



ELSEVIER

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

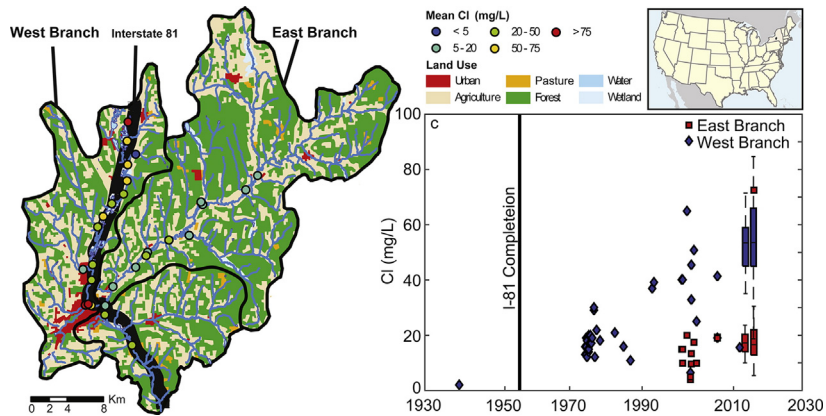
Chloride sources in urban and rural headwater catchments, central New York

Kristina Gutches^{a,*}, Li Jin^b, Laura Lautz^a, Stephen B. Shaw^c, Xiaoli Zhou^a, Zunli Lu^a^a Syracuse University, Department of Earth Sciences, 204 Heroy Geology Laboratory, Syracuse, NY 13244, United States^b Geology Department, State University of New York College at Cortland, Cortland, NY 13045, United States^c Department of Environmental Resources Engineering, College of Environmental Science and Forestry, State University of New York, Syracuse, NY 13244, United States

HIGHLIGHTS

- Rising Cl concentrations since the construction of an interstate highway
- Identifying salinity sources with linear discriminant analysis and mixing model
- Road salt contamination in surface water and groundwater in central New York
- Elevated salinity related to urban areas and impervious surfaces
- Groundwater contributed to increased baseflow concentrations of Cl

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 6 March 2016

Received in revised form 25 April 2016

Accepted 26 April 2016

Available online xxx

Editor: D. Barcelo

Keywords:

Road salt

Chloride

Bromide

Linear discriminant analysis

Groundwater

ABSTRACT

Road salt used as a deicing agent in winter months has become an emerging contaminant to streams and groundwater. In central New York, road salts are applied heavily during winter months. Recognizing potential sources of salinity to a river may reveal processes controlling the salinization of freshwater systems, with implications for future management practices. The Tioughnioga River, located in central New York, is a headwater of the Susquehanna River, which flows into the Chesapeake Bay. Salinity of the Tioughnioga River water has been increasing since the late 1930s. In this study, water samples were collected weekly at the East and West Branches of the Tioughnioga River from 2012 to 2014. We characterize natural and anthropogenic sources of salinity in the Tioughnioga River, using two independent approaches: (1) chloride to bromide ratios (Cl/Br) and (2) linear discriminant analysis.

Ratios of Cl/Br suggest that road salt runoff influence is notable in both branches, but is more significant in the West Branch, consistent with a greater area of urban land. Linear discriminant analysis confirms the results of Cl/Br in the West Branch and further indicates presence of Appalachian Basin Brines in the East Branch, although their contribution may be volumetrically small. Longitudinal stream Cl concentration profiles indicate that sources of pollution are particularly concentrated around urban areas. Residence time of Cl in the watershed is estimated to be approximately 20 to 30 years using a mixing model, suggesting that stream Cl concentrations likely will continue to rise for several decades.

* Corresponding author.

E-mail address: kmgutche@syr.edu (K. Gutches).

1. Introduction

Since the application of de-icing salts to roadways became widespread in the United States during the 1950's, concentrations of chloride (Cl) in natural waters have risen at a dramatic rate (Kaushal et al., 2005; Kelly et al., 2008; Kelly et al., 2010a, 2010b; Corsi et al., 2015). Elevated concentrations of chloride are harmful to sensitive biota (Jackson and Jobbágy, 2005; Kaushal et al., 2005; Kelly et al., 2010a, 2010b), threaten to perturb riparian ecosystems (Daley et al., 2009), and can contaminate drinking water supplies (Ramakrishna and Viraraghavan, 2005; Jackson and Jobbágy, 2005; Mullaney et al., 2009; Jin et al., 2011). Concentrations of Cl have a high positive correlation with areas of urban land use due to the application of de-icing salts to paved surfaces (Cunningham et al., 2009; Ledford and Lautz, 2014). Besides road salt runoff, additional sources of salinity may include contamination by the natural migration of deep basin brines and animal waste, which has been the focus of several recent studies (Lautz et al., 2014; Lu et al., 2015; Panno et al., 2006; Davis et al., 1998).

Bromide (Br) and Cl have been used as conservative tracers in natural waters. Ratios of Cl/Br have been used in various studies to identify sources of salinity in surface water and groundwater (Panno et al., 2006; Davis et al., 1998; Freeman, 2007; Llewellyn et al. 2014), which have proven to be effective in detecting contamination of water related to halite dissolution due to its high concentration of Cl relative to Br. During the evaporation of seawater, halite will precipitate excluding Br from the crystal structure, leading to high Cl/Br ratios in sources originating from the dissolution of halite (e.g. road salt and septic effluent) (Freeman, 2007). The residual brine remaining after halite precipitation (e.g. Appalachian Basin Brines) will be enriched in Br, and thus have a low ratio of Cl/Br (Davis et al., 1998). This allows for ratios of Cl/Br to be used as a fingerprinting tool in identifying contamination by de-icing salts. Table 1 lists observed concentrations of Cl, Br, and ratios of Cl/Br for various sources of salinity to natural water systems.

Linear discriminant analysis (LDA) is a quantitative method to distinguish among different classes of data by creating linear combinations of variables that results in the greatest separation of classes. LDA is an effective statistical technique for discriminating among samples impacted by Appalachian Basin Brines (ABB), road salt, or animal waste (Lautz et al., 2014). In addition to classifying samples by endmembers, LDA also provides an estimate of certainty for the produced classification (Lautz et al., 2014).

The primary objective of our study is to characterize the sources of salinity in two branches, with contrasting land use, of the Tioughnioga River, in central New York. Previous studies have attributed the increase in Cl in the Tioughnioga River, as well as groundwater in central New York, to the application of road salts, agricultural runoff from dairy

farming, and effluent discharge from septic systems (Buller, 1978; Buller et al., 1978; Waller and Finch, 1982; Miller et al., 1998). However, prior work in the study area does not attempt to distinguish the impacts of road salt from different sources of salinity. We use both Cl/Br ratios and LDA as two independent means to differentiate among sources. We apply a previously developed LDA modeling approach (Lautz et al., 2014) to identify the most probable sources of salinity from ABB, road salts, and animal waste. In addition, we also examine annual and decadal scale temporal variations in longitudinal Cl concentration profiles, which sheds light on spatial distribution of Cl sources and residence time of Cl in the watershed.

2. Background

2.1. Study area

The Tioughnioga River watershed in central New York (Fig. 1) is a major headwater watershed of the Upper Susquehanna River Basin and the largest estuary in the United States, Chesapeake Bay, where the decline of water quality has warranted attention (Budda, 2008; Hetcher-Aguila and Eckhardt, 2006). As a headwater watershed, the Tioughnioga River provides the opportunity to understand the transport of contaminants downstream to the Susquehanna River Basin. The study area is chosen because of the watershed's location in New York State – where road salts are applied heavily during winter months and compiled literature data show a clear increase in chloride concentration in the Tioughnioga River over the last few decades (Fig. 2).

Two tributaries originating in central New York, converge in Cortland County to form the Tioughnioga River (Fig. 1a), a major tributary to the Susquehanna River. The watershed area in this study is approximately 1000 km², and spans 77% of the total area of Cortland County (U.S. Geological Survey, 1980). The Tioughnioga River watershed is located within the Appalachian Plateau physiographic province. Land use in the Tioughnioga River watershed is predominantly forest and agriculture (U.S. Geological Survey, 2001). Urban areas comprise a greater area of the West Branch watershed (Fig. 1b; Table 2). The city of Cortland is located in the watershed of the West Branch. The city of Cortland wastewater treatment plant is located downstream of all sampling locations (Fig. 1a).

Mean daily discharge was recorded at a USGS gaging station (Station Number: 01509000) located 0.4 km downstream of the confluence of East and West Branches. Maximum discharge values occur during summer rain events or spring snowmelt, while minimum discharge is during base flow conditions in the fall (Table 3). Precipitation measurements were acquired through the NOAA Climatic Data Center for the city of Cortland (Station ID: US1NYCR0010).

Table 1

Concentrations of Cl, Br, and ratios of Cl/Br in various sources of salinity. First line for each source of salinity includes the range of concentration values. The second line contains the mean value for each (Adapted from Lautz et al., 2014).

Sources of salinity	Cl (mg/L)	Br (µg/L)	Cl/Br
NYS road salt	9560–19,820	2117–4194	6214–11,050
	13,615	3301	9516
Compiled road salt data	420–31,640	100–4002	2780–131,938
	15,737	882	35,356
Septic effluent	21–5620	50–1040	292–14,585
	334	175	3208
Animal waste	127–2460	216–1413	555–3724
	624	660	2063
Landfill leachate	198–6170	1175–42,760	192–807
	2258	12,061	435
Formation water (including ABB)	5760–207,000	94,000–2,240,000	131–412
	84,067	864,371	240

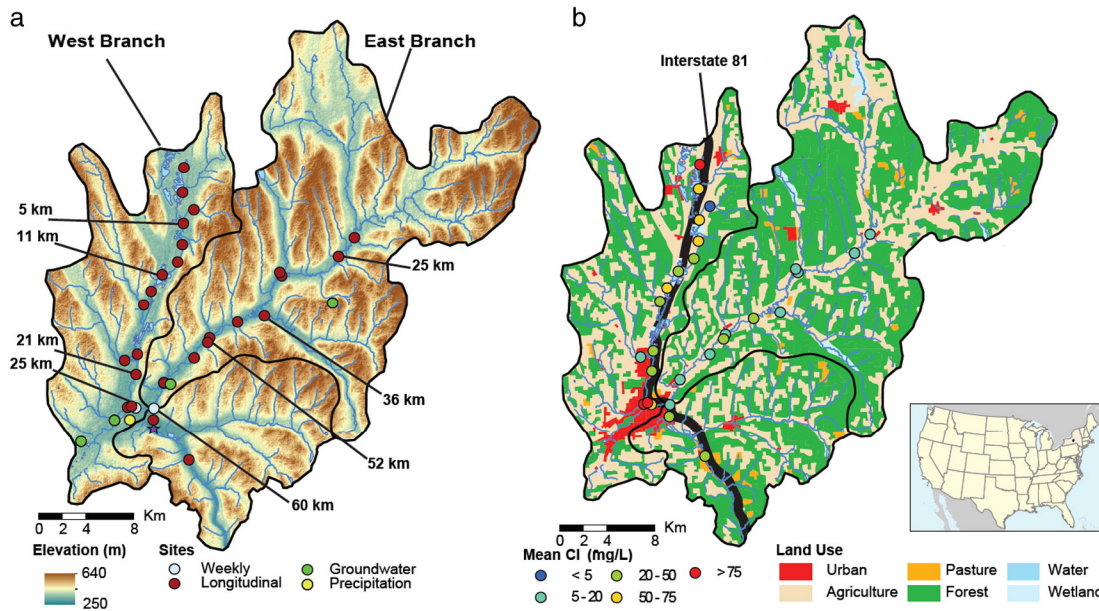


Fig. 1. (a) DEM site map of Tioughnioga river watershed showing location of sampling sites. Down channel distance is labeled. Purple star denotes location of city of Cortland wastewater treatment plant. (b) Land use classification of the Tioughnioga river watershed base on classification scheme suggested by Anderson et al., 1976. Mean concentrations of Cl in mg/L is denoted by colored circles at each site. Location of interstate highway I-81 is depicted by a black line. Site map shows the location of study area relative to contiguous United States. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.2. Geology

The river is underlain by an unconfined glacial-outwash aquifer comprised of sand and gravel and bounded laterally by less permeable till-covered bedrock hills. The underlying glacial aquifer system provides drinking water to inhabitants of the cities of Cortland, Homer, and surrounding communities (Miller, 2004). The aquifer overlies a lacustrine confining unit, underlain by sand and gravel, and Upper to Middle Devonian bedrock consisting predominantly of shale interbedded with siltstone, sandstone, and limestone (Table 3) (Miller et al., 1998; Miller, 2004). Groundwater in the area typically flows down valley (Buller et al., 1978). Previous studies within the watershed have demonstrated measureable groundwater discharge to the river through both seepage runs and model simulations (Miller et al., 1998; Reynolds, 1987; Buller et al., 1978).

2.3. Road salt application

Interstate Highway I-81 is a major US roadway in the Eastern United States. Road salts are applied at an average rate of 30 tons/lane mile to highways in the watershed area (Chris Bistocchi, Superintendent City of Cortland Public Works, personal communication). I-81 runs parallel to the West Branch. Road salt runoff from I-81 is likely a source of Cl to the watershed. It is likely that non-state roads administer de-icing salts at a lesser rate, so a value of 20 tons/lane mile was assumed for all non-state roads based on extrapolation from a rate of 15 tons/mile in the 1970's (Buller et al., 1978).

3. Methods

3.1. Sampling procedure

River water samples were collected from September 2012 through November 2014 in the Tioughnioga River watershed at 30 locations along the Tioughnioga River and four groundwater wells (Fig. 1a). Groundwater samples were collected 27 times between 2012 and 2014. One location in each branch was sampled weekly from September 2012 through November 2014 (n = 104). Longitudinal sampling of the rivers along the 30 locations was conducted six times in 2014 (n = 108). Sampling sites were selected based on accessibility and representativeness of locations within the watershed. Grab samples were collected under a variety of streamflow conditions, encompassing

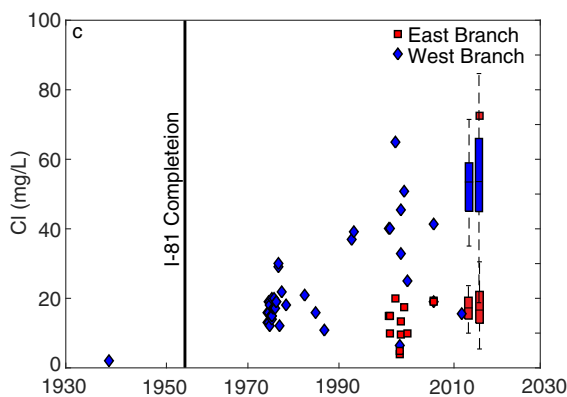


Fig. 2. Concentration of Cl in East and West Branches of the Tioughnioga since 1939 for the West Branch and 1998 for the East Branch (data source: Shindel et al., 1977; Buller, 1978; Miller et al., 1998; Reidy, 2015). Boxplots represent concentrations of Cl collected for this study for water years 2012–2013 and 2013–2014.

Table 2
Land use characteristics for East and West Branches of the Tioughnioga River, Cortland, New York (U.S. Geological Survey, 2001, 1980).

Land use	West Branch		East Branch	
	Area (km ²)	Area (%)	Area (km ²)	Area (%)
Urban	24	9	5	1
Agriculture	120	45	180	36
Forest	116	44	302	61
Wetland	4	1	8	2

Table 3

Watershed characteristics for the Tioughnioga River Watershed, Cortland, New York (Miller et al., 1998; Miller, 2004; U.S. Department of Agriculture, National Agricultural Statistical Service, 2014).

Watershed characteristics		
Total area (km ²)	–	1000
Population	Cortland County	49,000
	City of Cortland	19,000
Mean daily discharge (m ³ /s)	2012	1.2–127
	2013	3.7–98.8
Unconsolidated material thickness (m)	Unconfined glacial outwash aquifer	12–24
	Lacustrine confining unit (till)	0.3–47
	Confined sand and gravel aquifer	0.3–52

baseflow, snowmelt, and stormflow conditions. Precipitation samples were collected at one location following rainfall events.

Water samples were collected in prewashed bottles and filled to the top of the bottle to eliminate headspace. Samples were filtered with a 0.45- μ m filter and split into bottles for anion, and cation. Samples were stored between 0 °C to 4 °C. Samples analyzed for cations were acidified with a 5% HNO₃ solution before refrigeration. Samples for anions were frozen and thawed before analysis.

3.2. Analytical methods

Major cations and anions (Ca, Na, Mg, K, Cl, SO₄, and NO₃) were measured on an ion chromatograph (IC) using a Dionex ICS-1100 for cations and a Dionex ICS-2100 for anions. The system was calibrated with five internal laboratory standards for cations and five internal laboratory standards for anions prior to each run. Concentrations of Iodine (I) and Br were measured on a Bruker Aurora M90 inductively coupled plasma mass spectrometer (ICP-MS). Fresh calibration standards were prepared before the measurements. Blanks were monitored every three samples and calibration standards were run every six samples. Repeat sample runs typically varied by less than 5%. The detection limit of concentrations of Br measured on ICP-MS was below 10 ppb.

3.3. Multivariate statistical analysis

We use multivariate statistical analysis as one additional approach to identify the most probable sources of salinity in the water samples. LDA is a statistical method used to categorize unknown samples into known groups. A previously developed LDA model (Lautz et al., 2014) is adapted for this study. The model is written in MATLAB and incorporates concentrations of seven solutes (I, Na, K, Mg, Ca, Cl, and Br) into a stochastic mixing model, coupled with Monte Carlo simulation and LDA.

Separate statistical models are run for each branch. Each model first creates a sample of synthetic low salinity water samples ($n = 3000$), based on the observed multivariate log-normal distribution of solute concentrations (means and covariance matrix) for samples of low salinity water ($n = 9$ and 21 for East and West Branches, respectively). Measured river water samples are divided into groups of low salinity (samples with concentrations of Cl less than 10.5 mg/L for the East Branch and less than 42 mg/L Cl for the West Branch) or high salinity (samples with concentrations of Cl greater than 10.5 mg/L for the East Branch and greater than 42 mg/L for the West Branch) for this purpose. Samples are then randomly drawn from the synthetic low salinity data and mixed with varying proportions of waters from saline endmembers to create a training dataset comprised of synthetic populations of high salinity groundwater with different, known salinity sources. LDA is then trained on the synthetic high salinity data and used to classify measured samples into the synthetic high salinity population from which they have the highest probability of originating from. More details on the modeling approach used here can be found in Lautz et al. (2014).

Three possible sources of salinity to river water are considered: animal waste, road salt runoff, and groundwater from surrounding counties (Steuben, Chemung, Tioga, Broome, and Chenango Counties) that had been previously classified as influenced by ABB by the same model (Lautz et al., 2014). The endmember concentrations were obtained from published data for each source (Howard and Beck, 1993; Granato, 1996; Foos, 2003; Panno et al., 2005; Panno et al., 2006; Kelly et al., 2010a, 2010b; Ledford and Lautz, 2014). Additional endmembers considered in the literature (e.g. landfill leachate, septic effluent, acid mine drainage) are not known to exist to any sizable extent in the study area, thus they are not included as sources in the model exercise.

3.4. Mass balance and residence time of chloride

In order to assess the retention of Cl in the watershed we first developed a simple Cl mass balance approach. The Cl mass balance of the Tioughnioga River watershed can be derived by subtracting the total mass of Cl applied within the watershed from the Cl load leaving the watershed through river discharge. The difference between inflow and outflow results in an annual mass of Cl stored within the watershed. Retained Cl is likely to accumulate in groundwater, lakes, wetlands, and vegetation throughout the study area. To calculate the mass of Cl applied to the study area each year, we multiply road types and road lane lengths by their respective application rates (Winters, 2015; Bitocchi, 2013). Outflow of Cl is derived by calculating the total load of Cl leaving the watershed through river discharge for the year. The total load of Cl is equivalent to the annual sum of average daily concentration of Cl in the river multiplied by daily mean river discharge. Outflow is then subtracted from inflow to get the total mass of Cl resulting from the application of de-icing salts to roadways that remains in the watershed each year.

Daily flow data for Tioughnioga River tributaries only exists for the West Branch between 1966 and 1986 (USGS gauging station number: 01,508,803). Based on comparisons between Tioughnioga River discharge and discharge of the West Branch Tioughnioga River, it was determined that the West Branch contributes roughly 30 to 50% to the total discharge of the Tioughnioga River. In order to encompass the variation in contribution to the flow data that is available for our study interval, we vary the proportion of discharge that the West Branch contributes between 30 and 50% of the mean daily discharge of the Tioughnioga River to estimate the possible range of Cl loads.

We apply a previously developed mixing model (Shaw et al., 2012) to further investigate the relationships between Cl inputs and concentrations of Cl in surface water discharge. The model assumes a variable rate of road salt application that increases gradually over time until it attains a near constant level of application. The model (Eq. 1) calculates the residence time of Cl using five parameters: the year that road salting began in the watershed (t_0), the initial concentration of Cl in the river prior to the onset of widespread application of de-icing salts to roadways (C_0), the maximum concentration of recharge water to the system (C_∞), a rate constant concerning the increase in rates of road salt application (α), and the average residence time of Cl in the watershed in years (K).

$$C = C_\infty [1 - \exp(-kt^*)] - \frac{(C_\infty - C_0)}{1 - \frac{\alpha}{k}} [\exp(\alpha t^*) - \exp(-kt^*)] + C_0 \exp(-kt^*) \quad (1)$$

Parameter values were decided based on available data for the watershed. The model is calibrated to minimize the sum-of-squares between predicted and observed concentrations of Cl in the river and obtain a best fit. Background concentrations (C_0) of Cl were approximately 2 mg/L and were obtained from data published in previous studies (Buller, 1978). Because the initial model was applied to a watershed (Fall Creek watershed) adjacent to the Tioughnioga River watershed, the year that road salting began (t_0) and the increase in road salt

application rates over time (α) are assumed to be equal to the values derived in the original study of 1955 and 0.07 year^{-1} , respectively (Shaw et al., 2012). Because of the slight uncertainty in the actual α in this watershed, an alternate rate 0.05 year^{-1} is also considered. We determined the maximum concentration of recharge water (C_{∞}) to the system by dividing the annual load of Cl that is not lost to direct wash off (approximately 90% of the total annual load) by annual recharge (assumed annual recharge = annual base flow). The maximum concentration of recharge water used was 60 mg/L , calculated from 25,800 metric tons of annual Cl load is not lost to wash off divided by $3.8 \times 10^8 \text{ m}^3$ of annual base flow. We compiled historic observations of Cl measured during baseflow in the West Branch of the Tioughnioga River in order to assess the performance of the model (Waller and Finch, 1982; Shindel et al., 1977; Buller et al., 1978; Miller et al., 1998; Cortland County Soil and Water Conservation District, 2015). Individual data points are shown in Fig. 1c. A total of 54 point measurements in the West Branch were obtained from records spanning the years 1930 to 2014.

4. Results

4.1. Halogen concentrations

Concentrations of Cl in surface water are generally higher in the West Branch than in the East Branch of the Tioughnioga River (Table 4). Groundwater concentrations of Cl show similar West-East contrast, with higher values in the West Branch. Low concentrations of Cl often occur under high flow conditions such as rainfall and snowmelt events in both branches (Fig. 3a). High concentrations of Cl in river water are commonly associated with low flow conditions. Concentrations of Cl in groundwater of the West Branch are highest during spring of 2014. Concentrations of Br are higher in the West Branch than in the East Branch on most dates. A similar relationship applies to concentrations of Br in groundwater in the two watersheds (Table 4). Concentrations of Br are low during high flow events. High concentrations of Br occur under low flow conditions (Fig. 3b).

4.2. Ratios of Cl/Br

Ratios of Cl/Br plotted against Cl show the evolution of water chemistry and mixing trends between pristine and contaminated sources (Panno et al., 2006; Davis et al., 1998; Johnson et al., 2015). We apply this approach to our river water samples (Fig. 4). The mixing lines illustrate boundaries on the range of concentrations observed in water samples, relative to that of the road salt runoff (Fig. 4). Higher concentrations of Cl and Cl/Br ratios are observed in the West Branch.

A two-endmember mixing model was created to further define the mixing relationships. We use concentrations of Cl and Br in dilute road salt runoff reported for this area (Lautz et al., 2014) to define the road salt endmember in the mixing model. Solid road salt samples were collected from four highway salt depots in Broome, Chemung, Chenango, and Tioga Counties and diluted for analysis with DI water (Lautz et al., 2014). Because the river water naturally mixes with road salt runoff diluted to different degrees, we create four additional mixing trends by increasing Cl and Br concentrations in the runoff endmember ($2\times$, $5\times$, $8\times$, and $10\times$) while keeping Cl/Br ratio the same in the endmember. Most

Table 4
Concentrations of Cl and Br measured in surface water and groundwater from September 2012 through November 2014.

	West Branch		East Branch	
	Surface water	Groundwater	Surface water	Groundwater
Range of Cl (mg/L)	19–85	6–99	4–73	6–37
Average Cl (mg/L)	52	61	18	14
Range of Br ($\mu\text{g/L}$)	12–43	10–41	9–44	14–25
Average Br ($\mu\text{g/L}$)	27	30	21	19

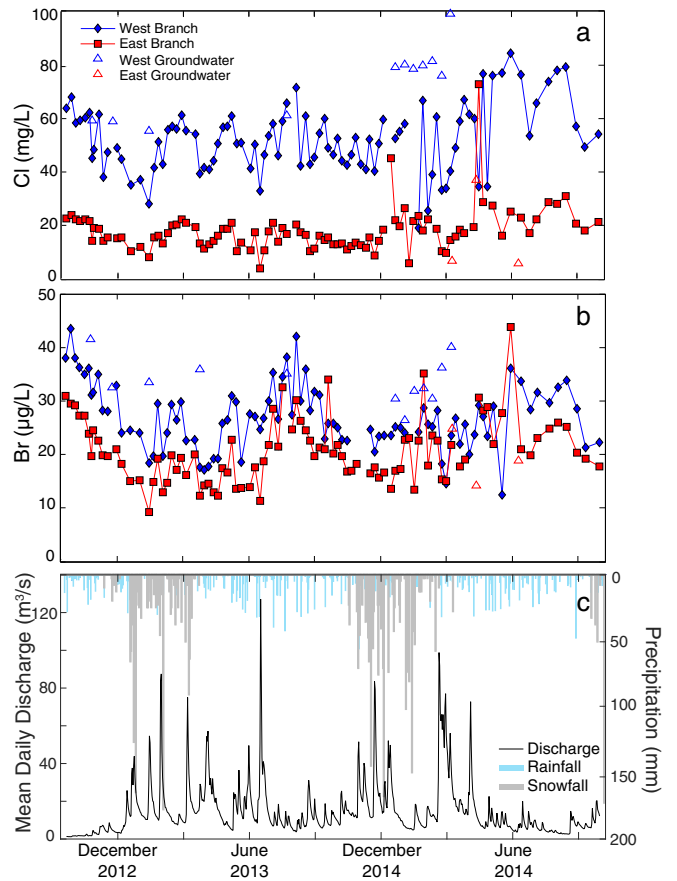


Fig. 3. Chloride (a), bromide (b), concentrations at weekly sampling sites from September 10th 2012 through November 29th 2014, and (c) precipitation and mean daily discharge of the Tioughnioga River (NOAA Climate Center Station ID: US1NYCR0010, USGS gauging Station No. 01509000).

samples fall within mixing lines of 5 to 10 times more concentrated than the dilute runoff, with a broader range in concentration values observed in the West Branch.

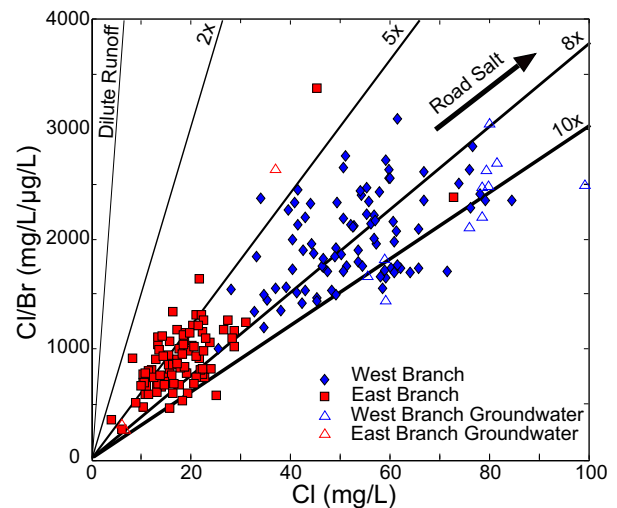


Fig. 4. Cl/Br ratios vs. Cl concentrations of river water and groundwater samples. Surface water and groundwater from East and West Branches follows mixing lines from pristine groundwater to road salt contaminated water. Each line indicates the degree of salinization (e.g. dilute runoff, 2 times more concentrated, 5, 8, and $10\times$ more concentrated than dilute runoff). Lines were determined through the two-endmember mixing scenario.

4.3. Multivariate statistical analysis

The LDA model generates two linear classifiers and accompanying scores for the training data and observed high salinity samples. The scores (Score 1 and Score 2) represent the combination of standardized and log transformed solute concentrations that result in the greatest separation of samples into different groups (Fig. 5). Score 1 separates samples mixed with ABB from road salt runoff. Score 1 exhibits a positive correlation with Br, similar to the results of prior works which have observed elevated levels of Br and I in brines relative to other sources of salinity (Davis et al., 1998; Panno et al., 2006; Warner et al., 2012; Lu et al., 2015). Score 2 separates animal waste from other endmembers. Score 2 values are positively correlated with K, Mg, and Ca ions. Animal waste can be enriched in K.

Because Score 1 serves to separate samples mixed with ABB from those mixed with road salts, samples with positive values for Score 1 are more likely to be classified as influenced by ABB, whereas samples with negative values for Score 1 likely represent mixing with road salt. Samples with scores that lie within overlapping regions of synthetic high salinity samples suggest that the endmembers are present in comparable amounts. For example, many of the water samples which were

classified as impacted by ABB appear to overlap with synthetic animal waste samples. The classification of samples as either animal waste affected waters or ABB affected waters results from the endmember with the greatest associated probability. Therefore, samples classified as impacted by road salts, have a greater probability associated with the synthetic road salt samples, than the probabilities associated with synthetic animal waste, or ABB samples. The classifications do not serve to discount mixtures of more than one source, but rather indicate the dominant source of salinity in a given water sample.

4.4. Classification by linear discriminant analysis

The results of the LDA model reveal that de-icing salts are not the sole source of salinity in the Tioughnioga River watershed (Fig. 6). Model output indicates that over 90% of the samples analyzed for the West Branch are impacted by road salts (2% ABB, 91% road salt, and 7% animal waste). Road salt is a dominant source of salinity in the East Branch, however the East Branch is also impacted by ABB, a source notably more pronounced than in the West Branch (26% ABB, 54% road salt, and 20% animal waste). Samples with any missing values for solutes were not classified by the model and are plotted as “unclassified

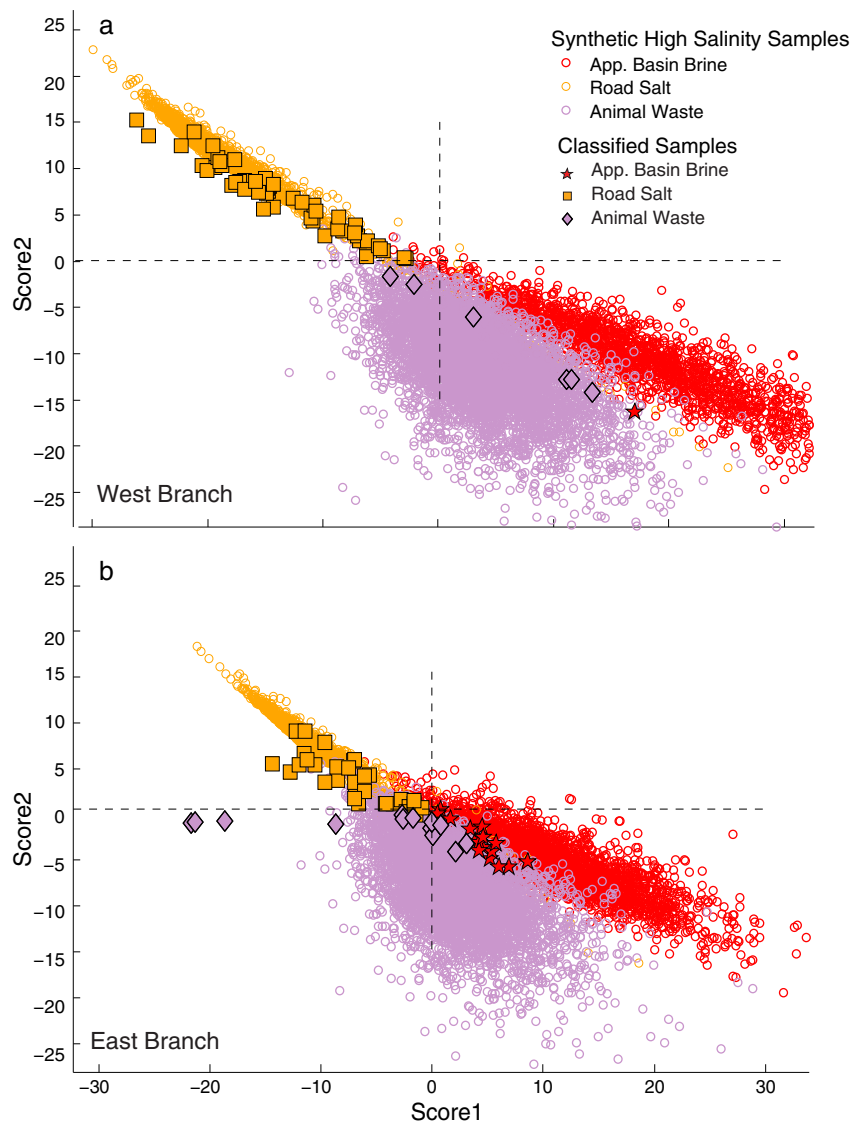


Fig. 5. Score 1 and Score 2 values of training data sets for each endmember. Score 1 and Score 2 values for West (a) and East Branch (b) classified samples are also shown. Only samples with information for all of the concerned solutes (I, Na, K, Ca, Mg, Cl, and Br) were considered.

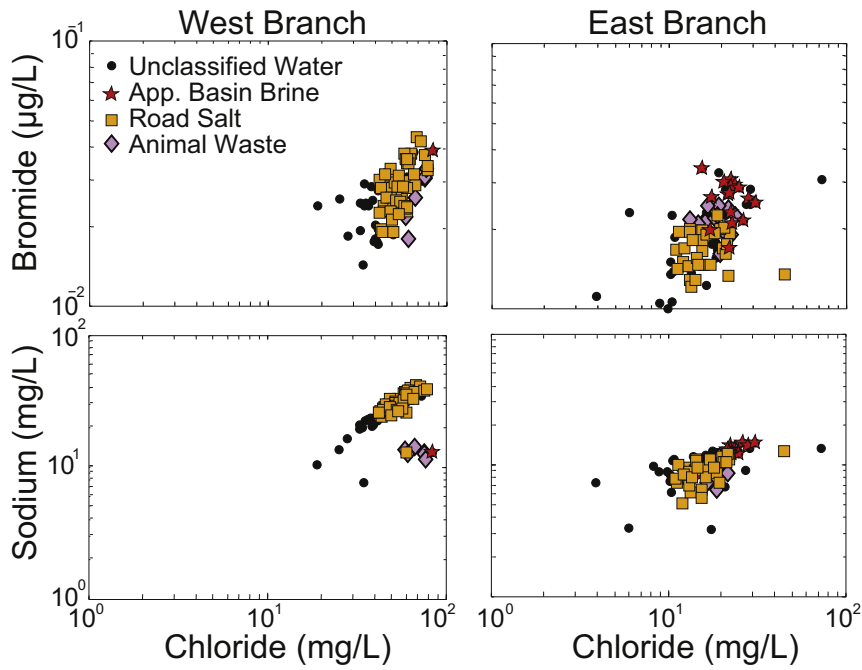


Fig. 6. Observations of unclassified and classified river water samples. Unclassified samples were excluded from LDA due to missing values of concentrations of solutes.

groundwater,” on the accompanying diagram (Fig. 6). It is likely that mixing of several sources of salinity contributes to the observed concentrations of Cl in water samples at a given time.

4.5. Temporal and spatial variations in longitudinal profiles

Concentrations of Cl range between 5 and 87 mg/L from the source down to the confluence in the West Branch, and from 6 to 32 mg/L in

the East Branch. At a downstream distance of 26 km from the source two major tributaries enter the West Branch. The tributaries pass through urban areas before their confluence with the Tioughnioga River (Fig. 7). Cl concentrations increase by up to 35 mg/L following the confluence. Field observations reveal that these tributaries do not contribute sizable amounts of water to the West Branch during winter months. Spatial variability is less pronounced in the East Branch. At approximately 60 km downstream an increase in

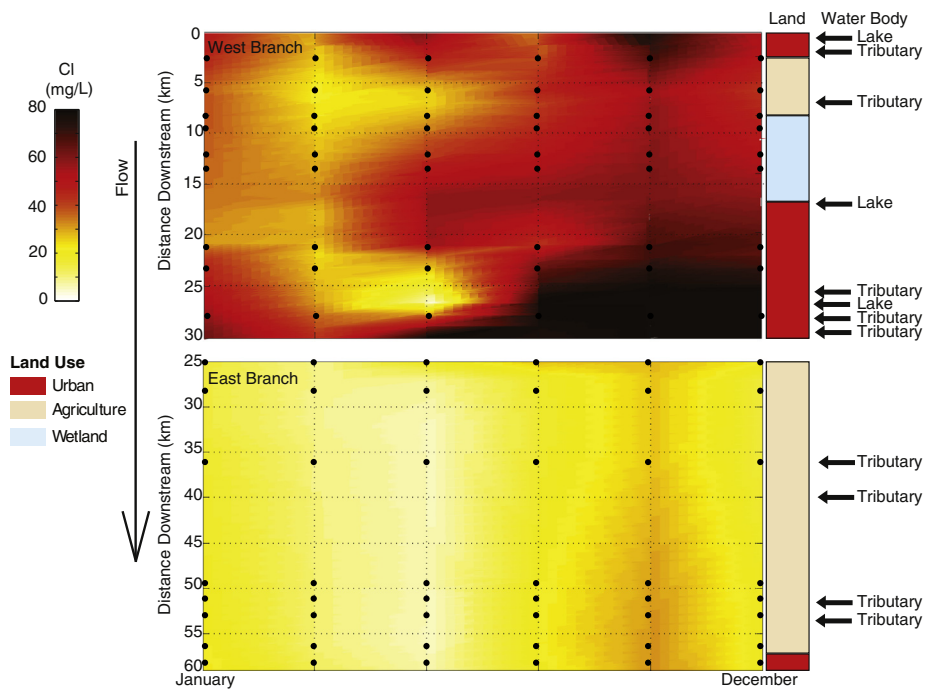


Fig. 7. Downstream concentrations of Cl for West and East Branches Tioughnioga River from January 2014 through December 2014. Points signify date and location of sample collection. Colored column indicates land use. Arrows mark the location of confluences with tributaries and outlets of lakes with the main channel. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

concentrations of Cl can be observed that coincides with increasing areas of urban land.

4.6. Residence time model

To better understand the length of time that de-icing salts can persist in the Tioughnioga River watershed, we modify an existing model to derive estimates of residence time of Cl (Shaw et al., 2012). The increase in concentrations of Cl over time in the West Branch Tioughnioga River ranges from 2 mg/L to 20 mg/L in 1930 and 1976 to the 2012–2014 average of 52 mg/L. Historic concentrations of Cl measured during baseflow conditions are weighted to discharge observations and averaged to create a flow-weighted mean Cl value. This value is then fit to a line derived by Eq. 1 to determine the residence time of Cl in the Tioughnioga River watershed (Fig. 8). Flow-weighted mean Cl concentrations between 1975 and 2010 that do not fall along modeled ranges were calculated for years with missing data or measured during periods of high flow. Based on uncertainties in historical road salt application rates, a number of simulations were performed in which α , C_{∞} , and t_0 were varied (Table 5). The best-fit of Eq. 1 to observed concentrations of Cl in river water can be achieved with residence times (k^{-1}) of 20 to 30 years (Fig. 8).

5. Discussion

The average concentration of Cl measured in the West Branch for this study is more than double of Cl concentrations in the East Branch, likely as a result of road salt usage (Fig. 1b). Concentrations of Cl measured in East and West Branches of the Tioughnioga River have increased since the 1950's (Fig. 2). During the summer of 2014, concentrations of Cl in the West Branch are notably higher than those observed during the winter months (Fig. 3a). This is likely the result of the combined effects of a greater total snowfall in 2013 winter and a lower summer precipitation rates in 2014 (Fig. 3c). Because snowfall and road salt application have a positive relationship, it is probable that a greater mass of de-icing salts was applied to roadways during the winter of 2013 (Gardner and Royer, 2010). Higher precipitation rates during 2012–2013 may have contributed to the subsequent dilution of concentrations of Cl. Elevated ratios of Cl/Br in surface water and groundwater from the Tioughnioga River watershed indicate that road salt is a dominant source of salinity, particularly in the West

Branch. The position of water samples relative to mixing lines suggests that the runoff of road salt to the East and West Branches of the Tioughnioga River can be as much as 5 to 10 times more concentrated than previously reported (Fig. 4) (Lautz et al., 2014). Results of LDA further confirm the impacts of road salt on the Tioughnioga River.

Potential explanations for the differences described above include a variety of both anthropogenic and climatic factors that may affect the transport of road salt to rivers, such as application rates, land use, proximity to roadways, snowmelt rates, and vegetation (Buttle and Labadia, 1999; Lovett et al., 2005; Findlay and Kelly, 2011; Shaw et al., 2012; Rhodes and Guswa, 2016). Bedrock weathering and Cl enrichment due to irrigation water return flow are not considered to be major sources of salinity to the watershed. Based on the 2012 Census of Agriculture (USDA NASS, 2014), Cortland County had over 50,000 acres of total cropland but only 81 acres were irrigated at any point during the season. Therefore, we would expect negligible amounts of Cl due to irrigation return flow. The majority of either reach is underlain by recent alluvium or glacial outwash. Bedrock exposure in either study area is minimal, thus we have assumed that Cl contributions to surface water as a result of the chemical weathering of bedrock, are minimal relative to other sources. Here we explore potential causes for the observed temporal and spatial geochemical patterns and their future implications.

5.1. Impact of interstate highway 81 (I-81)

Application of deicing salting on I-81 should make substantial contributions to the observed high Cl levels in the West Branch of the Tioughnioga River, relative to the East Branch, although other factors may warrant additional discussions. Road salt has been shown to accumulate in snowbanks and soils adjacent to roads and other paved surfaces (Buttle and Labadia, 1999). Road salt can reach the river through either direct runoff from the road or accumulation in snowbanks and release during snowmelt (Buttle and Labadia, 1999; Gardner and Royer, 2010). Demers and Sage (1990) observe this process in the nearby central Adirondack region of New York in the late 1980's. The combined impacts of greater road salt application rates on highway roads and the greater road density in the West Branch control the differences in salinity across East and West Branches.

Mean annual Cl concentration increases as a function of urban land use (Kaushal et al., 2005; Novotny et al., 2008; Cunningham et al., 2009; Ledford and Lautz, 2014). Several studies have connected an increase in urbanization with rising concentrations of Cl (Rhodes et al., 2001; Demers and Sage, 1990; Cunningham et al., 2009; Gardner and Royer, 2010; Trowbridge et al., 2010). Taking into consideration the difference in land use across the two watersheds, it is probable that runoff of road salts from impervious surfaces in urban areas, and especially from Interstate 81, have contributed to both the overall rise in concentrations of Cl that have been observed and the differences in magnitude of Cl across the two branches (Fig. 1c). Additionally, the geochemical signature of road salt may mask the natural signatures of basin brines that would be observed in the absence of de-icing measures.

Concentrations of Cl in the West Branch are notably higher year-round, despite road salts only being applied during the winter months. Surface runoff and drainage systems do not entirely remove road salt from aquatic systems in urban to suburban settings (Cunningham et al., 2008; Findlay and Kelly, 2011). Lovett et al. (2005) demonstrate that the retention of Cl in vegetation can later serve as a source of Cl. In addition to storage in groundwater, uptake of Cl by vegetation in the Tioughnioga River watershed could provide a continual source of Cl to rivers and tributaries located in proximity to roadways, thereby maintaining high concentrations of Cl throughout the year. Soils and wetlands are a significant source of retention of road salt contamination (Rhodes and Guswa, 2016). As wetlands are present within the watersheds of either branch, remobilization of road salts from wetland areas

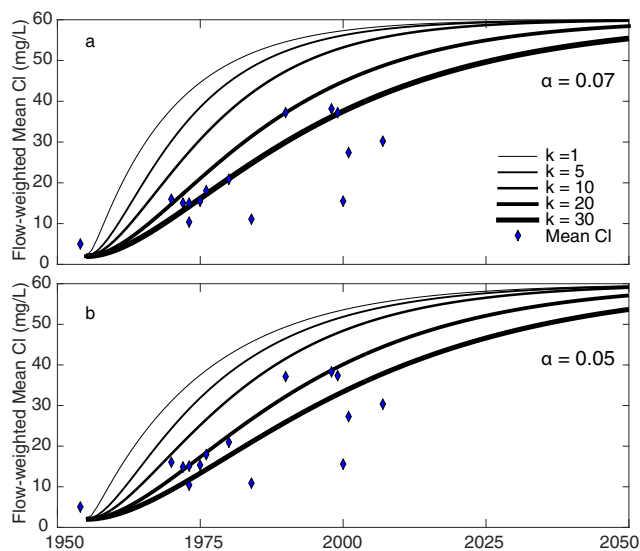


Fig. 8. Application of mixing model to the West Branch Tioughnioga River. Different curves indicate model output for different residence times (k^{-1}) ranging from 1 to 30 years for two different scenarios in the rate at which road salt application has increased in time: $\alpha = 0.07$ (a) and $\alpha = 0.05$ (b).

Table 5
Summary of sensitivity analysis of Cl residence time model parameters: constant for change in Cl application rates (α), and residence time (K^{-1}) in years. Year road salting began (t_0), initial concentration of Cl (C_0), and the maximum concentration of recharge water to the system (C_∞), were not varied across model runs. Their respective values are $t_0 = 1955$, $C_0 = 2$ mg/L, $C_\infty = 50$ mg/L (Buller, 1978, Shaw et al., 2012).

α (year $^{-1}$)	K^{-1} (year)	R ²	SE (mg/L)	RMSE (mg/L)	nRMSE
	1	0.58	1.55	24.22	0.73
0.07					
	5	0.73	1.55	19.39	0.59
0.07					
	10	0.85	1.54	13.11	0.40
0.07					
	20	0.92	1.48	4.89	0.15
0.07					
	30	0.93	1.55	3.30	0.10
0.07					
	1	0.70	4.24	18.21	0.55
0.05					
	5	0.81	3.34	13.67	0.41
0.05					
	10	0.89	2.40	8.26	0.25
0.05					
	20	0.93	1.45	2.90	0.09
0.05					
	30	0.94	2.07	5.41	0.16
0.05					

is likely an additional source of remobilized Cl. The retention of salt will be further discussed later.

5.2. Short-term sources related to land use type

Urban areas contribute saline waters to drinking water and surface water in areas where de-icing salts are applied to roads and other impervious surfaces such as sidewalks and parking lots (Kaushal et al., 2005; Kelly et al., 2008; Cunningham et al., 2008; Ledford and Lautz, 2014). Concentrations of Cl in streams and rivers in New York are positively correlated with impervious surface cover as a result of the use of de-icing salts (Ledford and Lautz, 2014). In this study, an increase in urbanization with down channel distance corresponds to elevated concentrations of Cl in East and West Branches of the Tioughnioga River (Fig. 8).

The spatial distribution of Cl in the West Branch reveals two locations in which nonpoint source pollution is increasingly concentrated (Fig. 8): Tully Lake – located approximately 2.5 km from the headwaters of the West Branch and adjacent to I-81 in the town of Tully, and urban areas within the town of Homer and the city of Cortland (23–27 km downstream). The State University of New York College at Cortland is located on a bedrock hill within the watershed of the West Branch. College campuses may apply de-icing salts at a greater rate than local and state agencies (Cunningham et al., 2008). Based on halogen ratios and LDA, urban tributaries bring waters contaminated by de-icing salts to the downstream reach of both branches.

Unlike the West Branch that has a consistent proximity to a major interstate highway, urban areas in the East Branch are concentrated in the downstream segment of the river. Increased concentrations of Cl in the downstream reach of the East Branch are due to the application of de-icing salts to impervious surfaces within the city of Cortland. Tributaries to the upstream reach of the East Branch lack a notable contribution from de-icing salts, and may have been influenced by alternate sources of salinity such as ABB or animal waste.

In the Tioughnioga River watershed, a higher percentage of urban land contributes a greater annual load (25,000 tons/year Cl) to waters of the West Branch compared to an annual load of only 12,000 tons/year Cl in the East. Daily flow data indicate that the West Branch contributes roughly 30 to 50% to the total discharge of the Tioughnioga River. Based on the percent contribution of the West Branch to the total discharge of the River, the results of mass balance calculations suggest that there is an overall storage of approximately 34–60% (12,500 to

22,500 tons/year Cl) of the total Cl applied to roadways annually. These are conservative estimates as they encompass variations in flow contribution of East and West Branches as described in previous sections.

In addition to the completion of Interstate 81, the growth of urban areas has contributed to an increase in application of de-icing salts to roadways in the study area. Waters contaminated by road salt may enter the river through direct runoff from roadways or can be stored in groundwater and released into the river over time. This has led to a substantial rise in concentrations of Cl in surface water and groundwater located near urban areas and roadways in the Tioughnioga River watershed, with long-term consequences.

5.3. Long-term retention of de-icing salts in aquifer

Elevated concentrations of Cl in summer months are indicative of retention and remobilization of Cl in groundwater, soils, vegetation, and wetlands (Demers and Sage, 1990; Kincaid and Findlay, 2006; Kelly et al., 2008; Gardner and Royer, 2010). This is observed in the stream chemistry of both branches, on at least a seasonal timescale. Long term retention of Cl in watersheds as a result of de-icing salt application to roadways is documented in numerous studies (e.g. Kelly et al., 2008; Novotny et al., 2009; Kelly et al., 2010a, 2010b; Jin et al., 2011; Shaw et al., 2012). Cl is stored in shallow groundwater and released into surface water over time, contributing to an overall increase in concentrations of Cl observed in streams and rivers in regions where road salts are applied over the past several decades (Ramakrishna and Viraraghavan, 2005; Novotny et al., 2008; Ostendorf et al., 2008; Novotny et al., 2009; Kelly et al., 2010a, 2010b). Furthermore, Gardner and Royer (2010) show an increase in stream water Cl, suggesting retention of Cl in urban sites, despite an otherwise relatively quick export. Based on the seasonal fluctuations in downstream Cl concentrations, mass balance, and residence time calculations, we suggest that there is long term retention of de-icing salts in the aquifer of our study area.

Our mass balance calculations are comparable to values derived in other studies of small, urban to suburban watersheds in the Snowbelt region (Paine, 1979; Howard and Haynes, 1993; Kelly et al., 2008). Paine (1979) found that as little as 50% of the total Cl contained in de-icing salts applied to urban areas and roadways was removed by overland flow in the Don River Watershed, Toronto, Canada. Howard and Haynes (1993) estimated only about 45% of Cl is removed annually by surface runoff in Toronto, and Bubeck et al. (1971) derive an estimate

of 41% Cl removed, with the remainder being stored in soils and groundwater.

Model results suggest a residence time of Cl of approximately 20 to 30 years. This estimate is similar to the residence time modeled in a nearby county of 40 to 70 years (Shaw et al., 2012). However, much longer residence times up to hundreds and thousands of years have been suggested in other studies (Novotny et al., 2009). If the application of road salts remains at the current rate, concentrations of Cl will continue to rise in the East and West Branches of the Tioughnioga River until leveling off around the year 2100 (Fig. 8). Based on the calculated residence times for the watershed, even if the application of de-icing salts to roadways were to decrease, we would continue to observe relatively high concentrations of stream Cl for decades as Cl stored in the subsurface is flushed into surface water. As urban populations grow and urban landscapes expand, salt application will become more widespread, further intensifying the observed effects.

6. Conclusions

Cl concentrations in Tioughnioga River waters has been increasing since the construction of an interstate highway. Halogen concentrations and ratios (Cl/Br) suggest that road salt runoff impacts both branches regardless of contrasting land use patterns. The West Branch exhibits a greater influence from de-icing salts, which is likely the result of a greater area of urban land and its proximity to a highly traveled highway. Discriminant analysis supports the results of halogen mixing model, and further indicates that ABB are mixing with stream water in the East Branch, although their contribution may be volumetrically minor. Seasonal changes in concentrations of Cl in longitudinal profiles suggest storage of Cl within the watershed and that urban areas are important nonpoint sources of Cl. An overall increase in baseflow concentrations of Cl in the West Branch, and calculated decadal residence times suggest the persistent influence of de-icing salts in river waters. Similar approaches can be adapted to better understand the controls of salinity in other natural water systems.

Acknowledgements

KG was supported by Syracuse University Water Fellowship and NRT: Education Model Program on Water-Energy Research (EM-POWER) at Syracuse University (DGE-1449617). SUNY Cortland faculty research program 2012–2013 provided partial funding for this work. We thank Zeno Levy, Sarah Ledford, and David Barclay for providing constructive feedback on this study. Patrick Reidy of Cortland County Soil and Water Conservation District provided assistance on field sampling and historic water quality data. We thank the three anonymous reviewers for suggestions that improved the manuscript and Damia Barceló for editorial handling.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.04.181>.

References

- Anderson, J.R., Hardy, E.E., Roach, J.T., Witmer, R.E., 1976. A land use and land cover classification system for use with remote sensor data. *Geol. Surv. Prof. Pap.* 864.
- Bitocchi, C., 2013. Personal Communication 26 December Department of Public Works, Cortland, New York, United States.
- Bubeck, R.C., Diment, W.H., Deck, B.L., Baldwin, A.L., Lipton, S.D., 1971. Runoff of deicing salt: effect on Irondequoit Bay, Rochester, New York. *Science* 172, 1128–1132.
- Budda, S., 2008. Summary report: upper Susquehanna subbasin survey: a water quality and biological assessment June–September 2007. Susquehanna River Basin Commission Technical Reports. Publication Number 260, pp. 1–32.
- Buller, W., 1978. Hydrologic Appraisal of the Water Resources of the Homer–Prelle Valley, New York. U. S. Geological Survey Water-Resources Investigations Open-File Report pp. 78–94.
- Buller, W., Nichols, W., Harsh, J.F., 1978. Quality and Movement of Ground Water in Otter Creek–Dry Creek Basin, Cortland County, New York. U. S. Geological Survey Water-Resources Investigations Open-File Report 78-3.
- Buttle, J.M., Labadia, C.F., 1999. Deicing salt accumulation and loss in highway snowbanks. *J. Environ. Qual.* 28, 155–164.
- Corsi, S.R., Cicco, L.A., Lutz, M.A., Hirsch, R.M., 2015. River chloride trends in snow-affected urban watersheds: increasing concentrations outpace urban growth rate and are common among all seasons. *Sci. Total Environ.* 508, 488–497.
- Cunningham, M.A., Snyder, E., Yonkin, D., Ross, M., Elsen, T., 2008. Accumulation of deicing salts in soils in an urban environment. *J. Urban Econ.* 11, 17–31.
- Cunningham, M.A., O'Reilly, C.M., Menking, K.M., Gillikin, D.P., Smith, K.C., Foley, C.M., Belli, S.L., Pregna, A.M., Schlessman, M.A., Batur, P., 2009. The suburban stream syndrome: evaluating land use and stream impairments in the suburbs. *Phys. Geogr.* 30 (3), 269–284.
- Daley, M.L., Potter, J.D., McDowell, W.H., 2009. Salinization of urbanizing New Hampshire streams and groundwater: effects of road salt and hydrologic variability. *J. N. Am. Benthol. Soc.* 28, 929–940.
- Davis, S.N., Whittemore, D.O., Fabryka-Martin, J., 1998. Uses of chloride/bromide ratios in studies of potable water. *Ground Water* 36 (2), 13.
- Demers, C.L., Sage, R.W., 1990. Effects of road deicing salt on Chloride levels in four Adirondack streams. *Water Air Soil Pollut.* 49, 369–371.
- Findlay, S.E.G., Kelly, V.R., 2011. Emerging indirect and long-term road salt effects on ecosystems. *Annals of the New York Academy of Sciences, Issue: The Year in Ecology and Conservation Biology*, pp. 58–68.
- Foos, A., 2003. Spatial distribution of road salt contamination of natural springs and seeps, Cuyahoga Falls, Ohio, USA. *Environ. Geol.* 44 (1), 14–19.
- Freeman, J.T., 2007. The use of bromide and chloride mass ratios to differentiate salt-dissolution and formation brines in shallow groundwaters of the Western Canadian Sedimentary Basin. *Hydrobiologia* 15 (7), 1377–1385.
- Gardner, K.M., Royer, T.V., 2010. Effect of road salt application on seasonal Chloride concentrations and toxicity in South-Central Indiana streams. *J. Environ. Qual.* 39, 1036–1042.
- Granato, G.E., 1996. Deicing chemicals as a source of constituents of highway runoff. Transportation Research Record 1533. National Research Council, Washington, D. C., pp. 50–58.
- Hetcher-Aguila, K.K., Eckhardt, D.A., 2006. Ground-water quality in the Upper Susquehanna River Basin, New York, 2004–2005. U.S. Geological Survey Open-File Report 2006-1161 p. 21 p.
- Howard, K.W.F., Beck, P.J., 1993. Hydrogeochemical implications of groundwater contamination by road deicing chemicals. *J. Contam. Hydrol.* 12 (3), 245–268.
- Howard, K.W.F., Haynes, J., 1993. Urban geology 3. Groundwater contamination due to road de-icing chemicals – salt balance implications. *Geosci. Can.* 20, 1–8.
- Jackson, R.B., Jobbágy, E.G., 2005. From icy roads to salty streams. *Proc. Natl. Acad. Sci. U. S. A.* 102 (41), 14487–14499.
- Jin, L., Whitehead, P., Siegel, D.I., Findlay, S., 2011. Salting our landscape: an integrated catchment model using readily accessible data to assess emerging road salt contamination to streams. *Environ. Pollut.* 159 (5), 1257–1265.
- Johnson, J.D., Graney, J.R., Capo, R.C., Stewart, B.W., 2015. Identification and quantification of basin brine and road salt sources in watersheds along the New York/Pennsylvania border, USA. *J. Appl. Geochem.* v. 60, 37–50.
- Kaushal, S.S., Groffman, P.M., Likens, G.E., Belt, K.T., Stack, W.P., Kelly, V.R., ... Fisher, G.T., 2005. Increased salinization of fresh water in the northeastern United States. *Proc. Natl. Acad. Sci. U. S. A.* 102 (38), 13517–13520 (<http://doi.org/10.1073/pnas.0506414102>).
- Kelly, V.R., Lovett, G.M., Weathers, K.C., Findlay, S.E.G., Strayer, D.L., Burns, D.J., Likens, G.E., 2008. Long-term sodium chloride retention in a rural watershed: legacy effects of road salt on streamwater concentration. *Environ. Sci. Technol.* 42 (2), 410–415 (<http://doi.org/10.1021/es0713911>).
- Kelly, V.R., Panno, S.V., Hackley, K.C., Hwang, H.H., Marinsek, A.T., Markus, M., 2010b. Using chloride and other ions to trace sewage and road salt in the Illinois Waterway. *Appl. Geochem.* 25 (5), 661–673.
- Kelly, V.R., Findlay, S.E.G., Schlesinger, W.H., Chatrchyan, A.M., Menking, K., 2010a. Road salt: moving toward the solution. *The Cary Institute of Ecosystem Studies*.
- Kincaid, D.W., Findlay, S.E.G., 2006. Sources of elevated chloride in local streams: groundwater and soils as potential reservoirs. *Water Air Soil Pollut.* 203 (1), 335–342.
- Lautz, L.K., Hoke, G.D., Lu, Z., Siegel, D.I., Christian, K., Kessler, J.D., Teale, N.G., 2014. Using discriminant analysis to determine sources of salinity in shallow groundwater prior to hydraulic fracturing. *Environ. Sci. Technol.* 48, 9061–9069.
- Ledford, S.H., Lautz, L.K., 2014. Floodplain connection buffers seasonal changes in urban stream water quality. *Hydrol. Process.* <http://dx.doi.org/10.1002/hyp.10210>.
- Llewellyn, G.T., 2014. Evidence and mechanisms for Appalachian Basin brine migration into shallow aquifers in NE Pennsylvania, USA. *Hydrogeology J.* 22, 1055–1066.
- Lovett, G.M., Likens, G.E., Buso, D.C., Driscoll, C.T., Bailey, S.W., 2005. The biogeochemistry of chloride at Hubbard Brook, New Hampshire, USA. *Big Data* 72, 191–232.
- Lu, Z., Hummel, S.T., Lautz, L.K., Hoke, G.D., Zhou, X., Leone, J., Siegel, D.I., 2015. Iodine as a sensitive tracer for detecting influence of organic-rich shale in shallow groundwater. *Appl. Geochem.* 60, 29–36. <http://dx.doi.org/10.1016/j.apgeochem.2014.10.019>.
- Miller, T.S., 2004. Hydrogeology and Simulation of Ground-Water Flow in a Glacial-Aquifer System at Cortland County, New York. U. S. Geological Survey Fact Sheet FS 054-03.
- Miller, T.S., Sherwood, D.A., Jeffers, P.M., Mueller, N., 1998. Hydrology, Water-Quality and Simulation of Ground-Water Flow in a Glacial Aquifer System, Cortland County, New York. U. S. Geological Survey Water-Resources Investigations Report 96-4255.
- Mullaney, J.R., Lorenz, D.L., Arntson, A.D., 2009. Chloride in Groundwater and Surface Water in Areas Underlain by the Glacial Aquifer System, Northern United States. U.S. Geological Survey Water Resources Scientific Investigations Report 2009-5086.

- Novotny, E.V., Murphy, D., Stefan, H.G., 2008. Increase of urban lake salinity by road deicing salt. *Sci. Total Environ.* 406, 131–144.
- Novotny, E.V., Sander, A.R., Mohseni, O., Stefan, H.G., 2009. Chloride ion transport and mass balance in a metropolitan area using road salt. *Water Resour. Res.* 45, W12410.
- Ostendorf, D.W., Rotaru, C., Hinlein, E.S., 2008. Steady groundwater transport of highway deicing agent constituents from an infiltration basin. *J. Irrig. Drain. Eng.* 134 (5), 630–637.
- Paine, L.R., 1979. Chlorides in the Don River Watershed Resulting From Road De-icing Salt: University of Toronto Institute for Environmental Studies. Snow and Ice Working Group Working Paper Publication No. SIC-3, p. 23 p.
- Panno, S.V., Hackey, K.C., Hwang, H.H., Greenberg, S.E., Krapac, I.G., Landsberger, S., O'Kelly, D.J., 2005. Database for the characterization and identification of the sources of sodium and chloride in the natural waters of Illinois. Illinois State Geological Survey. Open-File Series, p. 1.
- Panno, S.V., Hackley, K.C., Hwang, H.H., Greenberg, S.E., Krapac, I.G., Landsberger, S., O'Kelly, D.J., 2006. Characterization and identification of Na-Cl sources in ground water. *Ground Water* 44 (2), 176–187. <http://dx.doi.org/10.1111/j.1745-6584.2005.00127.x>.
- Ramakrishna, D.M., Viraraghavan, T., 2005. Environmental impacts of chemical deicers – a review. *Water Air Soil Pollut.* 155, 49–63.
- Reidy, P., Cortland County Soil and Water Conservation District, Cortland, New York, United States, 2015c. Personal Communication 12 November .
- Reynolds, R., 1987. Hydrogeology of the Surficial Outwash Aquifer at Cortland, Cortland County, New York. U.S. Geological Survey. Water Resources Investigations Open-File Report 85–4090.
- Rhodes, A.L., Newton, R.M., Pufall, A., 2001. Influences of land use on water quality of a diverse New England watershed. *Environ. Sci. Technol.* 35 (18), 3640–3645.
- Rhodes, A.L., Guswa, A.J., 2016. Storage and release of road-salt contamination from a calcareous lake-basin fen, western Massachusetts, U.S.A. *Sci. Total Environ.* v.545–546, 525–545.
- Shaw, S.B., Marjerison, R.D., Bouldin, D.R., Parlange, J., Walter, M.T., 2012. Simple model of changes in stream chloride levels attributable to road salt applications. *J. Environ. Eng.* 138 (1), 112–118.
- Shindel, H., Buller, W., Johnston, W.H., 1977. Water Resources in Western Cortland County, New York: Hydrological Data for 1972–1975 and Progress Report. U.S. Geological Survey Water-Resources Investigations Open-File Report 77–525.
- Trowbridge, P.R., Kahl, J.S., Sassan, D.A., Heath, D.L., Walsh, E.M., 2010. Relating road salt to exceedances of the water quality standard for chloride in New Hampshire Streams. *Environ. Sci. Technol.* 44 (13), 4903–4909.
- U.S. Department of Agriculture, National Agricultural Statistical Service, 2014i. 2012 Census of Agriculture. Washington, DC.
- U.S. Geological Survey, 1980. 1:2,000,000-scale Digital Line Graph, NYS Hydrography (1980). U.S. Geological Survey, Reston, VA.
- U.S. Geological Survey, 2001. 1:250,000 Scale Land Use and Land Cover, Binghamton Quadrangle (ARC Export: 1990). U.S. Geological Survey, Reston, VA.
- Waller, R.M., Finch, A.J., 1982. Atlas of eleven selected aquifers in New York. U. S. Geological Survey Water Resources Investigations Open-File Report 82–553.
- Warner, N.R., Jackson, R.B., Darrah, T.H., Obsorn, S.G., Down, A., Zhao, K.C., White, A., Vengosh, A., 2012. Geochemical evidence for possible natural migration of Marcellus Formation brine to shallow aquifers in Pennsylvania. *Proc. Natl. Acad. Sci. U. S. A.* 109 (30), 11961–11966.
- Winters, F., 2015. StreetSegment Public. Albany, NY, NYS GIS Program Office.