



# Patterns of c-q hysteresis loops and within an integrative pollutograph for selected inorganic and organic solutes and *E. coli* in an urban salted watershed during winter-early spring periods



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## ABSTRACT

Concentration – discharge (c-q) hysteresis loops are used to qualitatively understand solute transport pathways to streams. The majority of c-q studies involve non-urban areas in environmental settings such as the subtropics, mountains, and high latitude rivers. Only a few involve urban or urban salted watersheds. In this study, we explore c-q hysteresis plots and pollutographs for a variety of inorganic solutes ( $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{SiO}_2$ ,  $\text{NO}_3^-$ ), dissolved organic carbon and an indicator of the aromatic fraction ( $\text{SUVA}_{254}$ ), and a microbiological indicator (*E. coli*) in an urban salted watershed. The major hydrologic events are snow melts. The overarching hypothesis is that the hysteresis behavior can be explained by extending the pathway analysis (i.e., relative importance of storm event water,  $C_{SE}$ ; groundwater  $C_G$ ; and soil water,  $C_{SO}$ ) from the Evans-Davis classification scheme that describes six behaviors to account for differences in source locations and the biogeochemical behavior of the solutes along these pathways. Data sets for the years 2013, 2014, and 2015 were assembled from a series of undergraduate and graduate research projects performed over this period. The results of these studies indicate that: 1)  $\text{Cl}^-$  and  $\text{Na}^+$  exhibit a combination of C2 ( $C_{SE} > C_{SO} > C_G$ ) and C3 ( $C_G > C_{SE} > C_{SO}$ ) behavior during salting season and A1 ( $C_{SO} > C_G > C_{SE}$ ) and A2 ( $C_{SO} > C_{SE} > C_G$ ) behavior in non-salting times; 2)  $\text{SiO}_2$  shows A3 ( $C_G > C_{SO} > C_{SE}$ ) behavior in all events, 3)  $\text{K}^+$  changes from C2 to C1 ( $C_{SE} > C_G > C_{SO}$ ) with concentration depletion over subsequent events; 4)  $\text{NO}_3^-$  changes from A2 to C1 or C2 with concentration depletion over subsequent events; 5) DOC and  $\text{SUVA}_{254}$  exhibit C2 and A1 behavior, respectively; 6) *E. coli* changes from C2 to A2 over subsequent storms; 7)  $\text{Cl}^-$  and  $\text{Na}^+$  peak before the rising limb with a slight lag in the  $\text{Na}^+$  peak and 8) *E. coli* does not exhibit first-flush behavior. An integrative pollutograph for a snow melt event shows, 1)  $\text{K}^+$  and DOC peak together three times, unrelated to any additional event such as rain; 2) DOC becomes more aliphatic at its first peak, and 3)  $\text{NO}_3^-$  has a concentration decrease at the second DOC/ $\text{K}^+$  peak and peaks on the declining limb after the third DOC/ $\text{K}^+$  peak. These observations can be explained in terms of the c-q plots (e.g., importance of event water), environmental behavior (e.g., conservative solute), the nature of the urban landscape (e.g., pavement), and season (e.g., damped microbial activity). We interpret the multiple concentration peaks to indicate water masses originating from different compartments in the watershed are reaching the stream at different times and with different chemistries. These results extend the work of previous studies and may serve to help develop a fingerprint of solute behavior that can be used to more fully explore early season biogeochemical dynamics in an urban, salted, snow-melt dominated watershed.

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## 1. Introduction

Hysteresis reflects how a variable depends not only on time or rate, but on the history of variation. It reflects irreversibilities in controlling processes, for example, as commonly observed in

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magnetism and adsorption. Hysteresis loop graphs (Fig. 1a) have been used in stream hydrology to explore decoupling of a variety of physical or chemical concentrations (e.g., suspended sediments, solutes) versus discharge in streams as a function of hydrologic events such as storms and season changes (e.g., Williams, 1989; Kurashige, 1994; Gellis, 2013; Andermann et al., 2012; Creed et al., 2015; Fovet et al., 2015). In these cases, hysteresis arises when the concentrations on the rising limb of the hydrograph are not equal to the concentrations on the falling limb (Evans et al., 1999). The slope of the hysteresis loop over a stream hydrograph for events such as snow melt or storm is related to whether the concentrations are increased in the system due to flushing (positive slope) or decreased due to dilution (negative slope) (Fig. 1b). If the slope is zero, concentration and transport are considered to be in dynamic equilibrium. This condition is often referred to as chemostasis (Creed et al., 2015; Litt et al., 2015). The rotation direction of the loop has been related to whether the sources for concentrations are more local to the stream (clockwise) or more distal (counter clockwise) (e.g., Gellis, 2013; Creed et al., 2015). In other words, the concentration peak during an event occurs before the discharge peak in the case of the clockwise rotation and after the discharge peak in the case of the counter-clockwise rotation.

The concentration changes that occur in a river over the course of a hydrologic event can be related to the changes in the relative importance of transport pathways during the event (Fig. 2). Pathway I, direct precipitation input is not considered a major contributor to the mass of water or of chemical input into the river. Pathway II, surface runoff, is directly responsible for the early, rapid (i.e., first flush) concentration increases in the river. This water can profoundly change the chemistry of the river, but not necessarily

discharge. Increasing discharge is slightly delayed and is the result of Pathway II and the increasing importance of pathway III (interflow). During the falling limb, pathways IV (bankflow) and eventually V (deep base flow), become more dominant. Differentiating the contribution of these multiple pathways on solute concentrations is challenging (e.g., Creed et al., 2015; Evans and Davis, 1998).

To gain insights into the relative importance of changing pathways on solute concentrations, Evans and Davis (1998) proposed a more simplified three-component model (Fig. 2c) that involves surface event water (pathways II and III), soil water (pathways III and IV) and groundwater (pathway V). These pathways can be thought of as a measure of proximal (i.e., soil) or distal (i.e., groundwater) sources (e.g., Creed et al., 2015) or a distinction between direct and indirect transport (e.g., McElmurry et al., 2013). Using synthetic event hydrographs involving these three pathways, Evans and Davis (1998) developed a set of c-q hysteresis loops (Fig. 3) that show how the loop patterns change as a function of the relative importance of these three sources. Thus, one can infer the influence of these three components by constructing c-q hysteresis plots for a system and comparing the results to Evans and Davis's synthetic patterns. Many studies on both solute and suspended sediment concentrations have used this approach (e.g., Evans et al., 1999; Rose, 2003; Butturini et al., 2006; Baca, 2008; Aubert et al., 2013; Sun et al., 2014; Litt et al., 2015; Creed et al., 2015; Burt et al., 2015; Engel et al., 2016).

The majority of previous c-q studies involve non-urban areas in environmental settings such as the subtropics, mountains, and high latitude rivers (e.g., Goodman et al., 2011; Mann et al., 2012; Yang et al., 2013; Litt et al., 2015). Only a few c-q hysteresis studies involve urban (e.g., Rose, 2003) or salted watersheds (e.g., Sun et al., 2014). In this study, we continue our work on salted urban environments (e.g., Long et al., 2015) by exploring c-q hysteresis plots for a variety of inorganic solutes ( $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{SiO}_2$ ,  $\text{NO}_3^-$ ), dissolved organic carbon, an indicator of the aromatic fraction ( $\text{SUVA}_{254}$ ), and a microbiological indicator (*E. coli*). The overarching hypothesis is that the hysteresis behavior can be explained by extending the pathway analysis from the Evans-Davis classification scheme to account for both location of sources and the biogeochemical behavior of the solutes along these pathways. For example, in few systems would dissolved  $\text{SiO}_2$  have contaminant inputs. Thus, natural mineral sources would be dominant and we might expect the Evans-Davis classification of C3 (Fig. 3c) in which groundwater and soils water would be dominant over surface event water.

Few c-q studies (e.g., Evans et al., 1999; Fucik et al. 2012; Goodman et al., 2011; Long et al., 2015; Engel et al., 2016) have explored trends over a sequence of multiple events, within a sequence of events or watersheds greater than orders 1 or 2. In this study, we further extend the use of the c-q hysteresis technique and interpretations via the Evans-Davis classification by study of a 3rd order stream, that includes sequences of multiple events.

## 2. Materials and methods

### 2.1. Study area

The study watershed is the Red Cedar River Watershed, Michigan, USA (Fig. 4) which has an area of approximately 1194 km<sup>2</sup> and a length of 82.2 km. The watershed is a glaciated landscape characterized as medium textured glacial till with abundant eskers that comprises the Glacial Drift Aquifer (Westjohn et al., 1993). This aquifer and the underlying sandstone Saginaw Aquifer (Westjohn and Weaver, 1994) are the main aquifers in the watershed. At its confluence with the Grand River, the landuse is highly urbanized including the cities of Lansing and East Lansing and the campus of Michigan State University (MSU). The population of East Lansing is

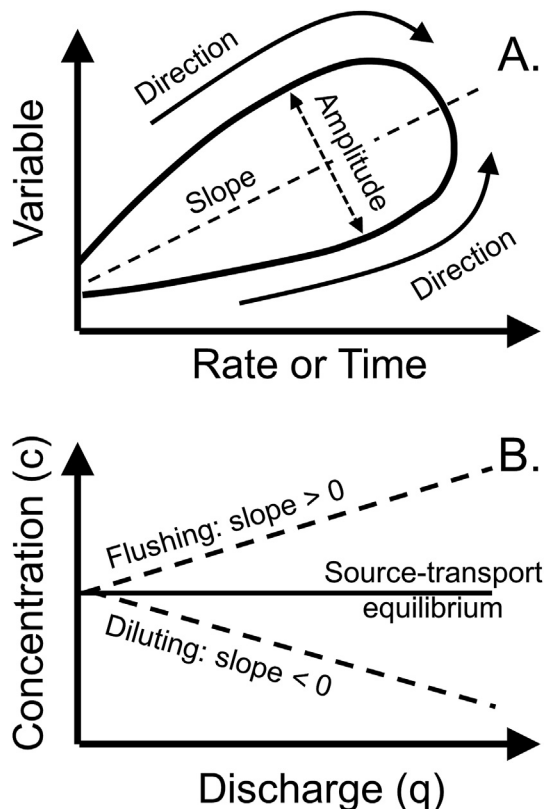
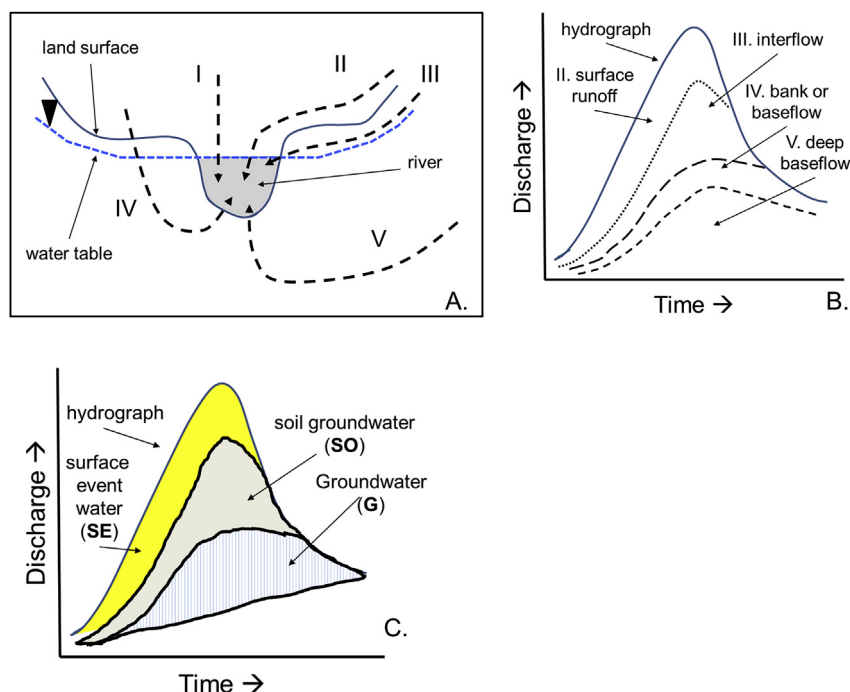
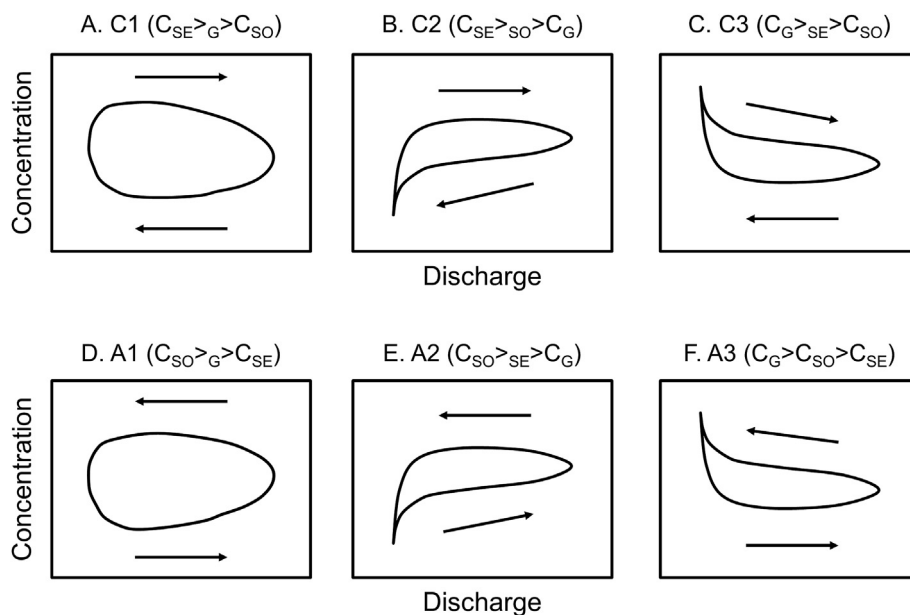


Fig. 1. Depiction of hysteresis loops. a. General nature of a hysteresis loop showing features such as slope, amplitude and direction, and directions. b. c-q plot showing interpretation process from slope of the hysteresis loop. Modified from Creed et al. (2015).



**Fig. 2.** Conceptual framework for the input of solutes to streams. a. pathways of water of water to streams where I. is direct precipitation input, II. is surface runoff, III is interflow, IV. is bank flow or baseflow, and V. deep baseflow; b. relative contributions of the various water pathways in a to the total stream hydrograph; and c. three component system (Evans and Davis, 1998) depicting surface event water (SE), soil groundwater (SO) and groundwater (G). Modified from Long et al. (2015).



**Fig. 3.** Synthetic event hysteresis loops and classification developed by Evans and Davis (1998) depicting how the slope of loop and rotation direction changes (clockwise, C; anti-clockwise, A) as a function of the relative imports of three components; surface event water (SE), soil water (SO), and groundwater (G). Modified from Evans and Davis (1998).

approximately 100,000 inhabitants during the time of the sampling, as MSU was in session. Upstream communities of Williamson, Okemos, Webberville and Fowlerville contribute another 30,000 inhabitants. Landuse/land cover is diverse consisting of grasslands (23%), wetlands (16%), forest (10%), agricultural (35%), and developed residential, commercial, and industrial land (14%). In portions of the watershed there is the potential for the influence of septic systems on river chemistry. However, much of the land is engineered to drain water from the soil by way of drain tiles, buried

pipes that collect and convey groundwater from the soil to the river. Urban areas are largely drained by storm sewers. Spring snowmelt and summer rains are normally the dominant hydrologic events for this river. When precipitation occurs, much of it runs off impervious surfaces and goes directly into storm drains. Waters drained by both drain tiles and storm sewers are not treated and run through pipes to outfalls along the river. A series of maps showing data relevant to the watershed, such as landuse distribution, population density, geology, can be found at <http://redcedarriver.weebly.com/>



Fig. 4. Map of the Red Cedar River, Michigan showing sampling site in East Lansing, Michigan. Map modified from [http://en.wikipedia.org/wiki/Red\\_Cedar\\_River\\_\(Michigan\)](http://en.wikipedia.org/wiki/Red_Cedar_River_(Michigan)). Last assessed December 7, 2016.

[map-gallery.html](#).

The data reported here originate from a collection of research and training activities that include graduate student projects and undergraduate student laboratory projects in an environmental geochemistry class offered at Michigan State University. Data sets from 2013, 2014, and 2015 have been selected because they offer 1) a variety of chemical species to be explored and 2) a temporal aspect (e.g., salting and non-salting periods). The graduate student projects and the class projects were not coordinated with respect to the data collected (i.e. parameters measured and sampling times) as they had different research goals, but sampling and analysis methods were identical. For example, the class projects focused on the behaviors of  $\text{Cl}^-$  as a conservative solute with contaminant sources (e.g., road salt) and  $\text{SiO}_2$  as a non-conservative (e.g., diatom uptake) with natural sources (e.g., mineral-water interactions). Total dissolved solids measurements were also obtained. The graduate projects focused on first flush and included solutes such as  $\text{NO}_3^-$  in addition to  $\text{Cl}^-$  but did not include  $\text{SiO}_2$ . In addition, as the graduate project evolved over time, more species were added (e.g.,  $\text{K}^+$ ).

Thus, even though the data sets are not comparable in all species, the combined analysis of the data affords insight into event c-q hysteresis behavior of  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{Na}^+/\text{Cl}^-$  molar ratios, total dissolved solids,  $\text{K}^+$ ,  $\text{SiO}_2$ ,  $\text{NO}_3^-$ , dissolved organic carbon,  $\text{SUVA}_{254}$ , and *E. coli* a salted urban environment. To the best of our knowledge, this is the first reporting of such behavior for *E. coli* in any system.

## 2.2. Sampling and analysis

The Red Cedar River sampling site was on the campus of MSU, which is a 3rd order stream at this point (Fig. 4). The advantage of this location was that samples could be rapidly transported to the laboratory for proper storage and subsequent analysis. From the class projects that extend back to 1999, we have learned that daily samples adequately characterize solute behavior during hydrologic events at this site, so most of that data is at this frequency. However, in the graduate student projects, two or three samples per day were collected over the first few days of the hydrographs to see if more information could be extracted about first flush. Our continued study of the Red Cedar has also revealed that the lag time between hydrologic event (e.g., rain, snow melt) and peak discharge is typically 2–3 days.

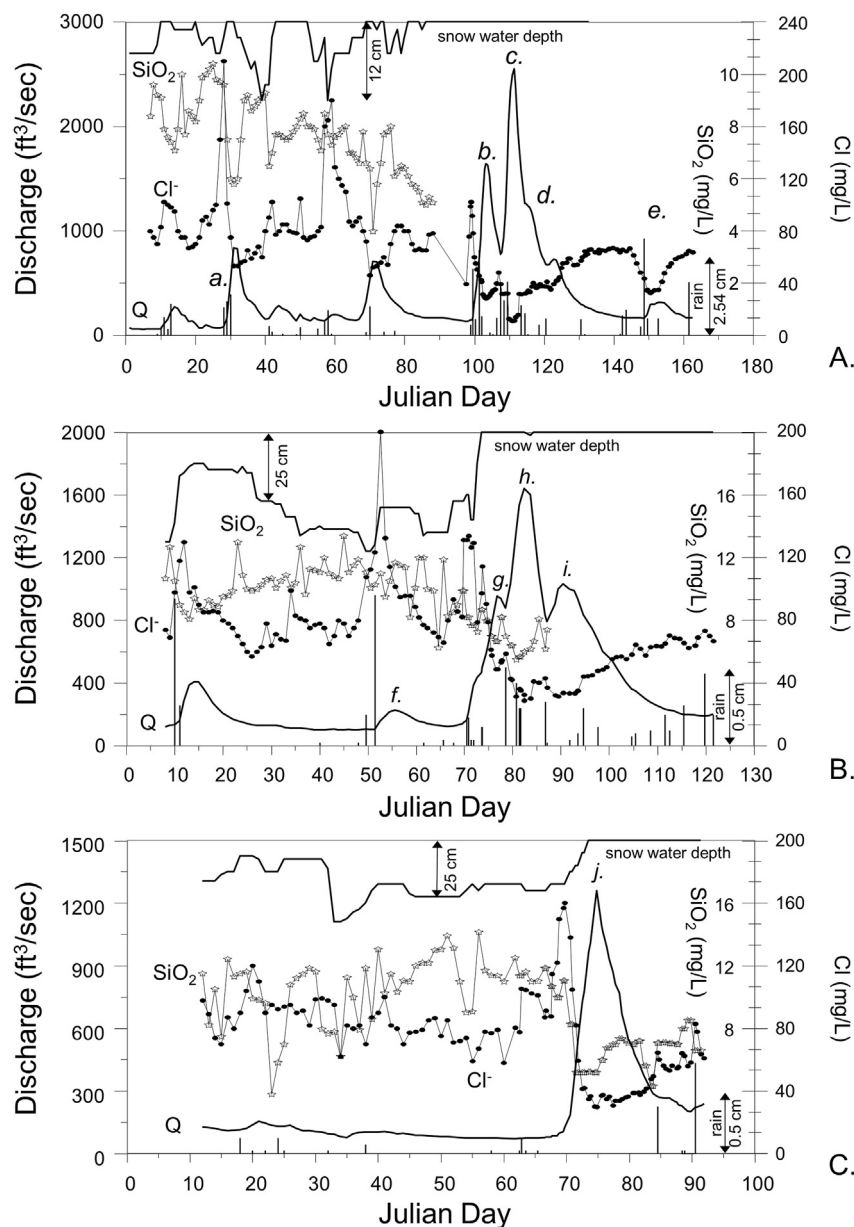
Although the two types of projects had different foci, measurement techniques were consistent for each parameter between studies. Samples were collected from the center of the river at a depth of about 30 cm at bridge crossings in appropriate pre-cleaned and river-rinsed bottles. Nitrate, chloride, sodium, potassium samples were collected in polyethylene bottles, filtered through 0.45  $\mu\text{m}$  Millipore filters, and after a short transit to the laboratory, stored at 4 °C until analysis. Nitrate and chloride concentrations were determined by ion chromatography using EPA method 300.1, while sodium and potassium were determined by emission spectroscopy using EPA method 273.1 (EPA-NERL,

1974). Some  $\text{Cl}^-$  analyses were done by specific ion electrode and it is the only solute to be measured by two techniques. When the two  $\text{Cl}^-$  data sets were combined to allow for the analysis of a longer time sequence (e.g., Fig. 5a, b, c), the data matched up and the data trend was continuous. Total dissolved solids concentrations were done at the time of collection using Myron L 4PII conductivity/TDS/resistivity meter. Silica was determined by the heteropoly blue method (USEPA, 1983) using the CHEMetrics vacu-vial system.

Samples for DOC (and  $\text{SUVA}_{254}$ ) were collected in acid-washed, ultra-pure water rinsed and baked glass bottles. Analysis was performed using a persulfate-digestion total organic carbon analyzer and ultraviolet absorbance photometry using EPA method 415.3. Samples for *E. coli* analysis were collected in 1-L sterile polypropylene bottles using defined substrate method Colilert-18TM Quanti-Tray 2000 (IDEXX Laboratories, Inc.). All

samples were measured in duplicate in three serial dilutions. Results are reported as MPN/100 mL (EPA 2007: IDEXX/Std. Methods 9223B).

Discharge measurements were obtained from the USGS gaging station (Hydrologic Unit 04050004) located along the river on the MSU campus. This station has been collecting 15 min discharge data since 1902. By using this station, the chemical data reflect the upper 900 km<sup>2</sup> of the Red Cedar watershed. As such, the site would be characterizing as a 3rd order stream. Precipitation data were collected from Michigan State University Enviro-weather (<http://www.agweather.geo.msu.edu/mawn/>), which has a station on the campus of MSU. Snow data (here we use snow water depth) was compiled from National Oceanic Atmospheric Administration's U.S. daily snowfall and snow depth data base (<https://www.ncdc.noaa.gov/snow-and-ice/daily-snow/>).



**Fig. 5.** Stream hydrographs for a. 2013, b. 2014, and c. 2015. Data sources are discussed in the text. Solid line is stream discharge (Q), solid dots are  $\text{Cl}^-$  concentrations, and open stars are  $\text{SiO}_2$  concentrations. Snow water depths are indicated on a reverse scale from the top of the graph and precipitation amounts indicate as vertical bars.



### 3. Results and discussion

#### 3.1. Stream hydrographs

The combined class project and research data sets comprise both snow melt and rain events (Fig. 5 a, b, and c). The 2013 (Fig. 5a) data cover the period January 7 to June 11 (Julian days 7–162) and is characterized by five major events. The first 3 are a combination of snow melt and rainwater, while the last two large events are rain driven. Relative to the other years, the snow pack was small. Total rain fall during this period was 12 cm. The 2014 data (Fig. 5b) cover the period January 8 to May 1 (Julian days 8–121). There are four events during this period with the highest discharge event driven by a major snow melt followed by a rain event. Total rain for the period was 2.5 cm. The time period for the 2015 data is January 12 to April 1 (Julian days 12–91). There was only one major event during this time period and was driven by snow melt. Total rain for the period was 0.5 cm.

#### 3.2. C-Q plots

##### 3.2.1. Chloride

There are no natural major sources for  $\text{Cl}^-$  such as halite deposits or upwelling brine in the Red Cedar River watershed (Long et al., 2015). A source for possible small amounts of  $\text{Cl}^-$  might be the  $\text{Cl}^-$  impurities in the ubiquitous presence of carbonates in the drift and bedrock aquifers (Wahrer et al., 1996; Meissner et al., 1996). Thus, the background concentration for dissolved  $\text{Cl}^-$  in the near surface aquifers for the lower peninsula of Michigan is less than 10 mg/L and typically on the order of 1–5 mg/L (Long et al., 2015). Chloride concentrations are clearly elevated in the river (Fig. 5 a, b, c) with road salt assumed to be the primary input (Long et al., 2015). Chloride is conservative in the environment (Hem, 1989) and easily can be flushed from landscape surfaces. Considering the dominant source for  $\text{Cl}^-$  in this system to be the surface application of road salt (typically halite), a C2 type of behavior ( $C_{SE} > C_{SO} > C_G$ ) with clockwise rotation and a positive slope of the hysteresis loop would be predicted which is characteristic of flushing.

Fifteen events involving  $\text{Cl}^-$  were recorded (Fig. 5 a, b, c). In this salted watershed,  $\text{Cl}^-$  exhibited a flushing characterized by a spike in its concentration at the start of the rain or snow melt events, e.g., events a and b (Fig. 5 a). The peaking of  $\text{Cl}^-$  concentrations before the discharge peak is typical for salted watershed (e.g., Cooper et al., 2014). As this occurs, river discharge is rising slowly. Chloride concentrations then decrease as river discharge rapidly increases and as the discharge reaches its peak, concentrations are diluted. This pattern is then followed by the recovery of discharge and  $\text{Cl}^-$  concentrations to pre-event. This first flush of  $\text{Cl}^-$  was observed in all events during or soon after the salting season (14). In the rain event during towards the end of the 2013 period, only  $\text{Cl}^-$  dilution occurs, as the residual road salt has been flushed from the surface.

The few c-q studies on  $\text{Cl}^-$  in streams reveal diverse behavior. For streams in Panama, dilution during the event was observed with no hysteresis (Litt et al., 2015). A clockwise rotation with a negative slope for the hysteresis loop (Type C3:  $C_G > C_{SE} > C_{SO}$ ) was observed for a watershed system in France (Aubert et al., 2013). However, the results may not be comparable as this was a seasonal study as opposed to one based on events. In a study of an urban area in Georgia, USA, for two streams over multiple events the dominant type was C3 but type A3 ( $C_G > C_{SO} > C_{SE}$ ) was also observed (Rose, 2003). The consistency in these studies was the evidence for dilution and the C3 type behavior.

The c-q plots for our data were generally consistent with the above observations in events during the salting period, for example,

as is seen in the clockwise dilution pattern in event e (Fig. 6a). It should be noted that  $\text{Cl}^-$  concentrations in this study were significantly higher than in studies reported above. In fact,  $\text{Cl}^-$  concentrations at our sampling point in the Red Cedar River never return to what we might consider the background range of less than 10 mg/L during our sampling period (e.g., Fig. 6a). For reference, reported groundwater concentrations in the area are quite variable ranging from less than 1 mg/L to over 100 mg/L (Slayton, 1982). This 42 sample data set shows a median value of 6 mg/L and a mode of 2 mg/L.

There was additional feature seen in our plots not seen in the other studies. This feature was the rise (clockwise rotation) in  $\text{Cl}^-$  concentrations at lower discharges prior to the rise in discharge due to the rain fall or snow melt event, which is directly related to the very early rapid first flush of  $\text{Cl}^-$  (Fig. 5a, b, and c). In the absence of this early flush of  $\text{Cl}^-$  (event e) (Fig. 6a), the anti-clockwise shape of the loop is interpreted to be A1 ( $C_{SO} > C_G > C_{SE}$ ) behavior. One might argue that this could also be type A3 ( $C_G > C_{SO} > C_{SE}$ ), however, Evans et al., 1999 interpret this shape to be indicative of A1 behavior for sulfate in their studies.

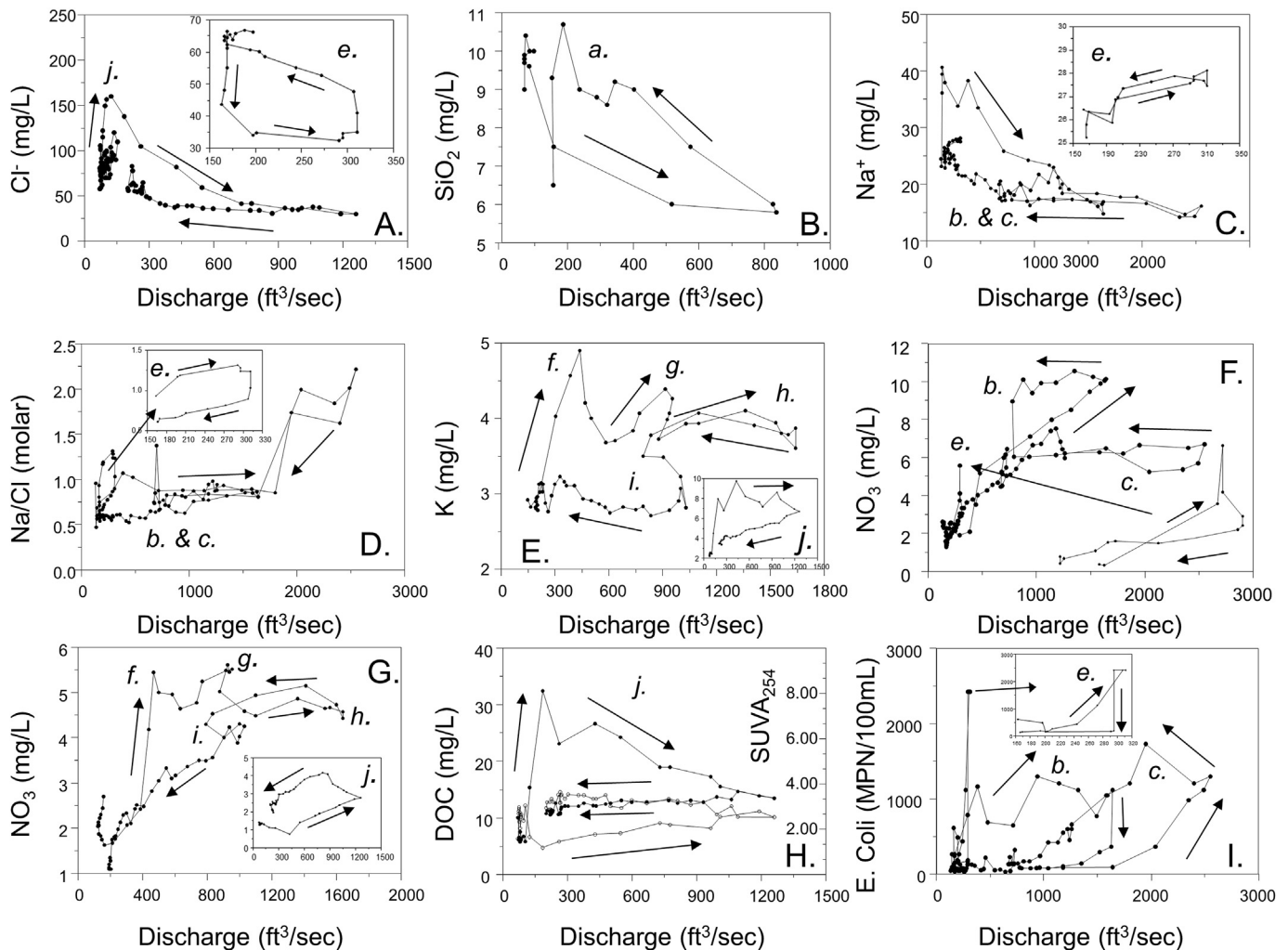
It would appear that the three component model does not fully capture the early rapid flush of  $\text{Cl}^-$  in this system during the salting season. This might indicate that the distinction between event water, soil water and groundwater is insufficient for urban systems of this type. This could relate to the large number of storm water drains that can quickly transport surface water to the river, and that this pathway was not revealed in the Georgia study due to the absence of the large halite source in the present study. The high solubility and conservative nature of  $\text{Cl}^-$  will cause it to be easily mobilized from the watershed surfaces (e.g., streets, parking lots) as well as being flushed from the plowed snow pack that might be enriched in road salt. This latter point may be demonstrated by the fact that the first flush of  $\text{Cl}^-$  is complete before the snow pack had completely melted (e.g., Fig. 5 a, b, and c). Thus, the characterization of  $\text{Cl}^-$  in an urban environment might be C2 behavior followed by C3 behavior during hydrologic events during road salting season. More work on developing the hydrologic models for this are needed. The change from the C2/C3 type to the A1 (perhaps A3) type would suggest that the landscape has been loaded over the many years of road salting and that a two component mixing model of dilute event water with more concentrated soil/ground water might apply (e.g., Evans and Davis, 1998; Rose, 2003).

The very early first flush behavior of  $\text{Cl}^-$  in a salted watershed has the potential to be useful as a tracer of other early flush of materials off of the watershed surface. We will include for comparison, the hydrograph patterns for  $\text{Cl}^-$  as we discuss the other solutes.

##### 3.2.2. Silica

The major sources for  $\text{SiO}_2$  in most watersheds are from the dissolution of aluminosilicates. Groundwater in sedimentary systems typically has  $\text{SiO}_2$  concentrations on the order of 10 mg/L, which is consistent with quartz equilibrium (Hem, 1989; Langmuir, 1997; Faure, 1998). Recent studies have shown the urban land used land cover can result in increased silica concentrations (e.g., Carey and Fulweiler, 2012, 2013). Our Red Cedar data show a consistent concentration pattern of values around 10 mg/L early in the year, with concentrations decreasing in Spring, most likely from diatom uptake (e.g., Wall et al., 1998; Grady et al., 2007; Berner and Berner, 2012). Because there are few major contaminant sources for  $\text{SiO}_2$  in the environment, we would anticipate its behavior to be rock dominated and exhibit a A3 type ( $C_G > C_{SO} > C_{SE}$ ) behavior.

There have only been a few c-q hysteresis studies for  $\text{SiO}_2$ . Evans et al. (1999) found that no hysteresis was the dominant pattern for



**Fig. 6.** c-q hysteresis diagrams for selected solutes and water quality parameters. Rotation of the hysteresis loop is indicated by arrows. Hydrologic events (Fig. 5) related to the loops are indicated. a.  $\text{Cl}^-$ ; b.  $\text{SiO}_2$ ; c.  $\text{Na}^+$ ; d.  $\text{Na}^+/\text{Cl}^-$ ; e.  $\text{K}^+$ ; f.  $\text{NO}_3^-$  2013 loop shape for event e is shown; g.  $\text{NO}_3^-$  for 2014; h. DOC; i. *E. coli*.

steams in the Catskills. In a study of urban and less urban streams in Georgia, USA (Rose, 2003), found evidence of C3 behavior for the more urban streams, half the observations were unclear and A3 behavior was found frequently for the less urban streams. On the other hand, House and Warwick (1998) found dissolved  $\text{SiO}_2$  to exhibit C3 behavior for rivers in a watershed dominated by agriculture and livestock farming. It appears from these studies the commonly observed behavior of  $\text{SiO}_2$  concentrations during storms is dilution with no first flush, which is consistent with the predicted behavior (e.g., Mann et al., 2012).

In all nine events for which we monitored  $\text{SiO}_2$ , the concentration decreased over the hydrologic event, with maximum dilution occurring just prior to the peak discharge (Fig. 5a and b, c). This is similar to the above findings. There was no first flush and the shape of the dilution curve was similar to that of  $\text{Cl}^-$ .

The c-q hysteresis diagrams for  $\text{SiO}_2$  all exhibit this dilution with an anticlockwise rotation characteristic of A3 type behavior, as can be seen in event a in 2013 (Fig. 6 b). Although the shape and rotation of the loops are consistent with the A3 classification, each shows a cross over to lower concentrations that do not return to the starting value. This is likely related to diatom activity with the otherwise conservative behavior of  $\text{SiO}_2$ . Thus, in this watershed,  $\text{SiO}_2$  behavior is largely explained by the expected dominance of rock sources.

### 3.2.3. Sodium and Na/Cl ratios

The primary sources for  $\text{Na}^+$  in near surface aquifers in the lower peninsula of Michigan are the same as for  $\text{Cl}^-$  (e.g., halite, upwelling of brine and impurities in the carbonates), but in addition, aluminosilicates can also be a natural source of  $\text{Na}^+$  (Hem, 1989).  $\text{Na}^+$  concentrations in near surface aquifers in the lower peninsula of Michigan unaffected by halite or brine are typically in the range 2–10 mg/L (Wahrer et al., 1996; Meissner et al., 1996), so it is not unexpected that the groundwater in this area shows a median concentration of 8 mg/L.

Sodium is not as conservative in the environment as  $\text{Cl}^-$  because its environmental behavior is influenced by exchange and sorption reactions (e.g., Foth, 1991; Shanley, 1994; Neal and Kirchner, 2000). In soils, some retardation with respect to  $\text{Cl}^-$  is expected and this differential transport has been suggested as the major mechanism decoupling dissolved  $\text{Cl}^-$  and  $\text{Na}^+$ , and causing  $\text{Na}^+/\text{Cl}^-$  molar ratios to be below 1 even after road salting (e.g., Dailey et al., 2014; Long et al., 2015). Thus, in the absence of the influence of road salts it is expected that the dominant source for  $\text{Na}^+$  will be soil minerals and hence c-q hysteresis loops will exhibit and either A1 or A3 behavior.

Previous  $\text{Na}^+$  c-q hysteresis loop studies in Georgia, USA show C3 behavior in the urban streams and an approximately equal combination of A3 and C3 behaviors in non-urban streams (Rose,

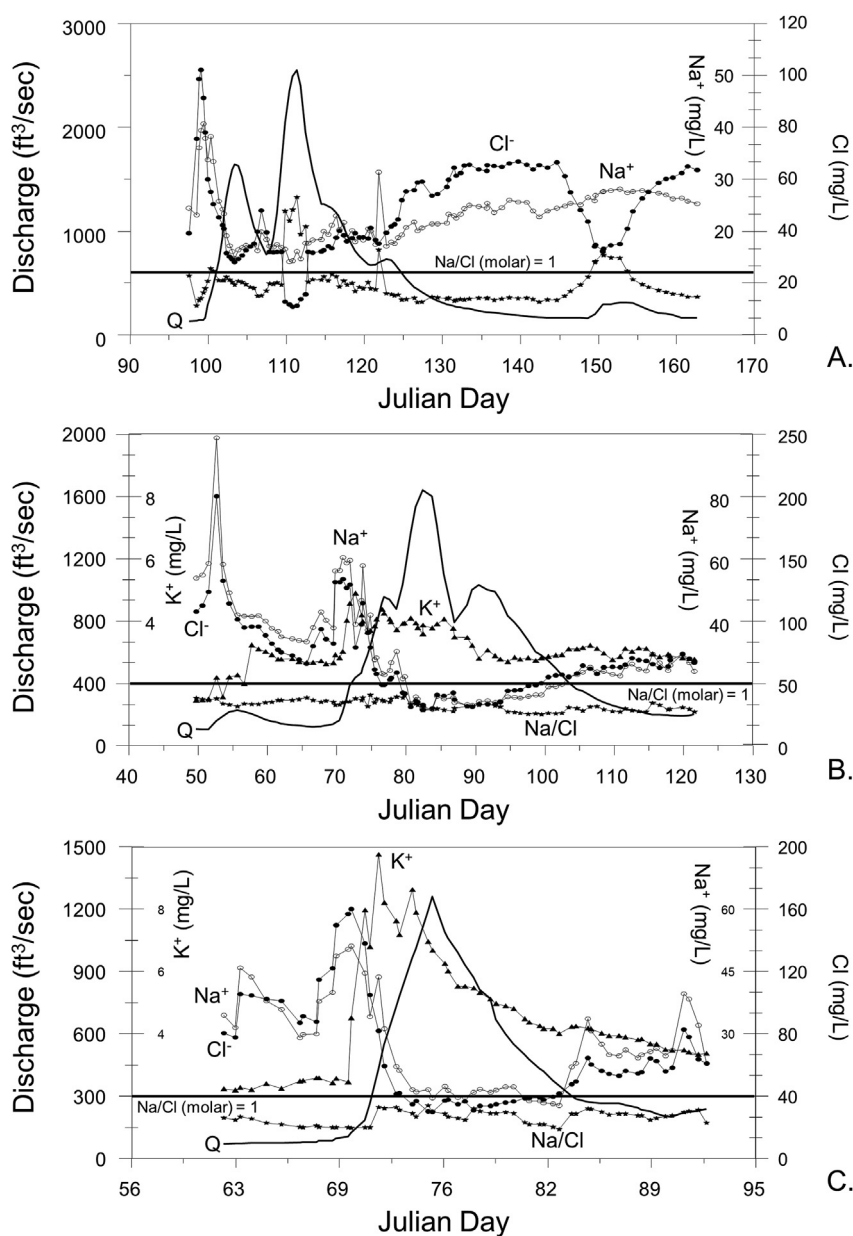
2003). A3 behavior characterized the Panama rivers (Litt et al., 2015). Evans et al. (1999) found no hysteresis for streams in the Catskill and Evans and Davis (1998) reported C2 and C3 behavior. Hood et al. (2006) also found C3 loops for watersheds in Oregon. There was no reported salting in these watersheds and most of them were not highly urbanized.

During the road salting period,  $\text{Na}^+$  has an early first flush similar to  $\text{Cl}^-$  (Fig. 7 a, b, and c). The concentration peaks in  $\text{Na}^+$  were slightly delayed when compared to that of  $\text{Cl}^-$ , again demonstrating the differential behavior of these two solutes, even for events involving short time scales and local flow paths. Sodium is subsequently diluted during peak discharge and recovers in concentration similar to  $\text{Cl}^-$ . However, sodium concentrations do not readily return to expected background levels (less than 10 mg/L), most like as a result of slow release of sorbed/exchanged

material (Long et al., 2015).

The shape and direction of the c-q hysteresis loop for  $\text{Na}^+$  is the same as for  $\text{Cl}^-$  during the salting period (e.g., events **b** and **c**, Fig. 6c), with again possibly both a C2 and C3 behaviors indicated. The shape and slope changes to A2 ( $C_{SO} > C_{SE} > C_G$ ) during the non-salting periods (event **j**, Fig. 6c). Although counter clockwise rotation is indicated, the degree of hysteresis is low.

The nature of changes in  $\text{Na}^+/\text{Cl}^-$  ratios during hydrologic events, including c-q hysteresis plots, at this site have been discussed in a previous paper (Long et al., 2015) for the 2013 data set and will only be briefly discussed here as they illustrate the differential environmental behavior of  $\text{Cl}^-$  and  $\text{Na}^+$  (Fig. 7 a, b, and c). Molar ratios of 1 are expected from the use of halite as a road deicer. The ratios observed in our studies show have values less than one in most cases, and they typically approach one during first flush. This



**Fig. 7.** Changes in  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$  concentrations and  $\text{Na}^+/\text{Cl}^-$  (molar) values over the stream hydrographs for a. 2013, b. 2014, and c. 2015. Data sources are discussed in the text. Solid line is stream discharge (Q), solid dots are  $\text{Cl}^-$  concentrations, open dots are  $\text{Na}^+$  concentrations, solid triangles are  $\text{K}^+$  concentrations, and solid stars are  $\text{Na}^+/\text{Cl}^-$  ratios. Line depicting  $\text{Na}^+/\text{Cl}^-$  (molar) ratio of 1 is depicted.



might be expected if the primary source is halite, and  $\text{Na}^+$  is depleted by sorption and exchange reactions. Another possibility is that the road salt being applied is not pure halite or is a mixture of halite with another salt such as sylvite (KCl) (e.g., Price and Szymanski, 2014). As we reported previously (Long et al., 2015), halite is the most common road salt used and is readily available in the State of Michigan. However, in 2015 we retrieved a sample of the deicer applied to the MSU campus roads and measured the  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{K}^+$  concentrations. The  $\text{Na}^+/\text{Cl}^-$  ratio of this material was slightly less than 0.5. The mean and medians of the  $\text{Na}^+/\text{Cl}^-$  ratios in the 2015 data set was 0.65 and 0.7 respectively. The higher ratios in the river indicate this salt is not the dominant source for these solutes and that a more halite-rich source is indicated. This does suggest that for studies of these solutes in salted environments, knowledge of the composition of the applied deicing material would be helpful in the interpretation of the data.

There have been few c-q studies involving  $\text{Na}^+/\text{Cl}^-$ . Sun et al., 2012, have shown that over time with increased road salting, the hysteresis changed from a counter clockwise loop to a clockwise loop. Our data are consistent with this observation in that recent loops are clockwise (e.g. Long et al., 2015, Fig. 6 d). Our data also show that the pattern of hysteresis changes from C2 type during the salting season to more of a C1/C2 type during the non-salting season, reflecting changes in the relative importance of pathways for  $\text{Na}^+$  and  $\text{Cl}^-$ .

### 3.2.4. Potassium

Natural sources of  $\text{K}^+$  in groundwater are the weathering of aluminosilicates and, therefore, concentrations less than 5 mg/L can be expected (Hem, 1989). This is consistent with our work on the near surface aquifers in the lower peninsula of Michigan and the study area groundwater's (Slayton, 1982; Wahrer et al., 1996; Meissner et al., 1996) that show concentration values between 1 and 3 mg/L (averaging around 2 mg/L). Thus, one might expect  $\text{C}_G$  and  $\text{C}_{\text{SO}}$  to be more dominant than  $\text{C}_{\text{SE}}$ . However,  $\text{K}^+$  concentrations can be elevated from throughfall and leaching from organic material and watershed surfaces (e.g., Likens et al., 1994; Berner and Berner, 2012; Jonczak et al., 2015). In addition,  $\text{K}^+$ -based fertilizers can contribute to elevated concentrations (e.g., Hamilton and Helsel, 1995; Griffioen, 2001). Thus,  $\text{K}^+$  flushing during an event is possible and  $\text{C}_{\text{SE}}$  would become more dominant than  $\text{C}_G$  and  $\text{C}_{\text{SO}}$ . This is the case for catchments in the Adirondacks where C1 ( $\text{C}_{\text{SE}} > \text{C}_G > \text{C}_{\text{SO}}$ ) behavior was the dominant type for  $\text{K}^+$  (Evans and Davis, 1998). Hood et al. (2006) also found clockwise rotations indicating either C1 or C2 behavior for streams in the H.J. Andrews Experimental forest, Oregon, USA. However, no hysteresis, including several cases of chemostatic behavior, was observed to be the dominant type for streams in the Catskills and Panama (Evans et al., 1999; Litt et al., 2015).

Concentrations of  $\text{K}^+$  peak during storm events and this peak comes after that of  $\text{Cl}^-$  and  $\text{Na}^+$ , but still occurs on the rising limb of the hydrographs (Fig. 7 b, c). Prior to the events, concentrations are at background levels (e.g., 1–3 mg/L). Concentrations are elevated (defined as above 2–3 mg/L) until after the events and then trend toward background. There is no evidence of a dilution pattern such as seen for  $\text{Cl}^-$  and  $\text{Na}^+$  and therefore road salts are most likely not contributing to elevated concentrations. For event **j** in 2015,  $\text{K}^+$  has three peaks, on the rising limb. During recession,  $\text{K}^+$  show a change in the dilution slope to indicate the addition of  $\text{K}^+$  to the systems, which is followed by continued dilution.

For both the 2014 and the 2105 events, hysteresis loops with clockwise rotation are observed. For event **j** in 2015 (Fig. 6 e), the hysteresis loop shows clear evidence of flushing and the three concentration peaks during the flushing event are seen. The behavior is C2 ( $\text{C}_{\text{SE}} > \text{C}_{\text{SO}} > \text{C}_G$ ). The 2014 loops (events **f**, **g**, **h**, **i**) are

more complicated because of the multiple discharge peaks. Most of the  $\text{K}^+$  is flushed out in event **f**. For each subsequent event, lower concentrations are found. Event **h** has little hysteresis and at event **i**, concentration are returning to background. The early events can be characterized as C2 type, and the last event is closer to C1 ( $\text{C}_{\text{SE}} > \text{C}_G > \text{C}_{\text{SO}}$ ).

These results are interpreted to indicate that the major source for the elevated  $\text{K}^+$  is from the leaching of organic matter. As mentioned, deicers most likely do not contribute  $\text{K}^+$  and through-fall and fertilizers would not be contributors this time of year. Pattern indicates that for the first event  $\text{K}^+$  release is relatively high with type C1 behavior. This suggests that organically derived  $\text{K}^+$  is being flushed by the surface event water. However, the pathway must be different from that of  $\text{Cl}^-$  as is evidenced by the lag of the  $\text{K}^+$  peak compared to the  $\text{Cl}^-$  peak. The lag can be explained by  $\text{K}^+$  being less conservative during transport (e.g., sorption/exchange reactions) than  $\text{Cl}^-$  and the sources within the watershed surface from which the  $\text{K}^+$  is derived. Chloride mainly originates from pavement allowing for quick release, while  $\text{K}^+$  is mainly released from non-pavement surfaces, (e.g., lawns, leaf litter). Thus, transit time is longer and more mineral surfaces are available for retardation.

### 3.2.5. Nitrate

Nitrate concentrations in natural groundwater are typically below 1 mg/L. Sources for elevated  $\text{NO}_3^-$  concentrations come primarily from human and animal wastes and fertilizers (Hem, 1989), all of which could be present in an urban area. Both hydrologic and biochemical processes such as nitrification and denitrification can play a role in regulating  $\text{NO}_3^-$  concentrations particularly within engineered drainage systems (e.g., Kaushal et al., 2011; Bettez and Groffman, 2012, 2013; Gallo et al., 2013). A recent study has shown that atmospheric deposition and fertilizers are the most dominant sources for  $\text{NO}_3^-$  in urban residential storm runoff and that the relative contribution of these sources changes over time (Yang and Toor, 2016). In this particular study, the increasing importance of a fertilizer source came mid to late summer. Given these possibilities one might expect the behavior of  $\text{NO}_3^-$  during hydrologic events to be C2 ( $\text{C}_{\text{SE}} > \text{C}_{\text{SO}} > \text{C}_G$ ). However, previous studies show no consistent pattern. Evans et al. (1999) found counterclockwise A2 and A1 behavior, from which they discussed the importance of mineralization and nitrification on  $\text{NO}_3^-$  concentrations. House and Warwick (1998) observed C3 behavior. In a snow melt – rain event study, Fucik et al. (2012) could not identify a consistent pattern, reporting both clockwise and anti-clockwise c-q loops. Similarly, Butturini et al. (2006) found both C2 and A1 type loops in a study of Mediterranean streams. Their results show little evidence of a lag but that the magnitude of the antecedent storm affected the  $\text{NO}_3^-$  behavior. Work in the H.J. Andrews Experimental Forest (Van Versveld et al., 2008) also showed little evidence of a  $\text{NO}_3^-$  peak lag behind the discharge peak. Aubert et al. (2013) observed A2 behavior in their monthly study and Carey et al. (2014) mostly C2 and C3 behavior in a suburbanizing watershed. Clearly season, landuse, and watershed hydrology play roles in  $\text{NO}_3^-$  behavior.

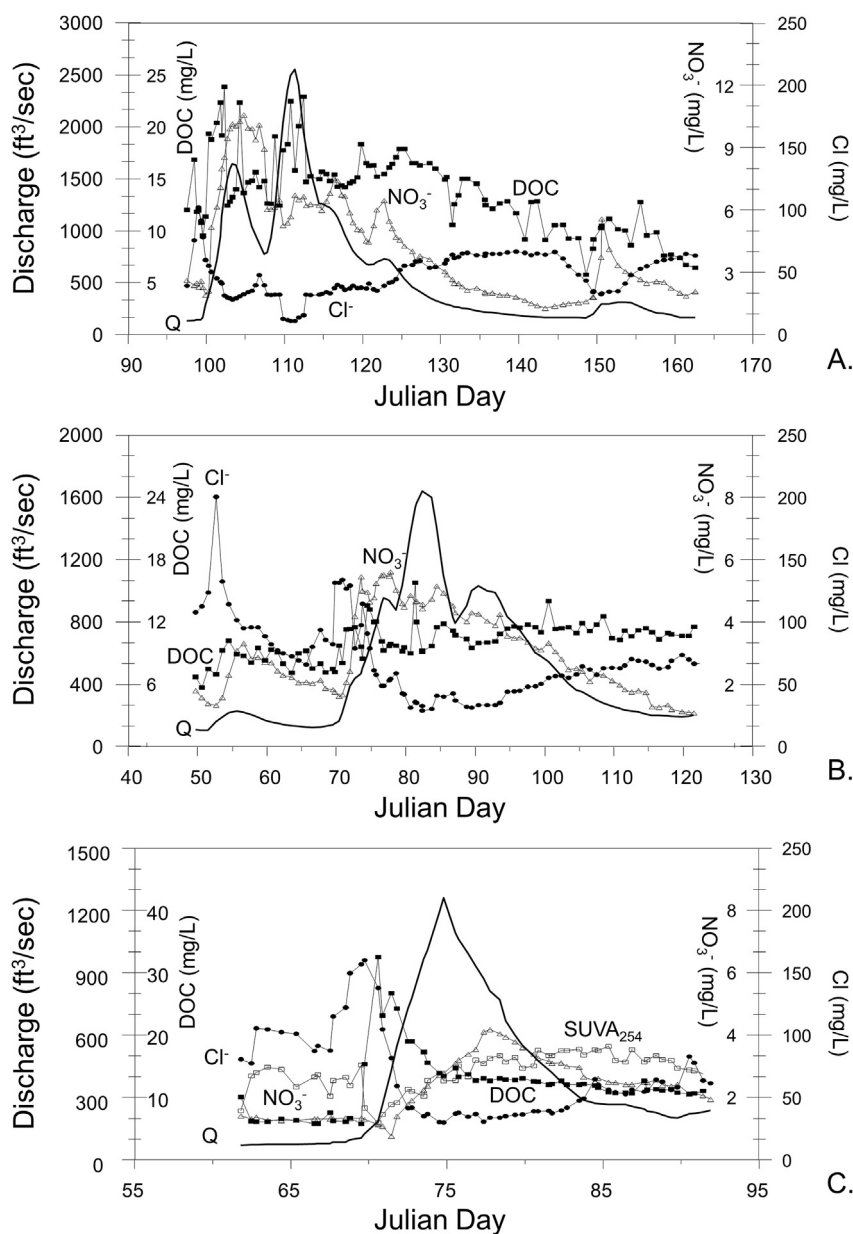
We also find different trends for  $\text{NO}_3^-$ . However, in all cases the  $\text{NO}_3^-$  peak and discharge peak did not coincide and a decrease in  $\text{NO}_3^-$  concentrations preceded the rise to the peak (Fig. 8 a, b, and c). We also found changes that occur during subsequent events. For example, in 2013 (events **b**, **c**, **e**) the c-q pattern changed from A2 to A1 to C2 respectively with decreases in concentrations (Fig. 6f). In 2014, over the course of events **f**, **g**, **h**, and **i**, the pattern changed from C2 to A1 to C1 with concentration depletion observed. The general shape of the loop for 2014 is very similar to that of  $\text{K}^+$  in 2014. It is the trend of concentration depletion over the course of

events that makes the over loop patterns similar. The A2 pattern characterizes event **j** in 2015 and it is interesting to note that the slight increase the concentration of  $K^+$  appears to coincide with the  $NO_3^-$  peak. A possible similarity in pattern amongst these results is that in the high discharge events or the highest event in a sequence of events (e.g., **b**, **c**, **h**, **j**) the c-q pattern is anti-clock wise regardless of whether A1 ( $C_{SO} > C_G > C_{SE}$ ) or A2 ( $C_{SO} > C_{SE} > C_G$ ).

### 3.2.6. Dissolved organic carbon and $SUVA_{254}$

The fate, quality, and transport of DOC is dependent on many variables such as source, temperature, stream order, microbiological processes, nutrient availability, influence of the hyporheic zone, hydrologic pathways, and sorption reactions (Agren et al., 2008; Zarnetske et al., 2011; Donn and Barron, 2013; McElmurry et al., 2013; Aubert et al., 2013; Creed et al., 2015). In the absence of

point or non-point sources (e.g., waste or stormwater discharges), it is the near surface soils that are the major source of DOC and this is reflected in that most c-q studies show the most common behavior for DOC over the hydrograph is C2 ( $C_{SE} > C_{SO} > C_G$ ) e.g., (Butturini et al., 2005, 2006; Hood et al., 2006; Van Versveld et al., 2008; Goodman et al., 2011; Mann et al., 2012; Creed et al., 2015). These studies also show that the trends of DOC and  $SUVA_{254}$  are similar and the aromaticity of DOC increases as a consequence of the hydrologic event. However, a study by Agren et al. (2008) found DOC and  $SUVA_{254}$  to behave differently: rather than the C2 or C3 loop reported in other studies, they found A3 ( $C_G > C_{SO} > C_{SE}$ ) behavior. This study involved snow melt events for boreal streams and the difference in DOC and  $SUVA$  behavior was attributed to the intensity of the melt event. The c-q studies also show that DOC trends are often related to those of  $K^+$  but not necessarily to  $NO_3^-$  (e.g.,



**Fig. 8.** Changes in  $Cl^-$ , DOC, and  $NO_3^-$  concentrations and  $SUVA_{254}$  values over the stream hydrographs for a. 2013, b. 2014, and c. 2015. Data sources are discussed in the text. Solid line is stream discharge ( $Q$ ), solid dots are  $Cl^-$  concentrations, solid squares are DOC concentrations, open triangles are  $NO_3^-$  concentrations, and open squares are for  $SUVA_{254}$  ( $L\ mg^{-1}\ cm^{-1}$ ).

Evans et al., 1999; Hood et al., 2006; Mann et al., 2012; Aubert et al., 2013).

We find in our study that the DOC concentration peaks lag those for  $\text{Cl}^-$  (Fig. 8 a, b, and c) and occur on the rising limb. Event **j** (Fig. 8 c.) shows evidence of three DOC concentration increases during the snow melt event. The first two are spikes in concentrations while the third is evidenced by a change in the concentration trajectory to an increased slope.  $\text{SUVA}_{254}$  has lower values (e.g., increase in aliphatic character) or a trend to a lower value as the DOC peaks and is lowest at the first DOC peak (Fig. 8c). We have found in general that the urban landscape is characterized by more aliphatic DOC than forest or agriculture (McElmurry et al., 2013). That alone cannot account for the decrease in  $\text{SUVA}_{254}$ . Rather, we suggest that this is a seasonal influence. As a consequence of the microbial decay of organic matter, aliphatic carbon can be preferentially consumed, leaving behind more aromatic structures (e.g., Marschner and Kalbitz, 2003). Thus, when water temperatures are high, decay reactions are stimulated and DOC flushed off of the landscape would have more of an aromatic character (McElmurry et al., 2013). In the early cold season, the flushed DOC would be more aliphatic, which would be the situation here and account for the initial decrease in  $\text{SUVA}_{254}$ .

The DOC peaks are concurrent with the peaks in  $\text{K}^+$  (Fig. 7 b, c). The three DOC/ $\text{K}^+$  peaks in event **j** must differ in origin from those in the events of 2014 in that these three peaks are not related to a specific hydrologic event such as rain. This suggests that during the snow melt event, water masses originating from different compartments in the watershed are reaching the stream at different times. In addition, the low concentration of  $\text{NO}_3^-$  at the second DOC/ $\text{K}^+$  peak, the potential variability in aromaticity amongst the peaks, and a  $\text{K}^+$  peak at the  $\text{NO}_3^-$  peak on the declining limb, indicates that the composition of these water masses are quite different. This is the subject of an ongoing study that may help to reveal sources and pathways.

The c-q loops for DOC show C1 ( $C_{\text{SE}} > C_{\text{G}} > C_{\text{SO}}$ ) or C2 ( $C_{\text{SE}} > C_{\text{SO}} > C_{\text{G}}$ ), but A1 ( $C_{\text{SO}} > C_{\text{G}} > C_{\text{SE}}$ ) for  $\text{SUVA}_{254}$ . One might interpret this to indicate that the storm event water is mobilizing the DOC but it is the soil water that is giving the DOC its character. The results are consistent with the previous studies in that DOC exhibits C1 behavior, but differs from most these studies in that we find, similar to observations of Agren et al. (2008), that  $\text{SUVA}_{254}$  behaves differently from that of DOC.

### 3.2.7. *E. coli*

*Escherichia coli* in the environment is an indicator of fecal contamination that is used to signal potential risk to human health (Ashbolt and Snozzi, 2001). The measurement itself does not differentiate the source (e.g., human, waterfowl) and there are many efforts underway to develop strategies to identify and assess the importance of different sources (source tracking) in both rural and urban watersheds (e.g., Wong and Xagorarakis, 2011; Srinivasan et al., 2011). To the best of our knowledge, the c-q hysteresis approach has not been used for *E. coli* and thus we do not know of any previous work that can be used for comparison purposes. However, there are a number of storm water studies that do provide some insight into what might be expected in urban environments.

Storm events generally produce an increase in *E. coli* concentrations in streams (Stea et al., 2015; Lee et al., 2014). However, the first flush behavior is complicated in that peak concentrations appear to occur at different times, do not seem to consistently correlate with any chemical parameter, can be higher for small hydrologic events than large ones (McCarthy, 2009; He et al., 2010; Oliver et al., 2015; Hathaway et al., 2015). While there is some evidence for dilution during the hydrologic event, this is also not consistent (Hathaway et al., 2015). These inconsistencies are likely

related to the complex interplay of biogeochemical and watershed properties that influence the fate and transport of *E. coli*. These properties include sunlight, temperature, nutrients, sources, land-use, nutrients, interactions with sediments, and growth and inactivity of microbe (Liu et al., 2006; He et al., 2010; Liao et al., 2016). There is also evidence that these other processes may be more important than transport (McCarthy et al., 2013).

Considering this complexity, it is difficult to predict specific behaviors. However, one might anticipate that the *E. coli* concentration peak will lag the  $\text{Cl}^-$  peak and not be correlated with other nutrients and that  $C_{\text{SE}}$  and  $C_{\text{SO}}$  would be more important than  $C_{\text{G}}$ . Our results for 2013 events **b**, **c**, **d** are consistent with this prediction and previous observations (Fig. 9). The *E. coli* peaks lag the  $\text{Cl}^-$  peak, they do not occur in a consistent position in the hydrograph and (for events **b** and **c**), and are not correlated with the  $\text{NO}_3^-$  peak. For event **e**, there may be indications of a similar source pathway for *E. coli* as  $\text{NO}_3^-$ . Event **e** also shows that a small event can flush higher amounts of *E. coli* than larger events. We point out that these *E. coli* events are not related to human sources and the source identification and c-q behavior is the subject of a future paper.

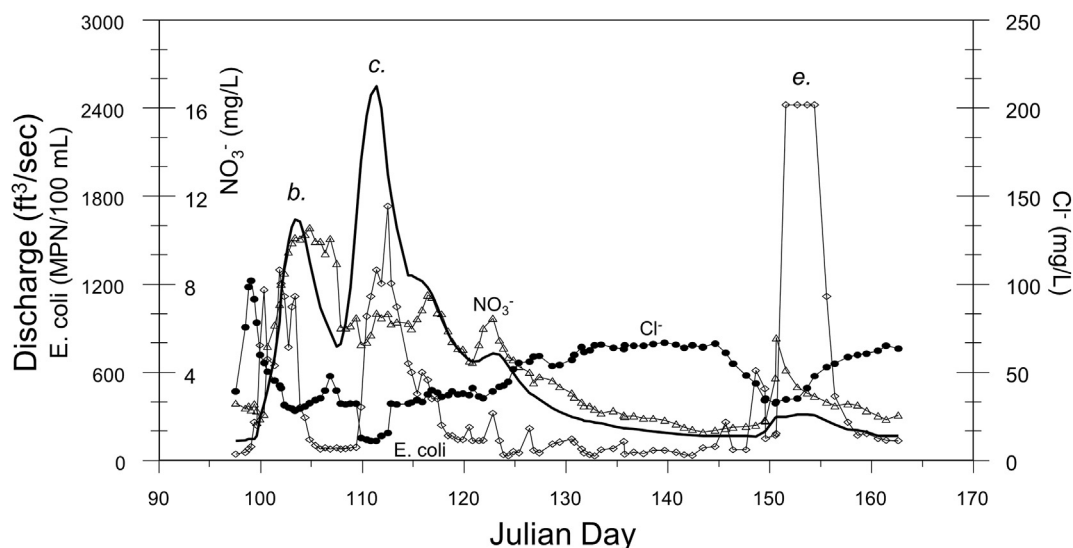
The c-q hysteresis type is variable. For event **b**, C2 ( $C_{\text{SE}} > C_{\text{SO}} > C_{\text{G}}$ ) behavior is indicated, but for event **c** type it is A2 ( $C_{\text{SO}} > C_{\text{SE}} > C_{\text{G}}$ ) and for **e** it is C2, but the shape is more complex for this large flush of *E. coli*. As expected, the importance of  $C_{\text{SE}}$  and  $C_{\text{SO}}$  for *E. coli* is indicated. The results also show, the possible influence of antecedent events on transport pathways (e.g., McCarthy et al., 2013; Chen and Chang, 2014; Oliver et al., 2015).

These results might indicate that *E. coli* is flushed from the surface (or proximal sources) during the first event. However, *E. coli* does not exhibit the early flush from the landscape as  $\text{Cl}^-$ . Rather there is a lag with respect for  $\text{Cl}^-$ , which is most likely due to retardation process (soil interactions) such as are observed for  $\text{K}^+$ . In the second event, the soil water pathway becomes more important. This type of analysis for *E. coli* is most likely too simplistic, given the complexities of understanding *E. coli* transport as noted above. However, we suggest that combining this type of approach with additional information to differentiate sources and as well as transport modeling, could be a fruitful path for future work. (e.g., Liu et al., 2006; Wong and Xagorarakis, 2011).

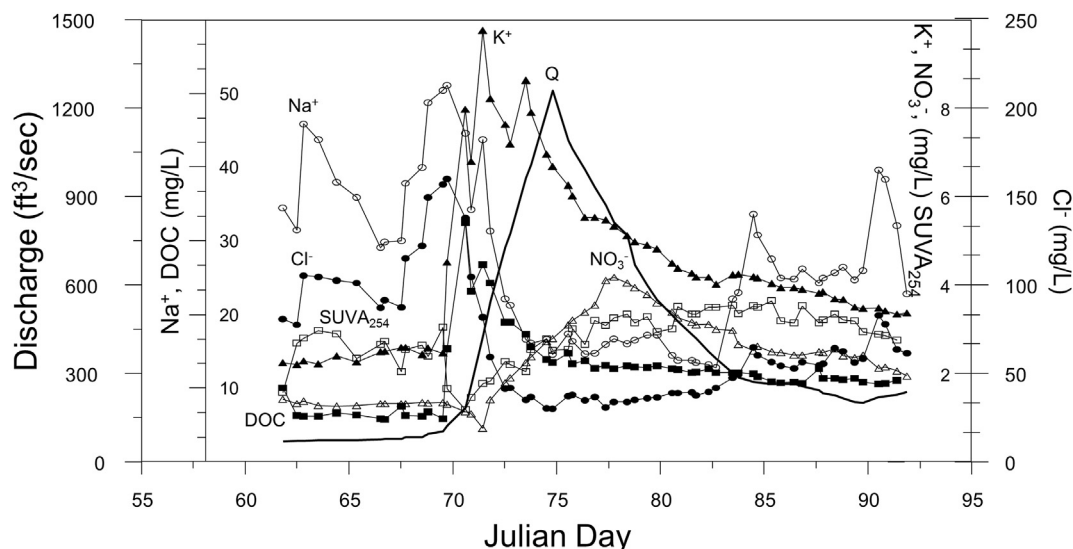
### 3.3. Integrative pollutograph

The previous discussion focused on the behavior of individual geochemical variables. Here we use event **j** (Fig. 10) as a summary of this behavior as well as exploring additional information that can be gained from the study of an integrative pollutograph. Even **j** is the major event (snow melt) for the measurement period of 2015 (Fig. 5 c) and thus concentration trends are not influenced by antecedent events. The following observations and explanations of the behavior of the geochemical variables are based on the above results and our previous interpretations:

1. Both  $\text{Cl}^-$  and  $\text{Na}^+$  peak before the rising limb of the discharge hydrograph with a slight lag in the  $\text{Na}^+$  peak compared to  $\text{Cl}^-$ . This can be explained by an environmental pathway that involves the influences of impervious surfaces allowing for the rapid flushing, the high solubilities of these solutes, and the less conservative behavior of  $\text{Na}^+$ . This rapid flushing is first flush.
2.  $\text{K}^+$  and DOC appear to have three correlated closely timed events on the rising limb that lag those of  $\text{Cl}^-$  and  $\text{Na}^+$ . These observations can be explained by the interaction of surface and near-surface water with organic matter, their less conservative nature compared to  $\text{Cl}^-$  and  $\text{Na}^+$ , and the influence of pervious surfaces such as soils that increases transit time.



**Fig. 9.** Diagram showing the concentration pattern of *E. coli* during the 2013 events. Solid line is stream discharge ( $Q$ ), solid dots are  $\text{Cl}^-$  concentrations, open diamonds are *E. coli* concentrations, and open dots triangles are  $\text{NO}_3^-$  concentrations.



**Fig. 10.** Summary diagram for event *i* in 2015. Solid line is stream discharge ( $Q$ ), solid dots are  $\text{Cl}^-$  concentrations, solid line, open dots are  $\text{Na}^+$  concentrations; solid triangle are  $\text{K}^+$  concentrations; open triangles are  $\text{NO}_3^-$  concentrations; solid squares are DOC concentrations, open square are  $\text{SUVA}_{254}$  concentrations in  $\text{L mg}^{-1} \text{C}^{-1} \text{m}^{-1}$ .

3.  $\text{SUVA}_{254}$  has a trajectory to a concentration low at the first  $\text{K}^+$ /DOC concentration peak. Values increase but show a lower trajectory at the second peak. Values again increase with a concentration low at the third  $\text{K}^+$  peak then increase again. At the third  $\text{K}^+$  peak, DOC concentrations exhibit a lower slope indicating a concentration increase rather than a peak. This in part can be explained by the urban landscape which appears to correlate with lower  $\text{SUVA}_{254}$  values in general and the flushing of DOC that is more aliphatic early in the cold season than later when warming brings the onset of significant microbial activity.
4. The  $\text{NO}_3^-$  peak lags the third  $\text{K}^+$ /DOC concentration peak on the declining limb of the hydrograph. In addition,  $\text{NO}_3^-$  has a concentration low at the second  $\text{K}^+$ /DOC peak. This can be explained by  $\text{NO}_3^-$  originating from more of a soil water source (e.g., slower transit time). The decrease is related to  $\text{NO}_3^-$  deficiency in the water mass accounting for the  $\text{K}^+$ /DOC peak and most likely is the results from the lack of significant nitrification

reactions early in the cold season. The lack of  $\text{NO}_3^-$  dilution at the peak  $\text{Cl}^-$  concentration is consistent with a low volume water mass entering the river that is not enough to affect the discharge, dilute the  $\text{NO}_3^-$  dilution, but highly concentrated in  $\text{Cl}^-$ . The  $\text{NO}_3^-$  and the  $\text{SUVA}_{254}$  concentration lows do not coincide, with  $\text{SUVA}_{254}$  on the first  $\text{K}^+$ /DOC peak and  $\text{NO}_3^-$  on the second.

5. The correlation of  $\text{K}^+$  and DOC is understandable in terms of  $\text{K}^+$  association with organic matter. However, the cause of the triple  $\text{K}^+$ /DOC concentration increases is made somewhat unclear because there are no specific hydrologic events (e.g., rain) that might have caused these pulses. What this behavior implies is that water masses reflecting different pathways are reaching the river at different times. The lack of correlation of the low  $\text{SUVA}_{254}$  values with the  $\text{NO}_3^-$  concentration low and the  $\text{NO}_3^-$  -  $\text{K}^+$  association on the declining limb might be evidence that



**Table 1**

Summary of the c-q hysteresis loop analysis for the water parameters studies. The classification scheme is based on that proposed by Evans and Davis (1998). NO is not observed.

Parameter	Season		Comment
	Salting	Non salting	
Cl <sup>-</sup>	C2/C3	A1	Unique to salted environments. Can be tracer for very early flush.
SiO <sub>2</sub>	A3	A3	Rock source lead to no influence of urban.
Na <sup>+</sup>	C2/C3	A2	Unique to salted environments
Na <sup>+</sup> /Cl <sup>-</sup>	C2	C1/C2	
K <sup>+</sup>	C2 to C1	NO	Depletion over subsequent events.
NO <sub>3</sub> <sup>-</sup>	A2 to A1 C2 to A1 to C1	C2	A2 or A1 is common for first event or large event. Depletion over subsequent events.
DOC	C1 or C2	NO	Multiple events not observed.
SUVA <sub>254</sub>	A1	NO	Multiple events not observed. Changes may reflect the urban environment.
<i>E. coli</i>	C2 to A2	NO	Maybe helpful for source tracking and modelling.

these water masses are chemically different, again reflecting these different pathways.

6. Unfortunately, we did not have *E. coli* measurements for event **j**. However, we did observe for other events that *E. coli* did not exhibit first flush.

#### 4. Summary and conclusions

In this study we characterized the behaviors of selected chemical and microbiological parameters during snow melt and rain events in an urban watershed using a combination of c-q hysteresis loop plots following the Evans and Davis (1998) classification scheme and pollutographs. Two types of fingerprints were observed. The first fingerprint involves the results of the c-q hysteresis analyses that are summarized in Table 1. Results show the following behaviors for: 1) Cl<sup>-</sup> and Na<sup>+</sup> show a combination C2-C3 behavior during salting season and A1 and A2 behavior in non-salting; 2) SiO<sub>2</sub> shows A3 behavior in all events, 3) Na<sup>+</sup>/Cl<sup>-</sup> shows C2 or C1 behavior, 4) K<sup>+</sup> changes from C2 to C1 with concentration depletion over subsequent events; 5) NO<sub>3</sub><sup>-</sup> changes from A2 to C1 or C2 with concentration depletion over subsequent events; 6) DOC and SUVA<sub>254</sub> C2 and A1, respectively; and 7) *E. coli* changes from C2 to A2 over subsequent storms.

The second fingerprint involves the pollutographs and there are two aspects to this. One aspect is the behavior of the individual parameter during the course of the event and the occurrence of its peak with respect to the hydrograph peak. Using Cl<sup>-</sup> as the conservative parameter that indicates the early first flush for comparison and knowledge of sources, one can infer the importance of biogeochemical processes in transport such as the retardation of Na<sup>+</sup> and K<sup>+</sup>. Integrative pollutographs lead to the second aspect, in which for example they reveal that different locations/pathways contribute to the changes in the biogeochemistry of the stream over the course of an event.

These results extend the work of previous studies and may serve to help develop a fingerprint of solute behavior that can be used to more fully explore early season biogeochemical dynamics in an urban, salted, snow-melt dominated watershed. Although event **j** might be used to characterize an overall framework for such a fingerprint, a better understanding of the temporal dynamics is needed. This need arises, not only, for example, from the changes in behavior of parameters such as NO<sub>3</sub><sup>-</sup> and *E. coli* over successive events, but also from the observations of the triple K<sup>+</sup>/DOC concentration increases with no related hydrologic event. The latter illustrates the complexity of understanding biogeochemical dynamics in an urban watershed with potentially many different types of pervious and impervious surfaces and of pathways.

We hope that this work sets the stage for additional work in a diversity of urban environments that incorporates more systematic

studies than we were able to do here (i.e., complete data sets for hydrographs), different seasons and the transition between seasons including the influence of the hyporheic zone, and integration of other physical-chemical and microbiological parameters.

Finally, we conclude that the use of the Evans and Davis (1998) classification scheme provides information that is both useful in terms of understanding process and in developing quantitative models. However, the interpretations must also take into account the biogeochemical behavior of the solute or microbial agent in the environment.

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