloride and pH (Fig. 16). This is the opposite of what would be expected for Cu, Cd and Zn. Previous studies have shown that Cd and Zn would increase in the dissolved phase, or decrease in K_d , with increased chloride, while Cu would be expected to show little change. All four heavy metals presented increase with the second decrease in chloride concentration. When compared to pH, the log K_d values show the same relationship as they do when compared to chloride. This is the opposite of what would be expected, as decreased pH leads to desorption of metals from surfaces into the dissolved phase, which would lead to a decrease in K_d values.

On January 14, 2006 the K_d values for Cu, Cd and Zn decrease as Chloride initially decreases (Fig. 17). Log K_d values of these parameters then increase as chloride continues to decrease. This shows a decrease of these metals to the dissolved phase with increased chloride concentration. Log K_d of Pb demonstrates little response to the initial decrease in chloride concentration, but increases noticeably as chloride continues to decrease. K_d values of these parameters demonstrate the same relationship with pH as with chloride concentration on January 14, 2006.

On January 18, 2006 all four metals presented show a positive correlation between their log K_d values and chloride concentration (Fig. 18). This trend is represented by the overall decrease in K_d values as chloride concentration decreases throughout the storm. This suggests an overall increase in Cu, Cd, Pb and Zn concentrations toward the dissolved phase with decreased chloride. These heavy metals show the same relationship with pH as in the two previously mentioned storm events, representing a decrease in concentrations toward the dissolved phase with decreasing pH.

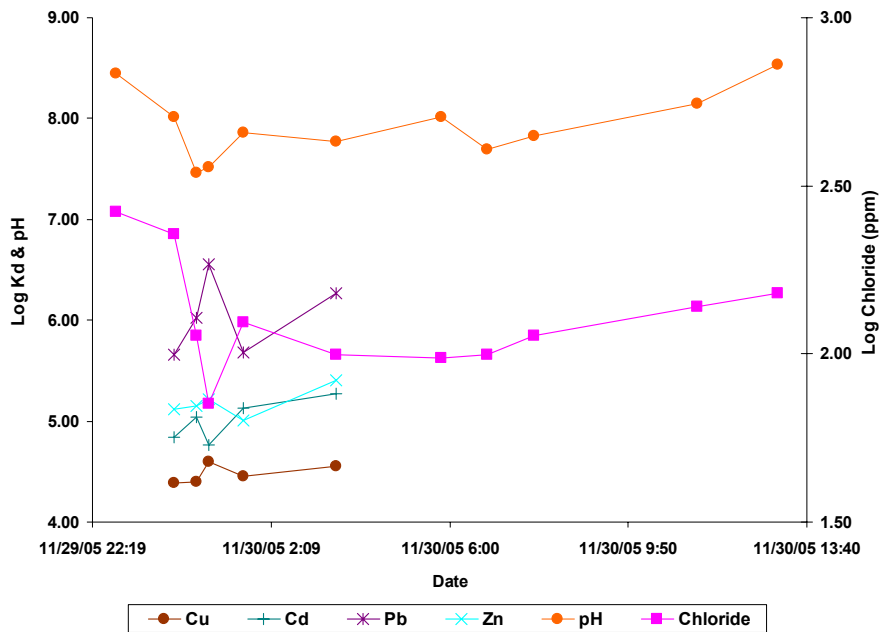


Figure 16. Time-Series of Log K_d for Cu, Cd, Pb and Zn, Chloride, and pH for the November 29-30, 2005 storm event.

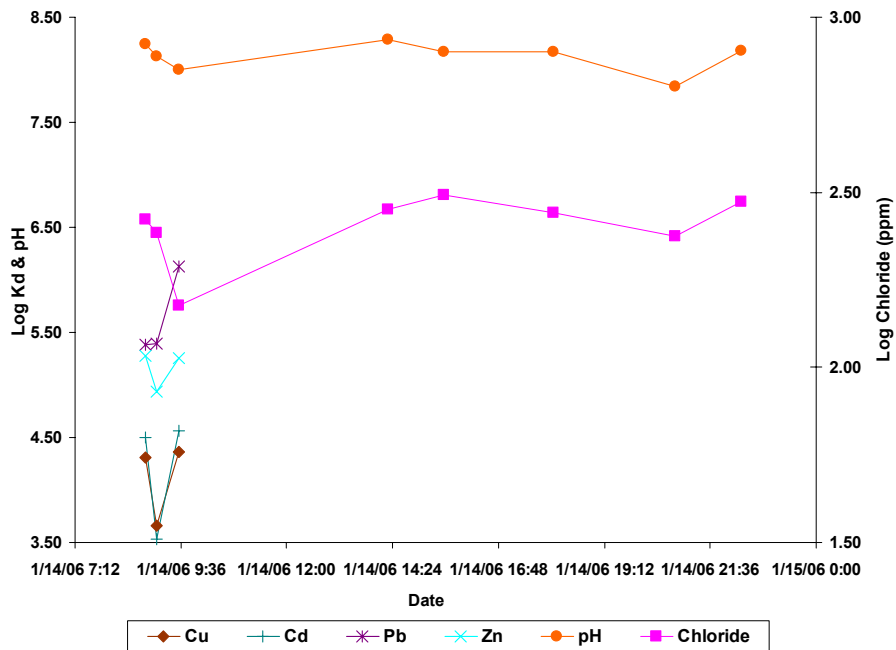


Figure 17. Time-Series of Log K_d for Cu, Cd, Pb and Zn, Chloride, and pH for the January 14, 2006 storm event.

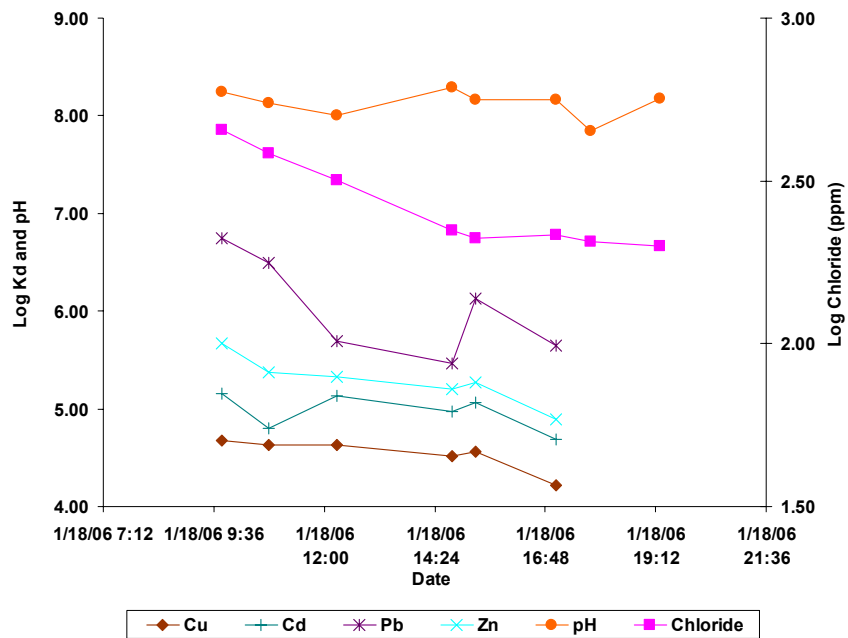


Figure 18. Time-Series of K_d for Cu, Cd, Pb and Zn, Chloride, and pH for the January 18, 2006 storm event.

5. Discussion

5.1 Chloride Trends in Patroon Creek

Major ion data support the conclusion by Erickson, 2004 that increased Na and Cl concentrations in Patroon Creek are due to the application of NaCl as road deicing salt. Spatial variation, for this study period also, shows that the North Branch of Patroon Creek has the highest concentrations of chloride. Seasonal variation was the same in that the highest concentrations of chloride were in the winter months with a second increase in July after a drop in the spring months. This increase is likely due to the release of chloride contaminated water stored in the reservoirs of the Patroon Creek Watershed during winter months.

5.2 Mean Metal Concentrations in Patroon Creek Compared to other Aquatic Systems

When compared to heavy metal concentrations measured in other urban streams, heavy metal concentrations from Patroon Creek are lower. Most metal concentrations in the total and dissolved fraction were well below regulatory values. In Table 12 the concentrations of Co, Cu, Zn, Cd, and Pb are compared to those of other systems. These include the Don River near Toronto, Canada, the Varuna River which is polluted with domestic waste, and landfill leachate from Southern Ontario. Also listed are NYSDEC Surface Water Standard concentrations of these metals in Class C streams.

The mean concentrations of total heavy metals in Patroon Creek as a watershed during this study are also mostly lower than those from a study by the Army Corp of Engineers on a small tributary to Patroon Creek that flows through the National Lead Industries site during 2002. The data for the FUSRAP study are presented as the mean concentrations

Table 13. Comparison of Total Heavy Metal concentrations in Patroon Creek with other polluted sites, in µg/L.

Site	Cobalt	Copper	Zinc	Cadmium	Lead
Patroon Creek	0.44	5.0	9.6	0.037	2.6
Varuna River	215	441	247	86	267
Landfill Leachate	-	n.d.	72	65	n.d.
Don River*	-	9.1	13.8	0.734	-
FUSRAP Study	0.276	28.3	27.6	0.3	13.6
NYSDEC Regulations	NS	200	2000	5	25

*Don River data is presented as the dissolved concentration.

Varuna River data from Aggarwal et al., 2000. Landfill Leachate data from Bolton & Evans, 1991. Don River data from Warren & Zimmerman, 1994.

of samples upstream and downstream from the NLI site in February and June 2002. For comparison this data is also presented in Table 13. Differences in data between the FUSRAP study and this study are likely due to the differences in sampling location. The FUSRAP study sampled only from a stream near the National Lead Industries site, which contains a concentrated amount of contaminated sediment that surface and groundwater flow through. Mean concentrations of heavy metals from Patroon Creek, however, represent the entire watershed which is as heavily contaminated.

Overall, the mean concentrations of heavy metals in the Patroon Creek Watershed are an order of magnitude or more less than many streams, and even regulatory values for its stream classification.

5.3 Effect of Chloride on Release of Total Heavy Metals into the Stream Environment

Chloride show little effect on the transport of total and dissolved heavy metal concentrations during the study period in Patroon Creek (Appendix VI). The lack of correlation of chloride concentration with the variation in concentration of these metals is likely due to the greater affinity of these metals for particulates over chloride. As many

of these metals form inner-sphere complexes with particle surfaces, it is unlikely for chloride to induce desorption of these metals (Sparks, 2003). Changes in pH are more likely to affect inner-sphere complexation, as decreases in pH have been shown to break these complexes. In Patroon Creek, the pH is well buffered making desorption due to pH unlikely. If chloride played a significant role in the desorption of heavy metals from particle surfaces and further transport through the Patroon Creek Watershed, these metals would have a noticeable correlation with chloride concentration in both their dissolved and total concentrations. This strong correlation would likely be due to the formation of chloride complexes.

5.4 Effects of Particulates on Heavy Metal release into the Stream Environment

Suspended particulate matter has been shown in Figure 11 to correlate well with many of the heavy metals that have been focused on (Cu, Cd, Zn, Pb). This corresponding trend gives evidence that these metals are likely being transported through the watershed system adsorbed to particulates.

Storm event samples show this same positive correlation with heavy metals when various parameters (Cl, SPM, Discharge, Dissolved, Total and Particulate Cd, Cu, Pb and Zn) are displayed temporally. During the November 30, 2005 storm event, total metal concentrations followed the same trend temporally as SPM, related to increased discharge. The initial concentration of these three variables is likely due to a “first-flush” phenomenon seen in urban streams. This phenomenon is defined as the runoff of a large percentage of the pollutant load during the initial stages of a storm event (Lee et al., 2004). Sanden et al. (1997) showed that the highest concentrations of Zn occur during the initial 200 minutes of a storm event, because of this “first-flush”.

Dissolved Cd, Cu, Pb and Zn concentrations follow a trend similar to chloride during the November 30, 2005 event. The similar trend is more likely due to the effect of release due to increased discharge during storms than the effect of chloride concentration on these metals (Fig. 12). This has been shown by the lack of correlation between dissolved metals and chloride (Appendix VI). During the January 14, and 18, 2006 storm events the same trend between SPM and total Zn and Pb occurs. Dissolved Cd, Cu, Pb and Zn concentrations for these two events, unlike during the November 30, 2005 storm, correspond to the trend of SPM. This may be due to the leaching of these metals from the particle surfaces, after they had been released into the stream, by a mechanism other than chloride complexation.

5.5 Chloride Effect on Heavy Metal Partitioning between the Dissolved and Suspended Phases

K_d values for Cd and Cu do not show a correlation with chloride that would suggest partitioning from the particulate to the dissolved phase of these metals is occurring (Fig. 15). If this were the case, the near linear negative correlation between chloride-complex forming metals and chloride, shown by Warren and Zimmerman (1994), would be evident. The lack of this correlation may be due to these metals being attached to organic particulates, and Fe and Mn oxide sediments. Amrhein et al. 1990, and Amrhein et al. 1993 showed that these two metals have a strong correlation with organic matter. Also they had shown that organic sediments are released with flushing by DI water after the application of 100 M NaCl. Zn and Pb however show some negative effect of chloride on their partitioning between the dissolved and particulate phases (Fig. 15A). In Warren and Zimmerman (1994) the leacheable and organic fractions of sediment showed the highest K_d for Cd and Zn with increased chloride. This

may be the case for Pb, as the leacheable fraction of heavy metals is representative of those on carbonates and in the leacheable fraction. Because the sediment digestion used in this study removed metals in a leacheable phase rather than a total digestion, it could be assumed that Pb was most associated with this sediment fraction. This may be the same reasoning for Zn partitioning shown in Figure 15A. These assumptions are only based on the results of previous studies, as the effect of sediment type in conjunction with chloride concentration variation on heavy metal behavior in Patroon Creek was not studied. The drastic change in the overall partitioning trend of Pb and Zn in Figure 15B when samples that were below the MDL were added, suggest that there is no overall effect on the partitioning of these metals with changing chloride concentration. This suggests that chloride may have an effect on partitioning under some circumstances but does not have a strong effect in Patroon Creek. Warren and Zimmerman (1994) presented their data under the conditions of Figure 14A, in which K_d values correlating with dissolved metal concentrations below the MDL were removed. This leads to a bias in their results away from lower metal concentrations in the dissolved phase. Their results may also show a drastic change in the partitioning trend if all data were presented.

One question that could arise about the lack of partitioning of heavy metals due to changes in chloride concentration is that there was not a long enough interaction time between adsorbed metals and the surrounding chloride enriched water. This would be due to the slower rate of reaction for this type of interaction, to break inner-sphere complexes. The slower kinetics of this type of reaction may explain the noticeable changes in partitioning of heavy metals seen in estuaries. The adsorbed metals may have been reacting with high chloride waters for extensive periods of time when they finally

settled in the location in which they were sampled from. This reasoning is not very likely for this study as samples were filtered and analyzed at time periods ranging from days to weeks after collection. This then, covers a variety of interaction times. Therefore whether a long or short reaction time was allowed, chloride showed little to no effect on the partitioning of heavy metals between the particulate and dissolved phases in the Patroon Creek Watershed. This fact could also have biased metal sorption toward particulates, due to the long interaction time with particulates in solution before filtration. This may have pulled metals that were in the dissolved phase at the time of collection into the particulate phase.

It would also be expected that K_d values in Figures 16 through 18 would increase with increases in pH and decrease as pH decreases, thus releasing heavy metals into the dissolved phase with decreasing pH values. This is due to the strong effect that pH has on the inner complexes that many heavy metals form. The concentrations of pH have small variations due to the Patroon Creek being a well buffered system, which then have little effect on heavy metals sorption processes.

5.6 Possible Bias Toward Low-Chloride Events

One possible problem in the analysis of samples used for the partitioning of heavy metals between the dissolved and suspended phases was the setting of the auto-sampler. The auto-sampler was programmed to begin collection of samples at an increase in stage height over .3 m. Based on the hydrographs of storms in which there was a noticeable increase in conductivity correlating with higher chloride concentrations, the discharge for these events was low and often times did not increase over .3 m (Fig 4-6). Because of this, partitioning results are biased more towards rain event conditions than storm events

in which chloride was high. If these events were more accounted for, partitioning results would have been more representative of icy conditions in which road salt was extensively applied.

5.7 Future Work

Some future work to fully understand the effect of chloride on transport of heavy metals in an urban watershed would include more intensive sampling at the beginning of a storm, sediment analysis, filtration of samples from all sites, larger partitioning samples, and programming the auto-sampler to collect samples under lower flow, or high specific conductivity conditions. More intensive sampling at the beginning of a storm would allow for more understanding of the relationship between chloride and trace metals during the “first-flush” phenomena. Sediment analysis would allow for the determination of what sediment types are more favorable to the partitioning to the dissolved phase of heavy metals with increasing chloride. Filtration of samples from all sites would allow for a wider understanding of possible chloride complexation and what type of partitioning is occurring throughout the watershed, and not only at the Gage. Collecting larger samples for partitioning analysis would presumably yield larger sediment fractions for partitioning analysis, particularly during winter storms where runoff and discharge are lower than other seasons. Finally, reprogramming the auto-sampler to sample under lower discharge conditions would lead to the collection of samples that are more representative of snow and ice conditions, as well as snow melt, when sodium chloride is at its highest in the stream environment.

6. Conclusions

Increases in chloride concentration due to increased application of NaCl to road surfaces as a deicing salt has been shown to increase the mobilization of heavy metals in both laboratory desktop studies and road side soil studies (Amrhein et al., 1992; Backstrom et al., 2004). This has also been observed in stream studies, noting that increases in NaCl as a road deicing salt increases the partitioning of heavy metals toward the dissolved phase. In Patroon Creek, however, when the effect of chloride on heavy metal transport and partitioning are considered on a watershed scale, this was not observed during the study period of October 2004 to March 2006. Answers to the objective questions based on the results of this study are presented as follows:

1. The largest concentrations of heavy metals were seen in the particulate phase as well as in total concentrations. This is shown by the strong correlations to SPM in Figure 11-14. This is likely due to the stronger affinity of heavy metals for particulate surfaces through inner-sphere complexation. Dissolved heavy metal concentrations were very small and were 2 to 3 orders of magnitude lower than NYS Standards for a Class C stream.
2. Figures 15-18 show that chloride has little effect on the partitioning of heavy metals between the dissolved and particulate phases. This may be due to the inner-sphere complexation mentioned in Conclusion 1. This may also be due to the phenomenon shown in Figures 5 and 6 in which storm events with higher specific conductance values related to chloride concentration did not occur during events with discharge values sufficient for triggering the auto-sampler. Therefore storm events that may have had chloride concentrations high enough to induce a

strong enough ionic strength to break inner-sphere complexes leading to more heavy metals in the dissolved phase, were not sampled.

3. Chloride was observed to have little to no effect on the aqueous transport of total and dissolved heavy metals in Patroon Creek. Suspended Particulate Matter was observed to have the greatest effect on the transport of Cd, Cu, Pb and Zn.

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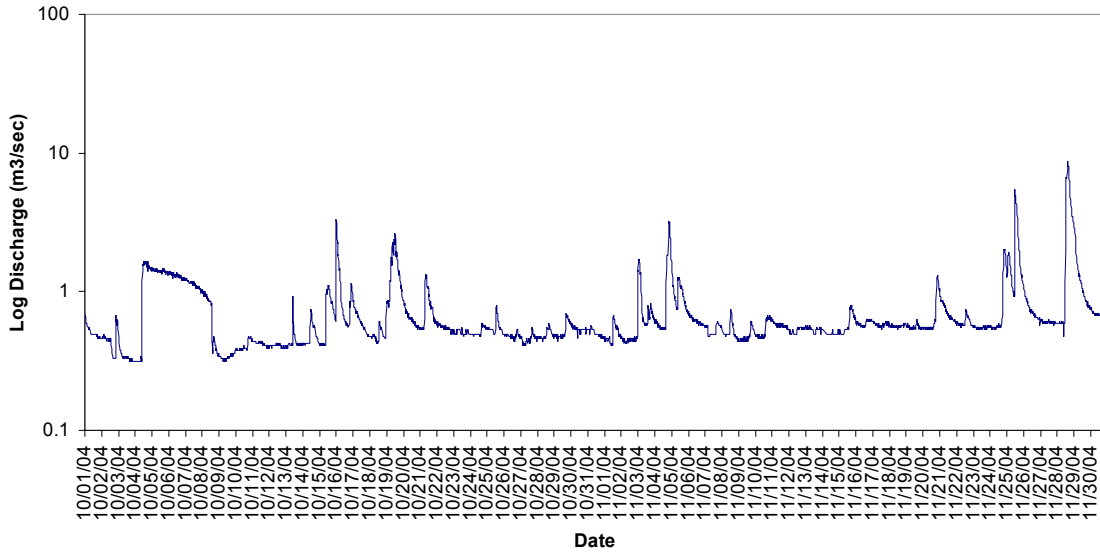
Appendix I. Peak Stream Flow Data for Patroon Creek

Water Year	Date	Gage* Height (m)	Stream-flow (m ³ /s)	Water Year	Date	Gage* Height (m)	Stream-flow (m ³ /s)
1979	Feb. 24, 1979	2.63	9.7635	2003	Jul. 21, 2003	1.25	11.32
1980	Oct. 03, 1979	2.78	11.1785	2004	Oct. 29, 2003	1.06	11.2068
1981	Feb. 20, 1981	2.65	9.905	2005	June 29, 2005	1.5	17.5177
1982	Aug. 09, 1982	2.97	12.735	2006	Jan. 18, 2006	1.27	14.2066
1983	Sep. 21, 1983	3.41	17.546				

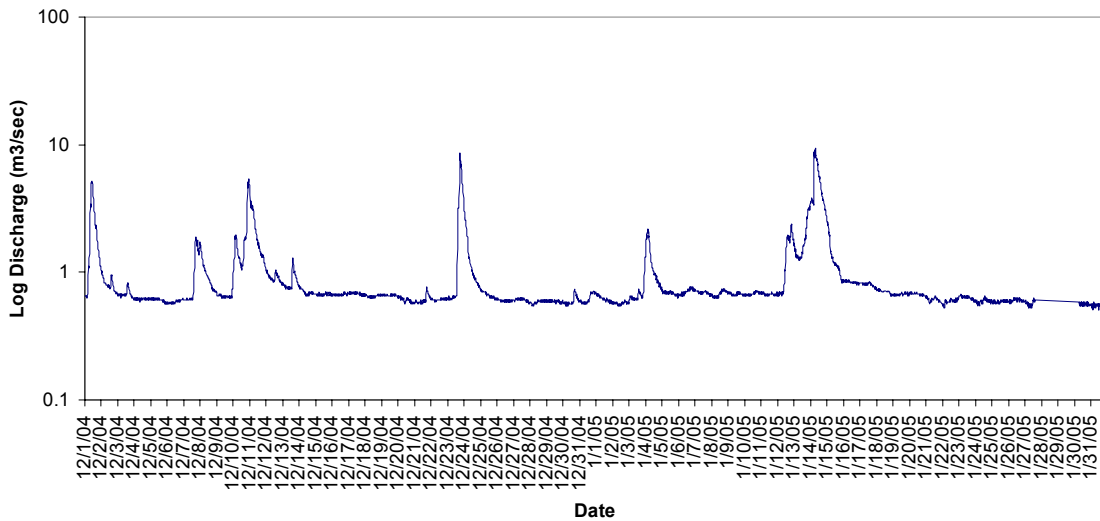
* datum change from 1979-1983 to 2003-present

Appendix V. Hydrographs for Patroon Creek from October 2004 to February 2006. Each hydrograph is 2 months of time, with date on the x-axis and discharge in m³/sec on the y-axis.

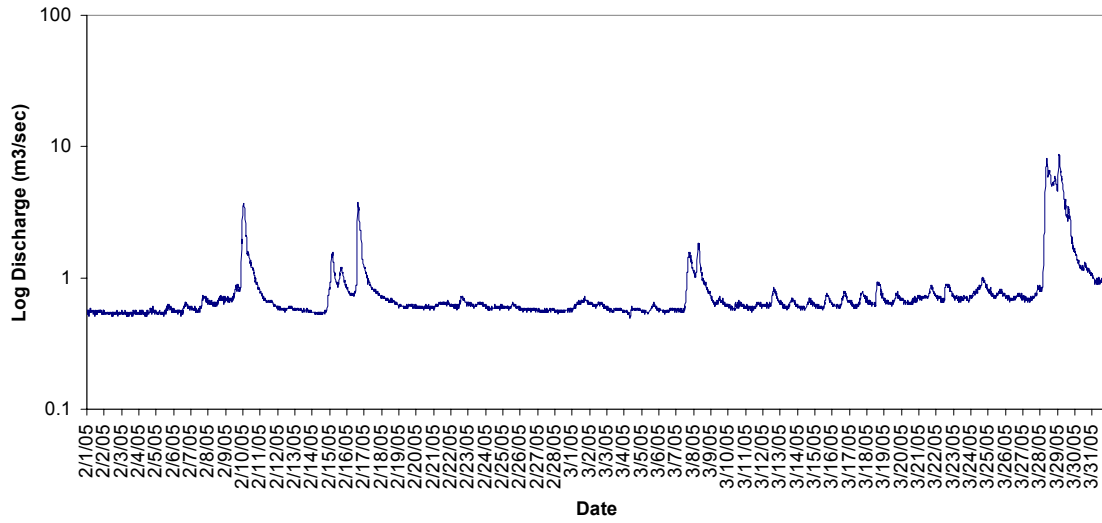
Patroon Creek Discharge, October and November 2004



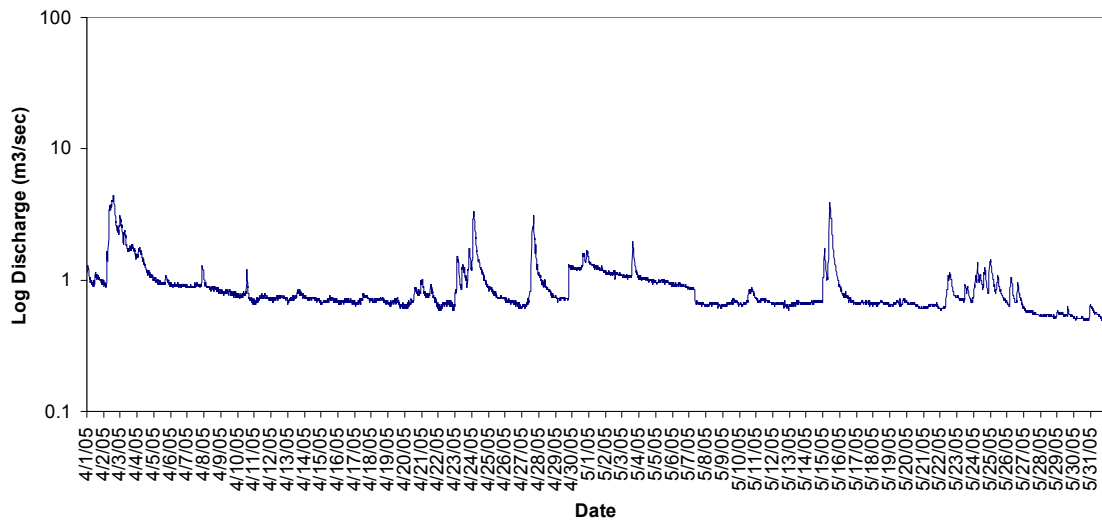
Patroon Creek Discharge, December 2004 and January, 2005



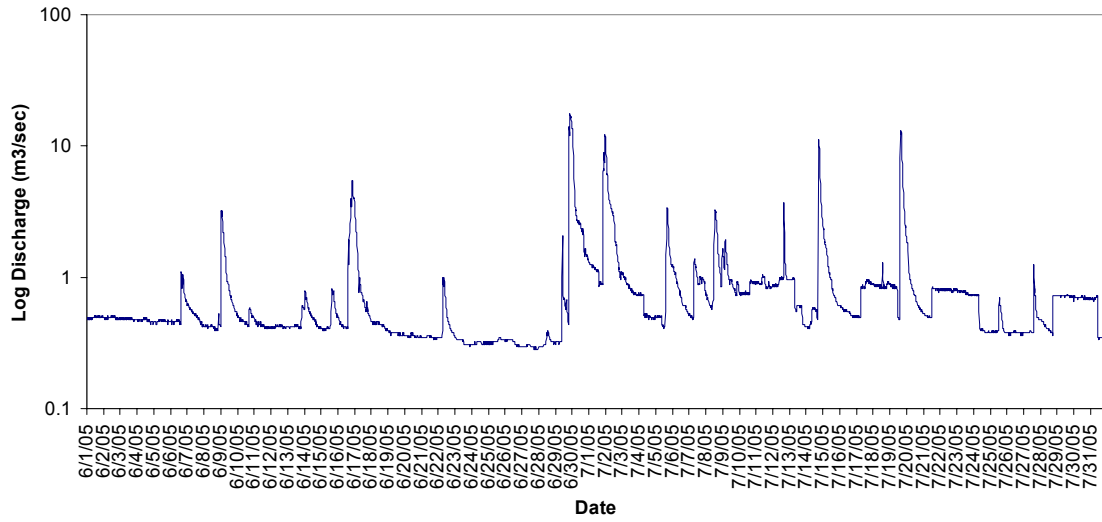
Patroon Creek Discharge, February and March 2005



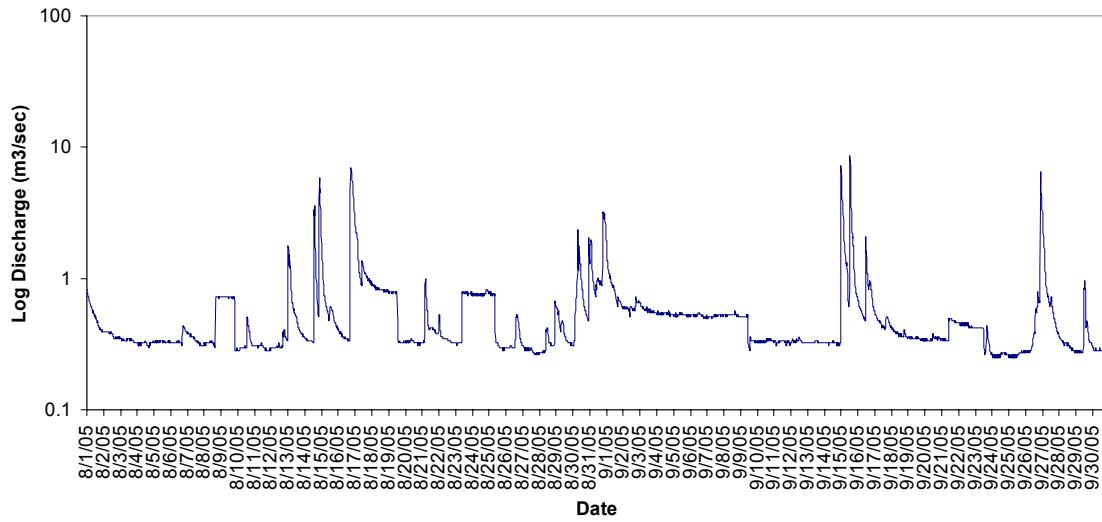
Patroon Creek Discharge, April and May 2005



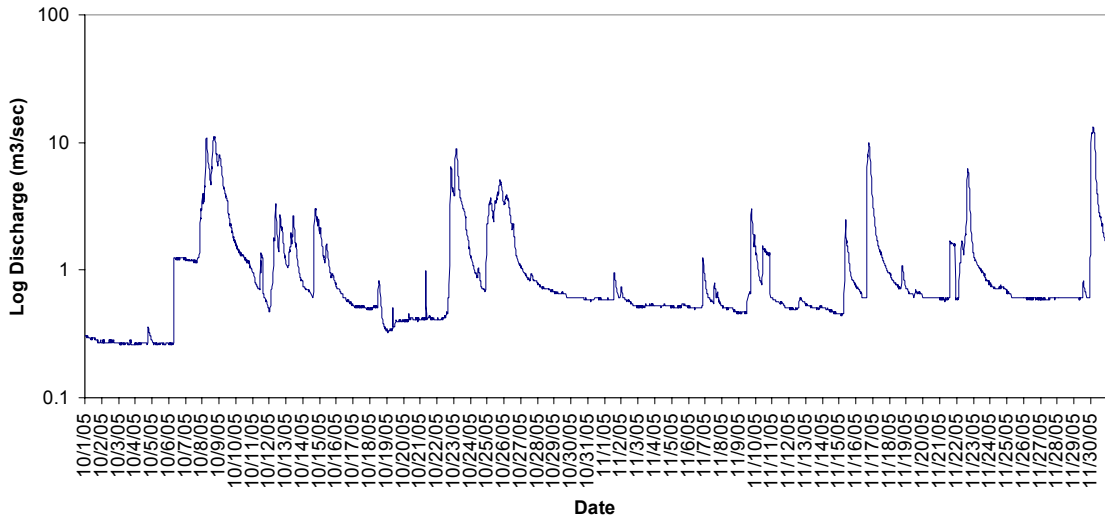
Patroon Creek Discharge, June and July 2005



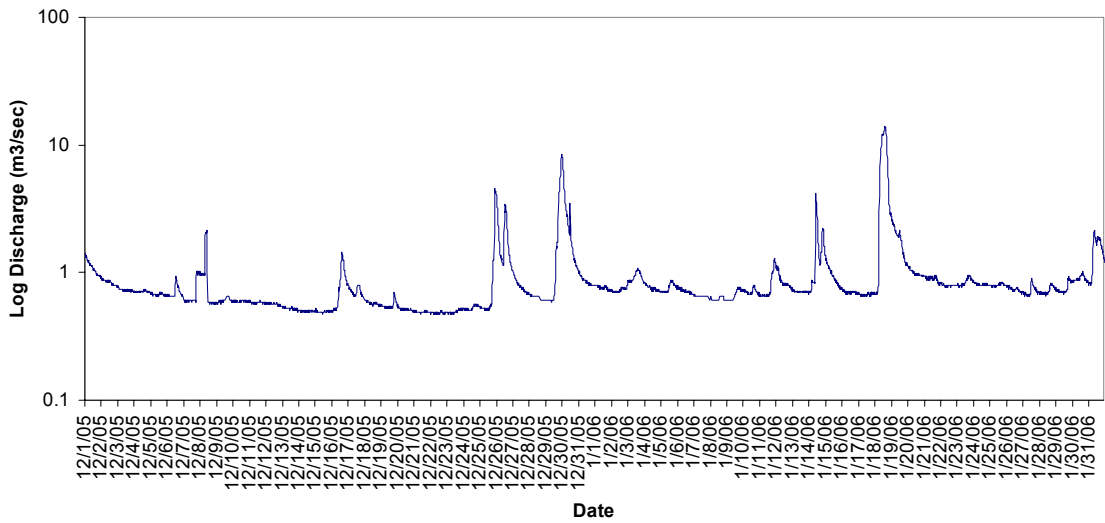
Patroon Creek Discharge, August and September 2005



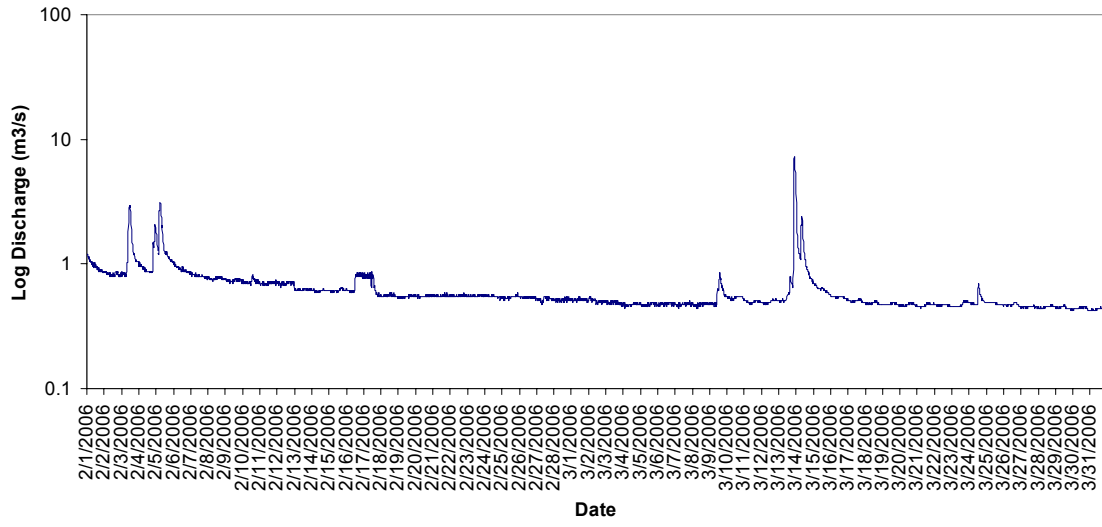
Patroon Creek Discharge, October and November 2005



Patroon Creek Discharge, December 2005 and January 2006

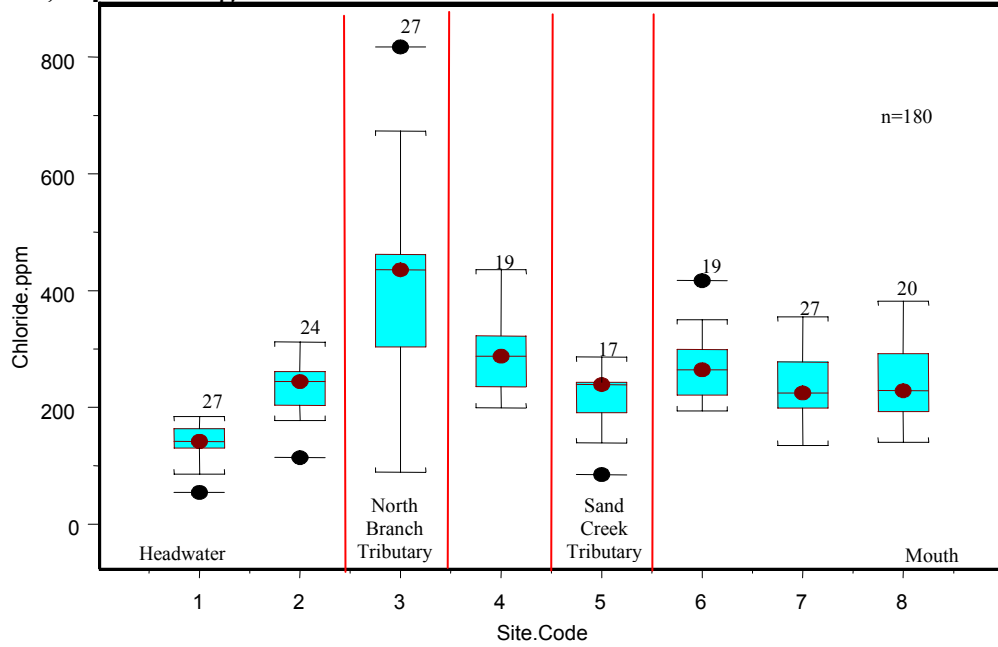


Patroon Creek Discharge, February and March, 2006

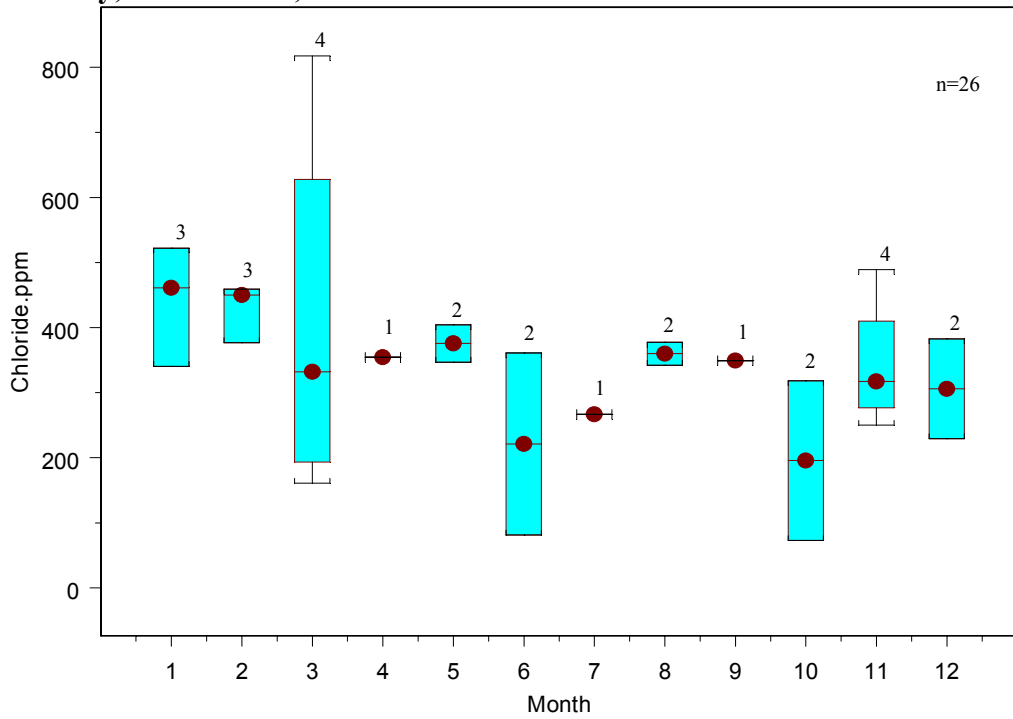


Appendix VI. Related Figures

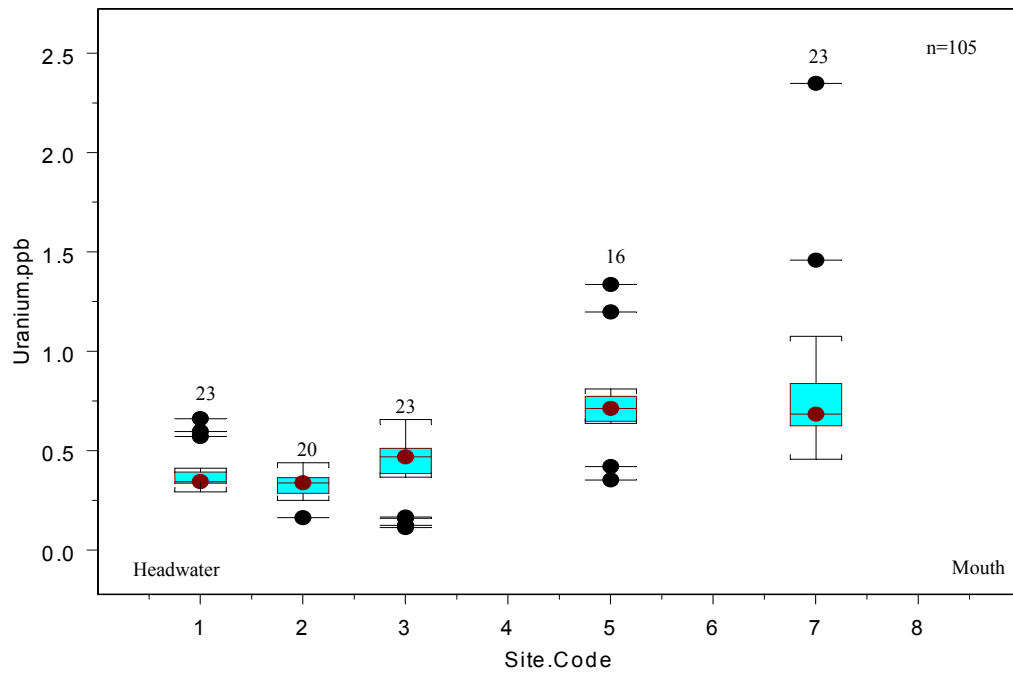
Spatial Variation of Chloride concentration in Patroon Creek Watershed from October, 2004 to March, 2006. Site Code is noted from 1, representing Rapp Rd, to 8, representing Erie Blvd.



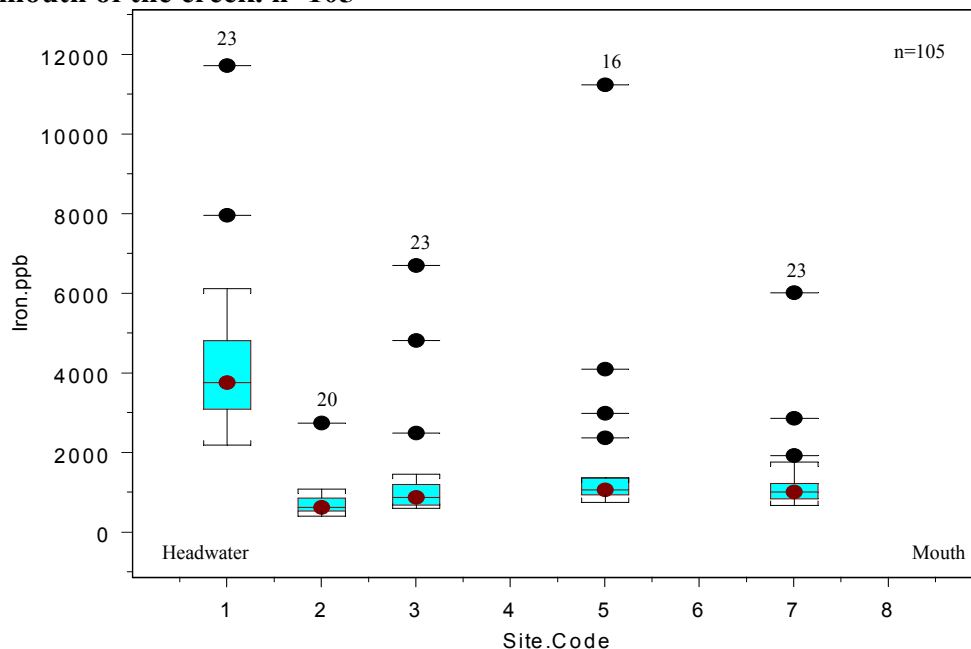
Chloride concentration as a function of month of the year from October, 2004 to March, 2006 at North Branch (Site 3). Month of the year is noted from month 1, January, to month 12, December. n=26



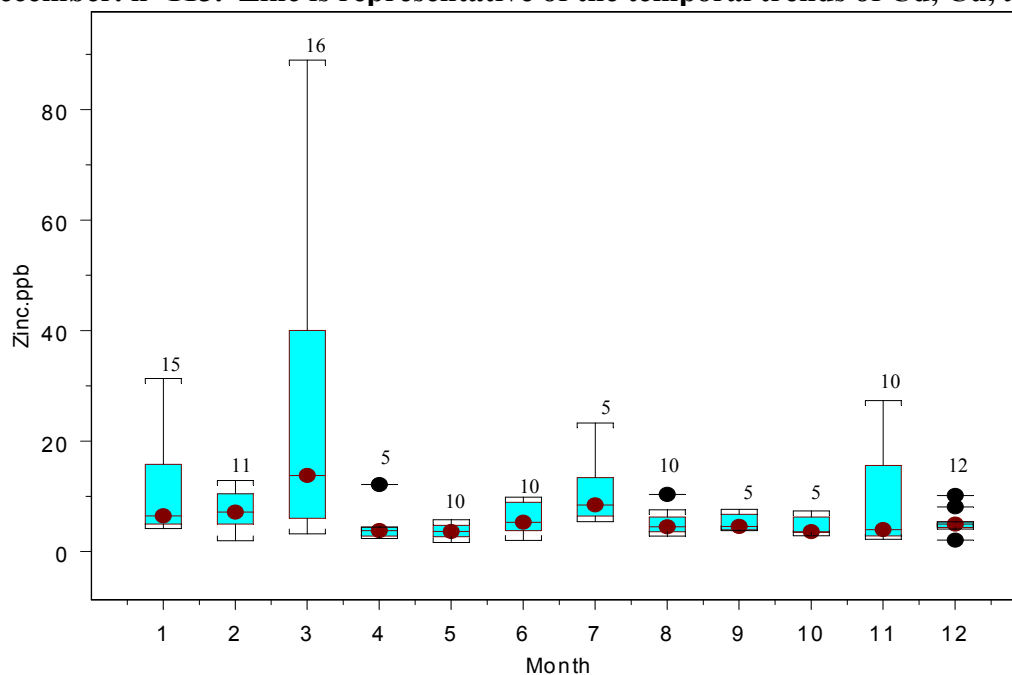
Uranium concentration as a function of site location along Patroon Creek from October, 2004 to March, 2006, from the headwaters at Site 1 to Site 8 near the mouth of the creek. n=105



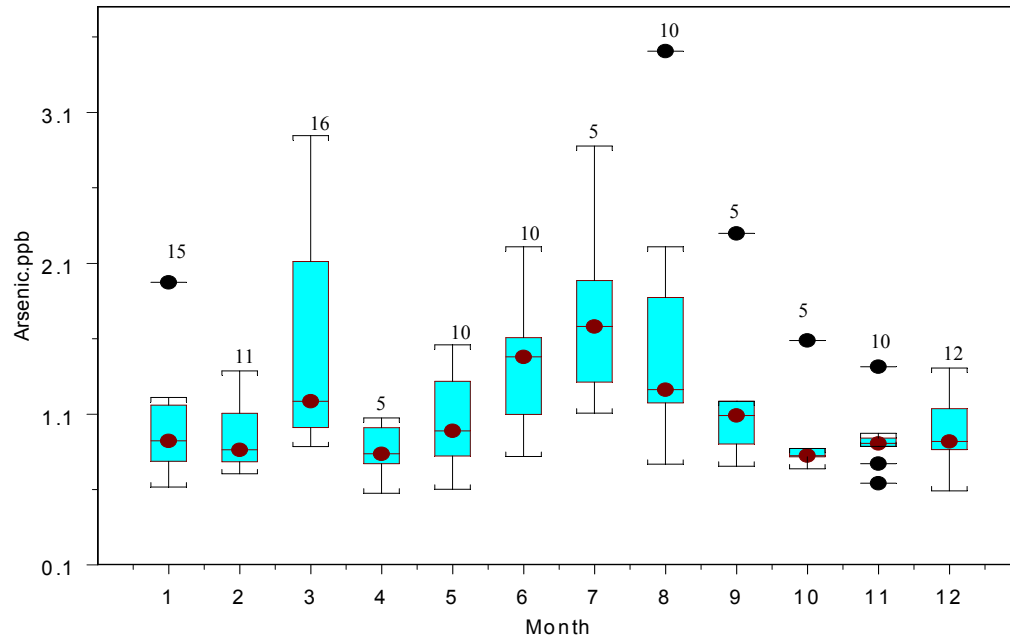
Iron concentration as a function of site location along Patroon Creek from October, 2004 to March, 2006, from the headwaters at Site 1 to Site 8 near the mouth of the creek. n=105



Zinc concentration as a function of the month of the year for all sites along Patroon Creek from December, 2004 to March, 2006, month 1 is January, and month 12 is December. n=113. Zinc is representative of the temporal trends of Cd, Cu, and Pb



Arsenic concentration as a function of the month of the year for all sites along Patroon Creek from December, 2004 to March, 2006, month 1 is January, and month 12 is December. N=113



Appendix IX. Related Writing

Uranium Trends in the Patroon Creek Watershed

Uranium, of all the metals studied, showed the most spatial variation in the watershed. This variation is likely due to atmospheric deposition of uranium from the National Lead Industries site. There is a noticeable increase of uranium in Appendix II downstream of the site, and a very noticeable increase at the Sand Creek site (Site 5), a tributary to Patroon that does not flow through the NLI site. This supports the idea that atmospheric deposition has occurred to the northwest of the site. Uranium, now in the surrounding soils (Arnason and Fletcher, 2003) is likely transported through the stream with the groundwater fraction of stream flow as suggested in Figure 10.

Relating results from Gage site to other sites in the Patroon Creek Watershed

Although there is only data for the effect of chloride concentration on the partitioning of heavy metals between the dissolved, and particulate phases from the Gage site, there are many assumptions that can be made regarding the other sites. This is due to the lack of spatial variation in concentration of many of the metals in question. Also the similarities in chloride concentrations support the idea that the results from the Gage site could be applied to the other sites, and the watershed as a whole. This however could be disputed because many of the storm events that had higher chloride concentrations did not produce enough suspended solids to confidently analyze them in regard to effect of chloride concentrations on the partitioning of heavy metals. Based on the mean and maximum value of chloride for samples analyzed for partitioning between the particulate and dissolved phases of these metals, North Branch samples are not well represented by

those from the Gage site for partitioning analysis. The mean concentration in partitioning samples from the Gage site was 221 ppm Cl, and the maximum value was 454 ppm Cl, which are representative of all other sites. The North Branch, however, has a mean value of near 450 ppm and a maximum of more than 800 ppm Cl. Therefore many inferences made for the samples at the Gage site are likely to apply to all others except for the North Branch site as its chloride values are almost twice those of the others, which may cause different results to occur.