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Abstract

The transport of solutes from their source to natural water systems is a critical control on the chemistry and potability of drinking water supplies. Therefore, developing a thorough understanding not only of contaminant sources, but also of the controls on the movement of solutes through catchments, is essential to providing accurate assessments of how future environmental stressors (e.g. land cover, population growth, and climate change) may affect water resources.

Halogens (specifically, chloride (Cl), bromide (Br), and iodine (I)) occur naturally at low levels in terrestrial aquatic ecosystems, and may also originate from a suite of anthropogenic sources. Due to their largely conservative behavior, and preferential incorporation into mineral crystal lattices during evaporation processes resulting from differences in ionic radii, ratios of Cl/Br are used to identify sources of salinity to freshwater systems. This approach can broadly distinguish endmember sources of salinity (e.g. road salts from basin brines) from one another, although has proven ineffective in distinguishing saline endmembers originating from the same processes (e.g. formation waters of different ages), thus warranting development of alternate approaches.

Elevated levels of Cl are harmful to sensitive biota, threaten riparian ecosystems, and may increase the corrosivity of affected waters. Anthropogenic practices may introduce Cl to drinking water supplies. Present-day controls on the salinization of freshwater systems have been rigorously evaluated. Although, prior to this dissertation, no future predictions of the impacts of continued deicing practices on freshwater salinization had incorporated changes in climate coupled with dynamic population and land use.

Iodinated disinfection by-products (I-DBPs) form when source waters containing halogens and organic matter are disinfected via chloramination during wastewater treatment processes. Despite the emergence of I-DBPs as highly toxic, teratogenic, and potentially carcinogenic agents, controls on the transport of iodine in terrestrial aquatic environments have yet to be fully constrained. As source water iodine is a major source of iodine in the formation of I-DBPs, developing a thorough understanding of the controls on the natural cycling of iodine in paired surface water-groundwater systems is essential to providing accurate assessments for the potential of adverse environmental and health effects following modern wastewater treatment practices. Individual components of the terrestrial aquatic iodine cycle have been studied extensively, although a single study has yet to evaluate variation of total dissolved iodine concentrations at the catchment scale across both time and space.

The purpose of this dissertation research was to evaluate the effects of anthropogenic and hydrogeologic processes on the fate of salinity and halogens at the catchment scale. We focus our efforts in the East and West Branches of the Tioughnioga River Watershed in Upstate New York State (NYS), USA. Spatially and temporally resolved series of major and trace halogens (Cl, Br, and I) were used in combination with graphical, statistical, and numerical approaches to elucidate controls on halogen sources and solute flow paths in headwater catchments with mixed land cover in temperate climates.

Salinity in the Tioughnioga River watershed has been increasing since the late 1930's. This trend increased precipitously after the completion of a major interstate highway (Interstate-81) in the West Branch catchment area during the 1950's. We used two independent approaches to characterized sources of Cl to both East and West Branches of the Tioughnioga River over a two-year interval: (1) Cl/Br ratios to graphically separate waters impacted by road salts from

other sources of contamination and (2) linear discriminant analysis (LDA) to quantitatively determine the most likely source of contamination to individual water samples. Ratios of Cl/Br suggested that road salt affected waters are present in both branches, but are more prominent in the West Branch, which has a greater percentage of urban land cover. LDA supports the results of Cl/Br in the West Branch and further reveals volumetrically minor contributions of Appalachian Basin Brines to surface waters in the East Branch. Downstream profiles of Cl concentrations in surface waters indicate that sources of pollution are concentrated around urban areas and may impact surface water chemistry year-round. We used a simple mixing model to estimate a residence time of Cl in the watershed of approximately 20 to 30 years, suggesting that stream Cl concentrations may continue to rise for several decades given no change in conditions. Assessment of the potential future impacts of continued de-icing practices is regularly evaluated using numerical and statistical models. These methods have undoubtedly advanced our understanding of the prolonged effects of de-icing practices on aquatic environments and drinking water quality. Although, these approaches have not incorporated future changes in climate that are projected to impact hydrogeology. To address this deficit, we use an INtegrated CAtchment (INCA) model to simulate Cl concentrations in the Tioughnioga River watershed. We ran the model over a baseline period (1961-1990) and over three future intervals (2010-2039; 2040-2069; 2070-2099) for future climate scenarios from a range of global climate models (GCMs). Model projections suggest that Cl concentrations in the catchment will continue to rise for several decades, before beginning to decline roughly mid-century, with all scenarios resulting in reduced winter snowfall totals and associated salt applications over the course of the 21st century. We attributed the delay in stream response to climate change and continued contribution of Cl from aquifers. By 2100, surface water Cl concentrations will decrease to below 1960's

values. Decreasing trends in average surface water Cl are moderate in catchments dominated by urban lands compared to those in forested catchments.

We evaluate the controls on contributions of iodine to surface water from different sources under variable hydrologic conditions across spatial and temporal scales in the Tioughnioga River watershed. Our findings reveal that iodine varies seasonally with temperature, suggesting a linkage to export of dissolved organic carbon. Iodine may be elevated temporarily during high flow events, resulting from near-stream subsurface storage during dry periods. Based on major ion analysis, LDA, and endmember mixing analysis, under low flow conditions, iodine in surface water likely originates from groundwater. Additionally, our findings illustrate that iodine varies significantly across a catchment, suggesting influence from local hydrologic controls. In addition to atmospheric deposition of iodine in rainwater, additional controls on transport may be linked to weathering of exposed rocks. Thus, we propose that terrestrial iodine fluxes in temperate forested catchments are closely tied to both surface sources and local hydrogeology and thus, suggest that waste water treatment facilities closely monitor source water iodine concentrations and adjust treatment practices accordingly.

This dissertation ultimately contributes to the growing and collective body of knowledge regarding halogen transport and sources in freshwater systems and provides valuable insights to future water resources security.

Evaluating the effects of hydrogeologic processes on the fate of salinity and halogens in
headwater catchments

by

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Dissertation

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Doctor of Philosophy in *Earth Sciences*

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Table of Contents

| | |
|--|----------|
| Abstract | i |
| Title Page | v |
| Acknowledgements | vii |
| List of Tables | xiii |
| List of Figures | xv |
| Chapter 1: Chloride sources in urban and rural headwater catchments, central New York | 1 |
| Abstract | 2 |
| 1. Introduction | 3 |
| 2. Background | 4 |
| 2.1 Background | 4 |
| 2.2 Geology | 5 |
| 2.3 Road Salt Application | 6 |
| 3 Methods | 6 |
| 3.1 Sampling Procedure | 6 |
| 3.2 Analytical Methods | 7 |
| 3.3 Multivariate Statistical Analysis | 8 |
| 3.4 Mass Balance and Residence Time of Chloride | 8 |

| | |
|---|-----------|
| 4. Results | 11 |
| 4.1. Halogen Concentrations | 11 |
| 4.2 Ratios of Cl/Br | 12 |
| 4.3 Multivariate Statistical Analysis | 12 |
| 4.4 Classification by Linear Discriminant Analysis | 13 |
| 4.5 Temporal and Spatial Variations in Longitudinal Profiles | 14 |
| 4.6 Residence Time Model | 14 |
| 5. Discussion | 15 |
| 5.1. Impact of Interstate Highway (I-81) | 16 |
| 5.2. Short-term Sources Related to Land Use Type | 18 |
| 5.3. Long-term Retention of De-icing Salts in Aquifer | 19 |
| 5. Conclusions | 21 |
| Acknowledgements | 21 |
| Tables | 23 |
| Figures | 28 |
| References | 36 |
| Chapter 2: Long-term Climatic and Anthropogenic Impacts on Stream Water Salinity in New York State: INCA Simulations Offer Cautious Optimism | 46 |
| Abstract | 47 |

| | |
|--|----|
| 1. Introduction | 48 |
| 2 Methods | 49 |
| 2.1 Site Description | 49 |
| 2.2 INCA-Cl Model Setup | 50 |
| 2.3 Model Calibration and Sensitivity Analysis | 53 |
| 2.4 Future Scenarios | 55 |
| 4. Results & Discussion | 56 |
| 4.1. Model Calibration | 56 |
| 4.2 Uncertainty & Sensitivity | 57 |
| 4.3 Baseline Simulations | 58 |
| 4.4 Future Climate-induced Changes to Stream Cl Concentrations | 59 |
| 4.5 Future Anthropogenic Impacts on Surface Water Cl | 61 |
| 4.6 Implications and Future Work | 63 |
| Funding Sources | 65 |
| Acknowledgements | 65 |
| Tables | 66 |
| Figures..... | 68 |
| Supporting Information | 72 |

| | |
|--|-----------|
| References | 86 |
| Chapter 3: Controls on Iodine Sources, Storage, and Transport in Forested Headwater | |
| Catchments | 96 |
| Abstract | 97 |
| 1. Introduction | 98 |
| 2 Methods | 100 |
| 2.1 Sample Collection | 100 |
| 2.2 Data Acquisition | 100 |
| 2.3 Iodine Leaching Experiments | 101 |
| 2.4 Analytical Methods | 102 |
| 3. Setting | 102 |
| 3.1 Land Use Classification | 103 |
| 3.2 Hydrogeology | 104 |
| 4. Results | 105 |
| 4.1. Water Samples | 105 |
| 4.2 Iodine Leaching | 106 |
| 4.3 Mass Balance | 107 |
| 5. Discussion | 108 |
| 5.1. Sources of Iodine | 108 |

| | |
|--|-----|
| 5.2 Event-based Iodine Flux | 112 |
| 5.3 Surface-subsurface Hydrogeologic Controls on in-stream Iodine..... | 113 |
| 5.4 Broader Impacts | 117 |
| 6. Conclusions | 118 |
| Acknowledgements | 119 |
| Tables | 120 |
| Figures | 123 |
| Supporting Information | 131 |
| References | 133 |
| Biographical Information | 145 |

List of Tables

Chapter 1

Table 1. Concentrations of Cl, Br, and ratios of Cl/Br in various sources of salinity

Table 2. Land use characteristics for East and West Branches of the Tioughnioga River, Cortland, New York

Table 3. Watershed characteristics for the Tioughnioga River Watershed, Cortland, New York

Table 4. Concentrations of Cl and Br measured in surface water and groundwater from 2012 – 2014 in the Tioughnioga River Catchment.

Table 5. Summary of sensitivity analysis of Cl residence time model parameters

Chapter 2

Table 1. Watershed characteristics for Tioughnioga River

Table 2. Results of sensitivity analysis obtained with best-fit model calibration

Table S1. Average annual Cl-loads during calibration period

Table S2. Descriptive Statistics for daily Cl concentrations during future simulation periods for reach 5

Table S3. Descriptive Statistics for daily Cl concentrations during future simulation periods for reach 11

Table S4. Descriptive statistics for daily Cl concentrations during baseline simulation period for reach 5 and 11

Table S5. Number of days that the baseline average annual precipitation as snowfall was exceeded for each model scenario

Table S6. Percent change from baseline in average annual total precipitation as snowfall and total precipitation for each INCA model scenario.

Table S7. INCA model calibration efficiencies

Chapter 3

Table 1. Hydrogeologic characteristics of East and West Branches of the Tioughnioga River

Table 2. Descriptive statistics for iodine concentrations measured in various water sources in the Tioughnioga River catchment from 2012 – 2014

Table 3. Results of cold-water extractable iodine leaching experiments and associated bedrock characteristics

List of Figures.

Chapter 1

Figure 1. Site maps of Tioughnioga River watershed38

Figure 2. Cl concentrations in East and West Branches of the Tioughnioga River since 1939 ...39

Figure 3. Chloride and bromide concentrations from 2012-2014 in East and West Branches of the Tioughnioga River40

Figure 4. Cl/Br ratios vs. Cl concentrations of Tioughnioga River watershed samples41

Figure 5. LDA scores and training datasets42

Figure 6. LDA classifications43

Figure 7. Downstream Cl concentration profiles for East and West Branches of the Tioughnioga River, 201444

Figure 8. Residence time mixing model results for the Tioughnioga River watershed45

Chapter 2

Figure 1. INCA reach structure and land use classification78

Figure 2. INCA calibration results from 2012 to 201579

Figure 3. INCA-Cl model results for reaches 5 and 1180

Figure 4. Mean monthly anomaly in surface water concentrations of Cl for reaches 5 and 1181

Figure S1. INCA Inputs for calibration period83

| | |
|--|----|
| Figure S2. Downscaled and bias-corrected GCM temperature and precipitation monthly anomalies for IPCC scenarios A2 and B2..... | 84 |
|--|----|

Chapter 3

| | |
|--|-----|
| Figure 1. Site map of study area showing location and type of sample sites | 135 |
| Figure 2. Concentrations of iodine measured weekly in East and West Branches of the Tioughnioga River, Cortland, NY | 136 |
| Figure 3. Log concentration-discharge (CQ) plots for downstream reaches of East and West Branches of the Tioughnioga River | 137 |
| Figure 4. Concentrations of iodine and corresponding stream temperature measured in East and West Branches of the Tioughnioga River | 138 |
| Figure 5. Event-based dissolved ion concentrations measured in East and West Branches of the Tioughnioga River during snowmelt and rainfall events | 139 |
| Figure 6. Site map of the Tioughnioga River showing average iodine concentrations, bedrock outcrops and distribution of wetlands | 140 |
| Figure 7. Downstream iodine concentration profiles for East and West Branches of the Tioughnioga River, 2016 | 141 |
| Figure 8. Conceptual model of terrestrial aquatic iodine cycle | 142 |
| Figure S1. Time series for major ions in East and West Branches of the Tioughnioga River ... | 143 |
| Figure S2. Geologic map of surrounding area and locations of bedrock sample collection | 144 |

Chapter 1:

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

Chapter 1 has been published as:

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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.

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. 2010, Corsi et al. 2015). Elevated concentrations of chloride are harmful to sensitive biota (Jackson and Jobbágy 2005, Kaushal et al. 2005, Kelly et al. 2010), 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. 2014, Panno 2006, Davis et al. 2001).

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, Llewelyn 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 1977, 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 (Buda 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 (Figure 1a), a major tributary to the Susquehanna River. The watershed area in this study is approximately 1,000 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 (Figure 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 (Figure 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).

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 1978, 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 (Figure 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 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- μm 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. 2010, and 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). 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: 01508803). 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 to 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).

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

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 3.8×10^8 m³ 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 Figure 1c. A total of 54 individual 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 (Figure 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 (Figure 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 (2x, 5x, 8x, and 10x) while keeping Cl/Br ratio the same in the endmember. Most 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.

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 (Figure 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 2006, Warner et al. 2012, Lu et al. 2014). 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 (Figure 6). Model output indicates that over 90 percent 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 groundwater,” on the accompanying diagram (Figure 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 (Figure 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 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 equation 1 to determine the residence time of Cl in the Tioughnioga River watershed (Figure 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 (Figure 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 (Figure 1b). Concentrations of Cl measured in East and West Branches of the Tioughnioga River have increased since the 1950's (Figure 2). During the summer of 2014, concentrations of Cl in the West Branch are notably higher than those observed during the winter months (Figure 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 (Figure 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 (Figure 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 Royers 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 (Figure 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 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 (Figure 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, 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. 2010, 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. 2010). Furthermore, Gardner and Royers (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 (Figure 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.

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Tables

Table 1. Concentrations of Cl, Br, and ratios of Cl/Br in various sources of salinity. The 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 ($\mu\text{g/L}$) | Cl/Br |
|---------------------------------|---------------------------|-------------------------------|--------------------------|
| NYS Road Salt | 9,560 – 19,820 13,615 | 2,117 – 4,194 3,301 | 6,214 – 11,050 9,516 |
| Compiled Road Salt Data | 420 – 31,640 15,737 | 100 – 4,002 882 | 2780 – 131,938 35,356 |
| Septic Effluent | 21 – 5,620 334 | 50 – 1,040 175 | 292 – 14,585 3,208 |
| Animal Waste | 127 – 2,460 624 | 216 – 1,413 660 | 555 – 3,724 2,063 |
| Landfill Leachate | 198 – 6,170 2,258 | 1,175 – 42,760 12,061 | 192 - 807 435 |
| Formation Water (including ABB) | 5,760 – 207,000 84,067 | 94,000 – 2,240,000 864,371 | 131 - 412 240 |

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. Census Bureau, 2014).

| Watershed Characteristics | | |
|--|------------------------------------|------------|
| Total Area (km ²) | - | 1,000 |
| 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 |

Table 4. Concentrations of Cl and Br measured in surface water and groundwater from

| | 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 (μ g/L) | 12 – 43 | 10 – 41 | 9 – 44 | 14 - 25 |
| Average Br (μ g/L) | 27 | 30 | 21 | 19 |

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 |
|--------------------------------|-----------------|----------------|-----------|-------------|-------|
| 0.07 | 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 |
| 0.05 | 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 |

Figures

Figure 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.

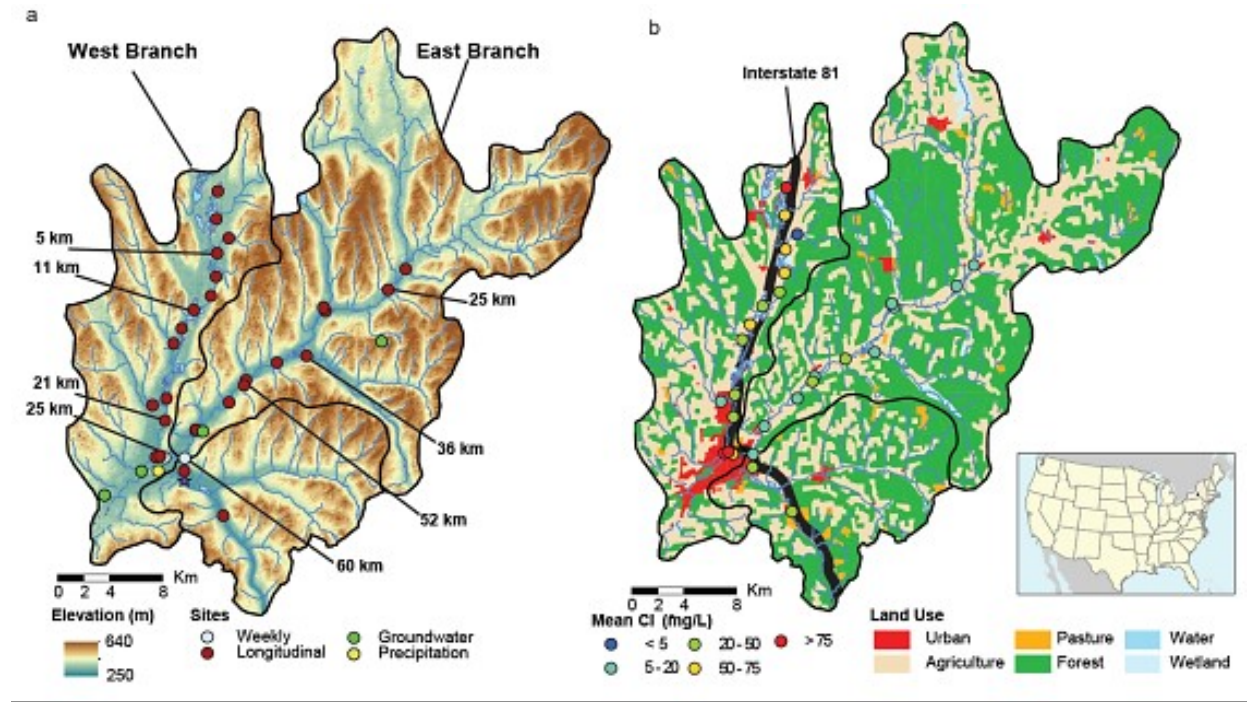


Figure 2. Concentration of Cl in East and West Branches of the Tioughnioga since 1939 for the West Branch and 1998 for the East Branch (data source: Shindel et al. 1977, Buller 1978, Miller et al. 1998, and Reidy 2015). Boxplots represent concentrations of Cl collected for this study for water years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

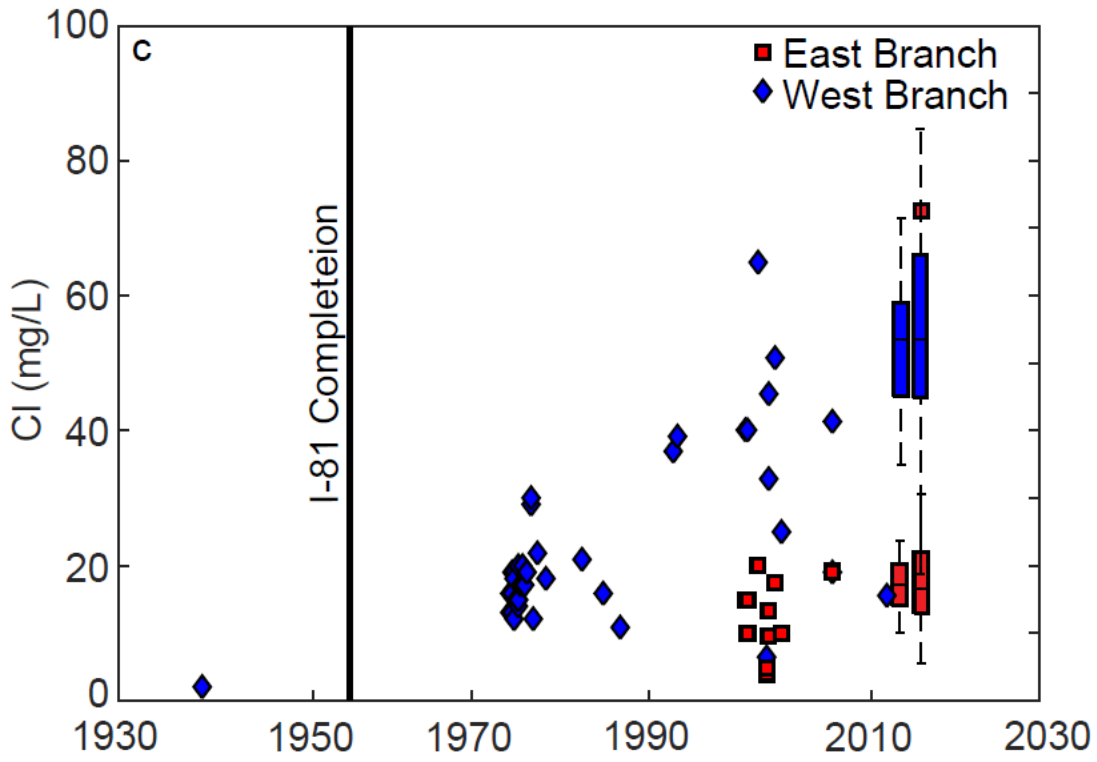


Figure 3. Chloride (a), bromide (b), concentrations at weekly sampling sites from September 10th, 2012 through November 29th, 2014, and (c) precipitation and mean daily discharge of the Toughnioga River (NOAA Climate Center Station ID: US1NYCR0010, USGS gauging station No. 01509000).

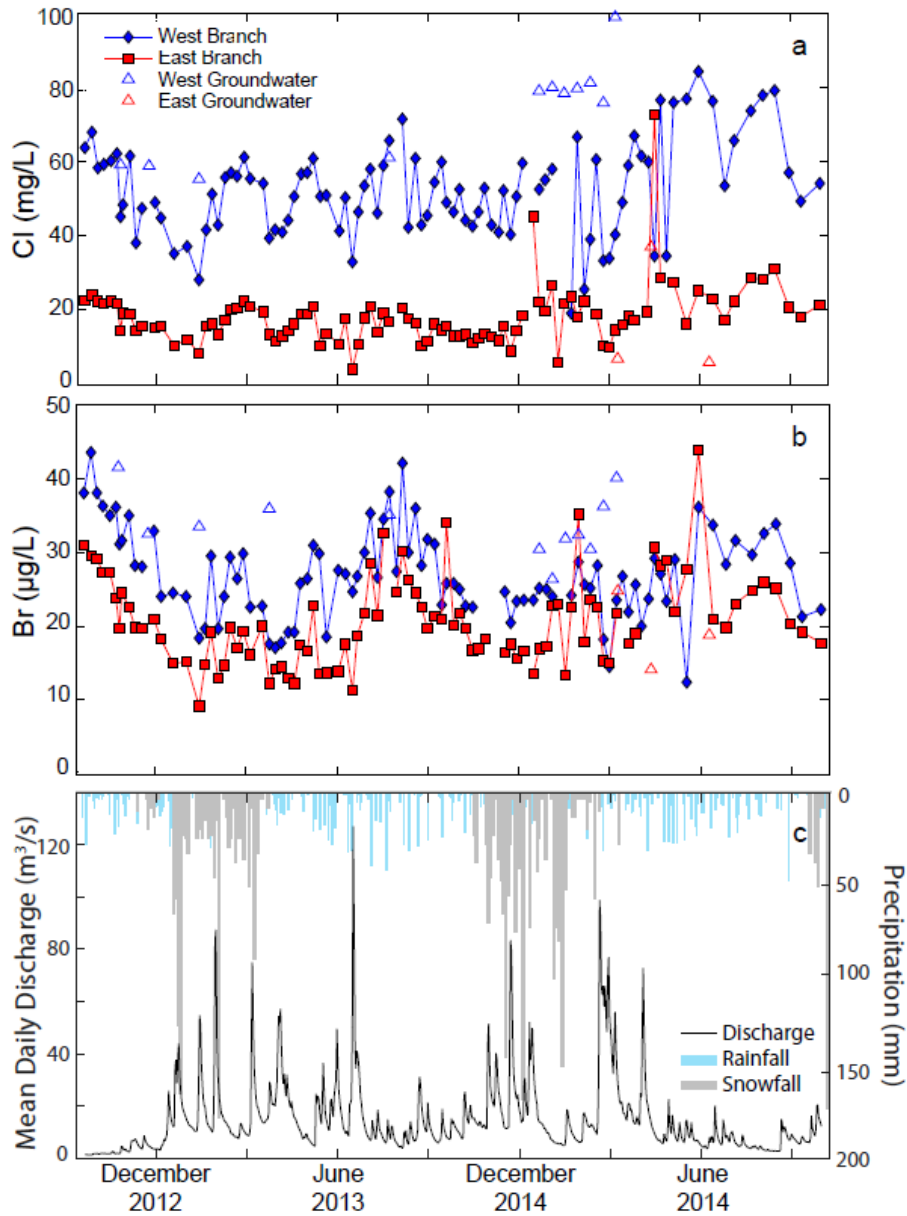


Figure 4. Cl/Br ratios vs. Cl concentrations of river water and groundwater samples. Surface water and groundwater from East and West Branches follows mixing lines from pristine groundwater to road salt contaminated water. Each line indicates the degree of salinization (e.g. dilute runoff, 2 times more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

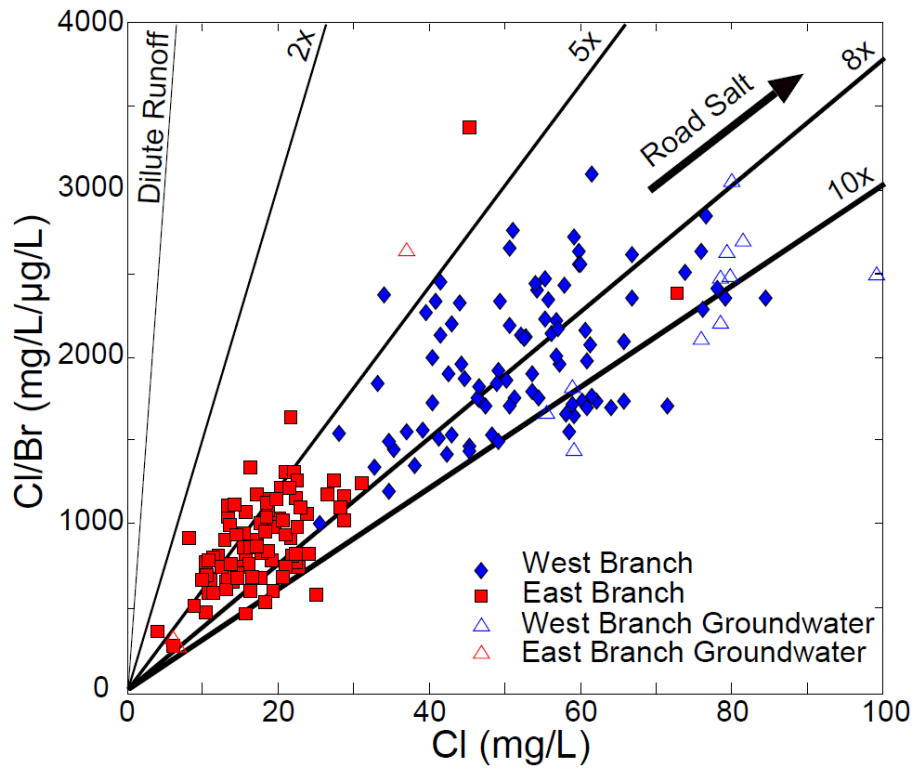


Figure 5. Score 1 and score 2 values of training data sets for each endmember. Score 1 and Score 2 values for West (a) and East Branch (b) classified samples are also shown. Only samples with information for all the concerned solutes (I, Na, K, Ca, Mg, Cl, and Br) were considered.

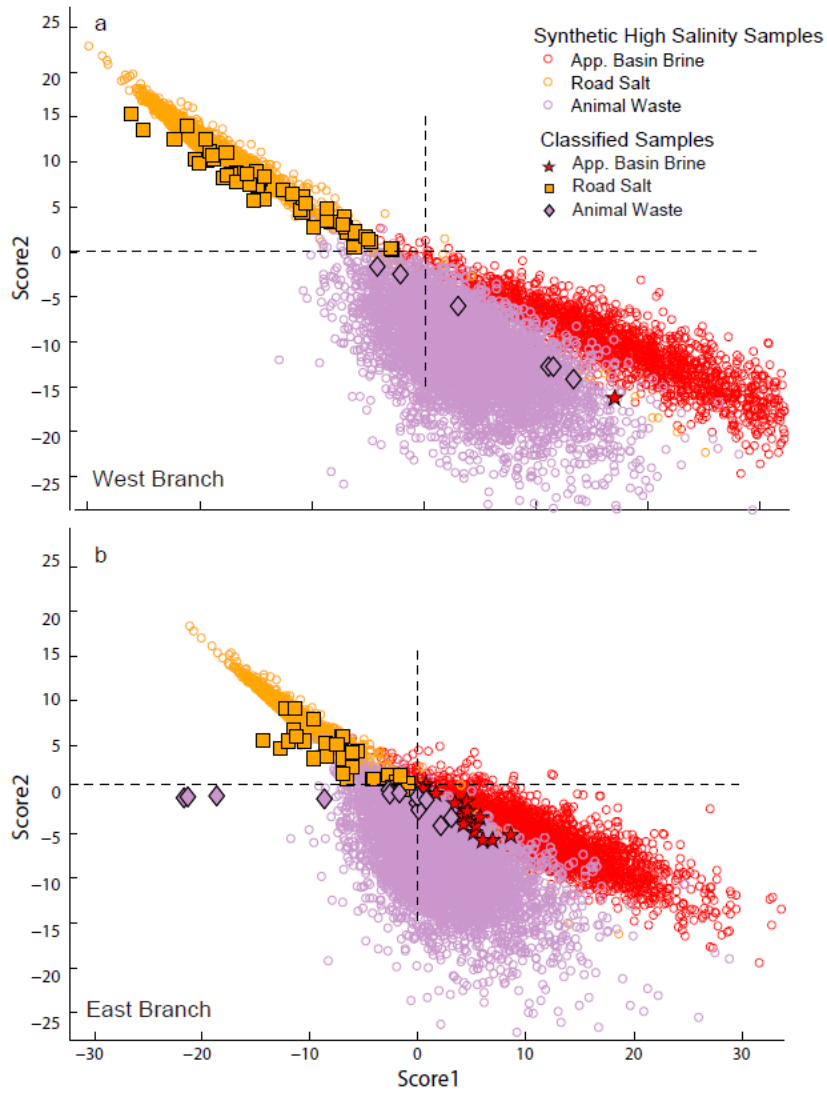


Figure 6. Observations of unclassified and classified river water samples. Unclassified samples were excluded from LDA due to missing values of concentrations of solutes.

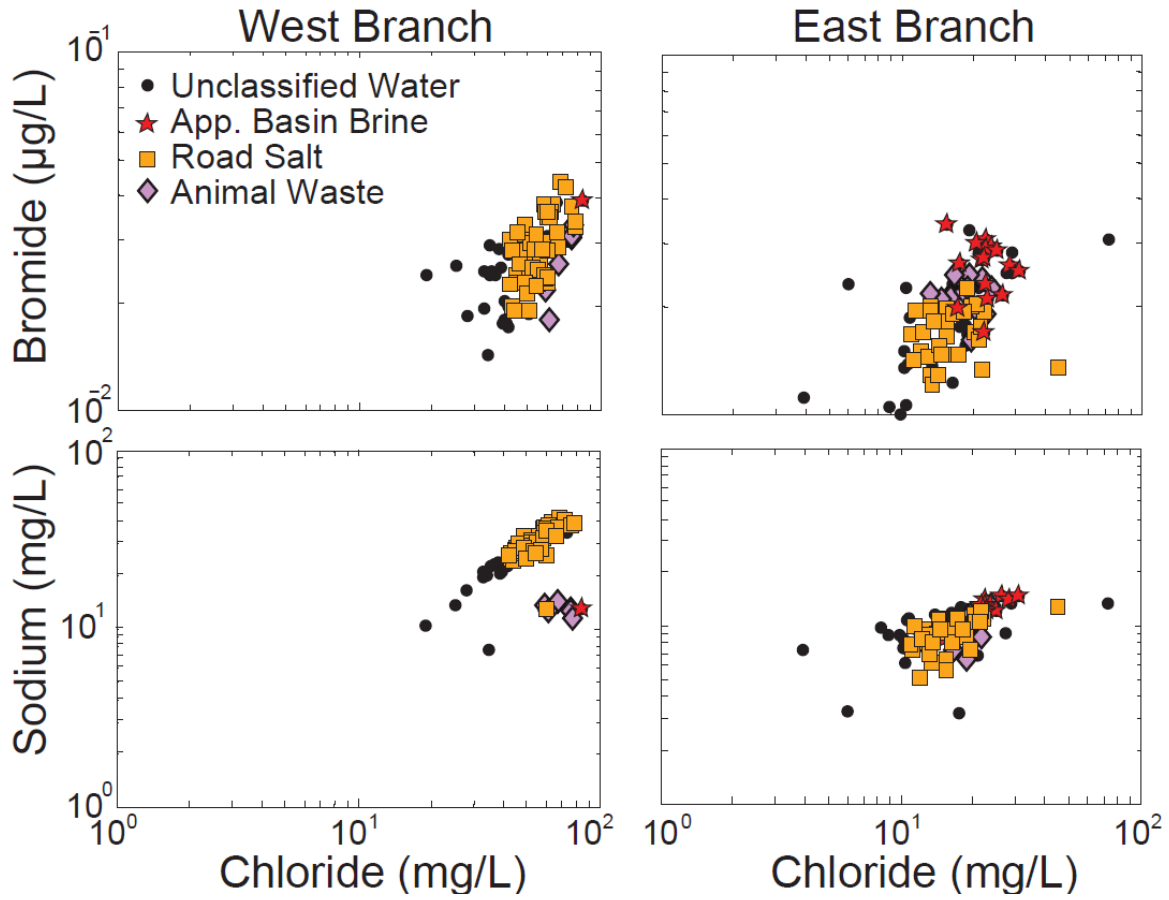


Figure 7. Downstream concentrations of Cl for West and East Branches Tioughnioga River from January 2014 through December 2014. Points signify date and location of sample collection. Colored column indicates land use. Arrows mark the location of confluences with tributaries and outlets of lakes with the main channel.

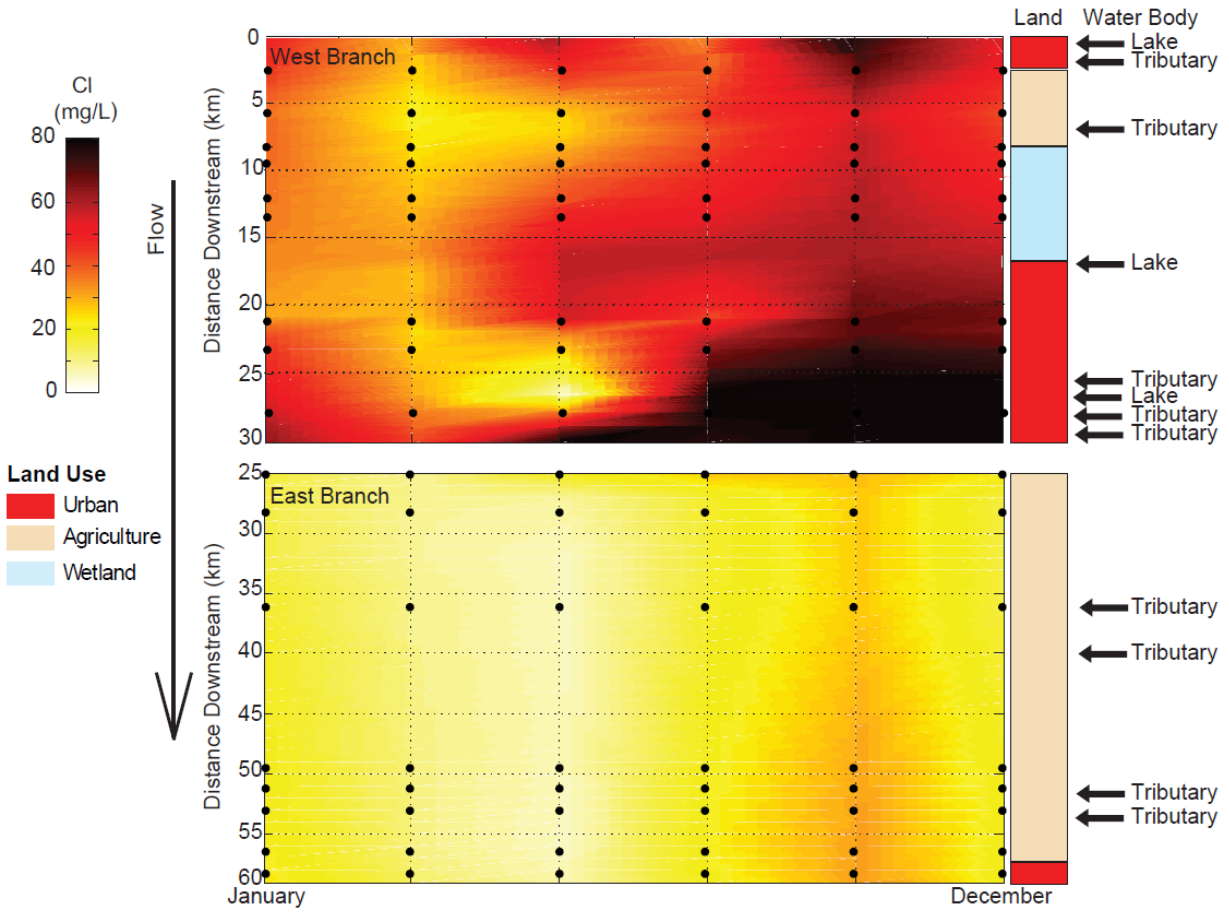
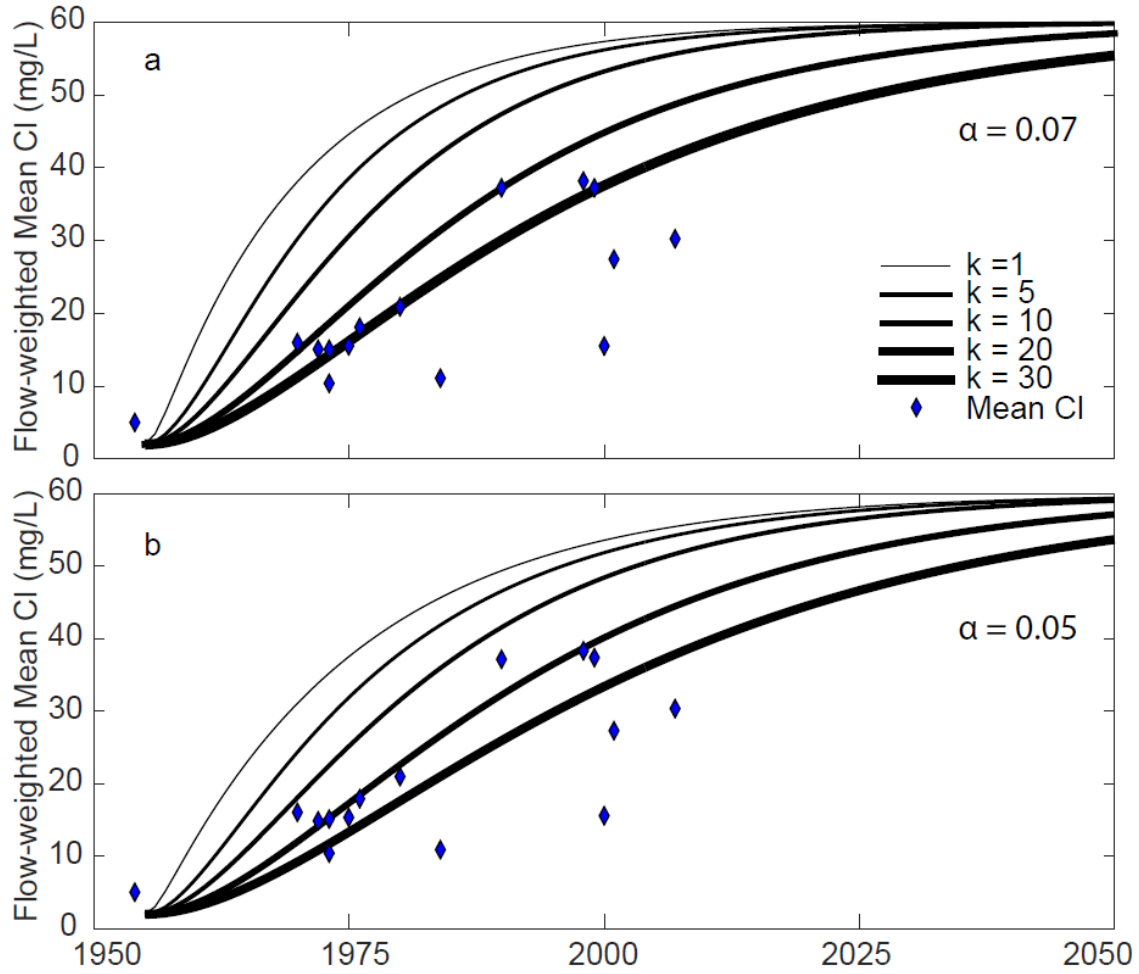


Figure 8. Application of mixing model to the West Branch Tioughnioga River. Different curves indicate model output for different residence times (k^{-1}) ranging from 1 to 30 years for two different scenarios in the rate at which road salt application has increased in time: $\alpha = 0.07$ (a) and $\alpha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



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Chapter 2:

Long-term climatic and anthropogenic impacts on stream water salinity in New York

State: INCA simulations offer cautious optimism

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Abstract

The long-term application of road salts has led to a rise in surface water chloride (Cl) concentrations. While models have been used to assess the potential future impacts of continued de-icing practices, prior approaches have not incorporated changes in climate that are projected to impact hydrogeology in the 21st century. We use an INtegrated CAthment (INCA) model to simulate Cl concentrations in the Tioughnioga River watershed. The model was run over a baseline period (1961-1990) and climate simulations from a range of GCMs run over three 30-year intervals (2010-2039; 2040-2069; 2070-2099). Model projections suggest that Cl concentrations in the two river branches will continue to rise for several decades, before beginning to decline around 2040-2069, with all GCM scenarios indicating reductions in snowfall and associated salt applications over the 21st century. The delay in stream response is most likely attributed to climate change and continued contribution of Cl from aquifers. By 2100, surface water Cl concentrations will decrease to below 1960's values. Catchments dominated by urban lands will experience a decrease in average surface water Cl, although moderate compared to more rural catchments.

1. Introduction

Concentrations of chloride (Cl) in surface water have risen at unprecedented rates since the application of de-icing salts to roads began in the 1950s (Kaushal et al., 2005, Kelly et al., 2008, Kelly et al., 2010a, Kelly et al., 2010b, Corsi et al., 2015). In New York State, 90-450 lbs. of road salt per lane mile of road are applied to highways during a given event (New York State Department of Transportation, 2012). Only approximately 10% of this salt is attached to vehicle traffic and transported away without entering local streams (Shaw et al., 2012). The rest enters adjacent catchments as non-point source pollution through surface runoff annually, contributing to a rise in baseline concentrations of Cl over time (Heisig, 2000, Perera et al., 2013). Elevated concentrations of Cl in surface water may threaten sensitive biota (Kaushal et al., 2005, Kelly et al., 2010a, Kelly et al., 2010b, Jackson and Jobbágy, 2005), increase corrosivity (Kaushal 2016, Kaushal et al., 2017), and jeopardize the quality of drinking water resources (Kaushal 2016, Kaushal et al., 2017, Rmakrishna and Viraraghaven, 2005, Mullaney et al., 2009, Jin et al., 2011).

Anthropogenic stressors on a catchment (such as urbanization and de-icing practices) can have long term effects on the potability of drinking water resources and terrestrial ecosystems (Kaushal et al., 2005, Kelly et al. 2008, Rhodes et al., 2001). Even more profound impacts on water chemistry are possible due to potential future changes to climate (Crossman et al., 2013, Whitehead et al., 2015). Many studies have employed basic mass balance or mixing models to understand the extent to which future changes in road salt usage might impact water quality (Shaw et al., 2012, Heisig 2000, Novtony et al., 2009, Gutchess et al., 2016). To date, few studies have provided predictions of water quality changes incorporating both future changes in climate and anthropogenic effects related to road salt usage. The INtegrated CAatchment (INCA)

family of models was initially developed for the assessment of nitrogen sources within mixed land-use catchments (Whitehead et al., 1998a, Whitehead et al., 1998b), but has since been expanded to simulate fluxes in phosphorus, carbon, mercury, and sediments in a variety of settings (Rankinen et al., 2002, Wade et al., 2002, Futter et al., 2007, Lazar et al. 2010, Whitehead et al., 2011, Futter et al., 2012, Jin et al., 2012). The INCA model framework employs process-based, reaction kinetic equations to simulate principle hydrologic and biogeochemical processes. The model is dynamic and features a mass-balance approach to track temporal and spatial variations across both land and stream components at daily time steps at the catchment scale.

Here we provide a present-day calibration and the first future simulation of stream Cl under a variety of climatic conditions, changes in land use, and snow management practices throughout the twenty-first century. We modify the INCA-N modeling framework to simulate daily fluxes in stream Cl- (hereby INCA-Cl) featuring a new multi-branched structure under sixteen different future scenarios (Whitehead et al., 2011, Jin et al., 2016). We apply the INCA-Cl model to a mixed land-use headwater stream network in New York State (Figure 1).

2. Methods

2.1. Site Description

The Tioughnioga River in central New York is a main headwater catchment to the Upper Susquehanna River Basin and Chesapeake Bay. Two main tributaries (East and West Branches of the Tioughnioga River) converge in Cortland County in central New York to form the Tioughnioga River. This study focuses on an approximately 900 km² (266 km² West Branch and 496 km² East Branch) segment of the upstream reach (U.S. Geological Survey, 1980) (Figure 1).

Land use in the Tioughnioga River watershed is dominated by forest and agriculture (U.S. Geological Survey, 2001). Urban land accounts for a greater proportion of area in the West Branch and is concentrated toward the catchment outlet. The West Branch flows adjacent to Interstate 81 for the entirety of its reach. Mean annual temperature and average annual precipitation in the City of Cortland are 8.1 °C and 99 cm, respectively (NOAA CDC GHCND: USC00301799). Snowfall typically occurs from October to April and accounts for a significant proportion of annual precipitation, with an average of 189 cm from 1900 – 2000 (NOAA CDC GHCND: USC00301799).

The river is underlain by a two-aquifer valley-fill system comprised of a surficial unconfined sand and gravel aquifer and a confined basal sand and gravel aquifer separated by a glaciolacustrine confining unit (Reynolds 1987, Miller et al., 1998, Kappel and Miller, 2003, Miller 2004). The aquifer system overlies organic rich shale interbedded with siltstone, sandstone, and limestone of Upper to Middle Devonian age (Reynolds 1987, Miller et al., 1998, Kappel and Miller, 2003, Miller 2004).. The aquifer provides drinking water to inhabitants of the cities of Cortland, Homer, and surrounding communities. It has been designated as a primary aquifer by the New York State Department of Environmental Conservation (NYS DEC) and as a sole source aquifer by the U.S. Environmental Protection Agency (US EPA) under the Safe Drinking Water Act (Miller 2004). Primary aquifers are recognized by the NYS DEC as highly productive aquifers utilized as municipal water supply sources. A sole source aquifer designation indicates that reasonable alternative drinking water sources do not exist.

2.2. INCA-CI Model Setup

INCA is a dynamic, semi-distributed, process-based solute transport model originally developed to assess sources of nitrogen in catchments (Whitehead et al., 1998a, Whitehead et al., 1998b)

The INCA Model was previously used to simulate stream Cl⁻ concentrations in a single stem main river that treats the tributaries as aggregated inputs (Jin et al., 2011). In this study, we modified an existing INCA-N model and incorporated the new multi-branched structure to simulate daily estimates of in-stream concentrations of Cl⁻ in the Tioughnioga River watershed. Within the model, Cl⁻ is transferred through the catchment by individual processes operating across five land use classes and a multi-reach river network. Inputs to INCA include daily time series of precipitation, temperature, hydrologically effective rainfall (HER) and soil moisture deficit (SMD). HER reflects the proportion of precipitation that eventually becomes surface runoff (i.e. after accounting for evapotranspiration and interception), whereas SMD is defined as the depth of water required to return soil water content to field capacity (maximum). HER and SMD were estimated using the Precipitation, Evapotranspiration and Runoff Simulator for Solute Transport (PERSiST) model by the processes outlined by Futter et al (2014). Daily precipitation and temperature estimates were calculated for 7 weather stations (NOAA Climatic Data Center) located within the catchment area using the Thiessen-polygon area-weighted approach (Thiessen 1911). Missing data were supplemented with area-weighted mean daily temperature and precipitation data generated by the Daymet single-pixel extraction tool (Thornton et al., 2017). The study area was divided into 11 reaches and associated sub-catchments. Reach boundaries were selected based on locations of measured water chemistry and USGS flow stations (Figure 1). Two main branches were simulated individually by splitting into multiple reaches to reflect the heterogeneity of the catchment with different land uses. Reaches 5 and 11 represent the mouth of the East and West branches, respectively (Figure 1). Sub-catchment delineation was derived using a digital elevation model in ArcGIS version 10.4. The percentage of each of five

land use classes (urban, highway, agriculture, wetland, and forest), total area, and reach length were also calculated for each sub-catchment (Table 1) in ArcGIS.

Cl⁻ inputs to the model included (1) atmospheric deposition of Cl⁻, (2) road salt application, and (3) water softener usage (SI Table S1). Daily loads of road salt application and water softener usage were determined based on area, 2000 U.S. census data, water usage, state road salt purchase records, and meteorological conditions. Natural atmospheric deposition rates of Cl⁻ were measured at the Aurora Research Farm in adjacent Cayuga County, New York (NY08) (National Atmospheric Deposition Program (NTN)). Based on the 2012-2015 average annual Cl⁻ deposition at this site, we calculated annual wet deposition of Cl⁻ to be 0.59 kg/ha/yr. This value was used as the deposition rate in the model. Dry deposition was calculated to be 0.20 kg/ha/yr, which represents the same proportion of total atmospheric Cl⁻ deposition as was observed in Cornwall NY, approximately 292 km from the southwest study area (Nichols 1999).

The new multi-branched INCA-Cl model setup allows for variable road salt application rates to reflect different salting practices for highway and local roads in each individual sub-catchment. Daily road salt application rates were derived from relationships between state road salt purchase records, land cover, and meteorological conditions. State road salt purchase records indicate that from 2012 through 2015 an average of 23,000 and 9,000 tons of road salt were purchased annually for application to urban areas and Interstate-81 in Cortland County, respectively (NYS Office of General Services, 2017). We used 60-68% of the purchased amounts as model input to reflect the proportion of Cortland County and Interstate-81 within the model area while accounting for an additional 10% loss via direct wash off (Shaw et al., 2012). In New York State, road salts are commonly applied when precipitation occurs at sub-zero (Celsius) temperature to prevent traffic accidents (NYS Department of Transportation, 2006). Thus, road salt applications

were calculated to be 76 days per year (on average) during the calibration period, using weather data. Daily Cl⁻ application rates were, then, estimated for both highway and urban land use classes of 38.7 and 21.4 kg Cl⁻/ha/d, respectively, based on the total number of sub-zero days, the total area of highway and urban land use classes.

Water softeners have been used in the Tioughnioga River watershed to combat water hardness issues for decades (Miller et al., 1998, Buller 1978, Buller et al., 1978). Daily Cl⁻ inputs from water softener for each sub-catchment were estimated based on per capita water and water softener use. We simplified estimates by assuming that all households in the study area use water softeners, as in previous studies (Kelly et al., 2008, Jin et al., 2011), which likely results in an overestimation. Based on US EPA estimates, we assumed average water consumption and water softener usage of 400 L/person/day and 125 kg/year, respectively (Kelly et al., 2008, U.S. Environmental Protection Agency). The amount of water softener used per sub-catchment was derived by multiplying the per capita-softener consumption by the population (SI Table S1).

Calculated inputs estimated that road salt accounts for approximately 87% of the total Cl⁻ inputs into the Tioughnioga River catchment from 2012-2015 (SI, Table 1). Prior studies suggested in addition to a dominant source of salinity from road salt, the natural migration of deeper, more saline groundwater could potentially contribute to stream water salinity especially at the summer baseline. However, given the insignificant volume (typically < 0.1%) (Gutchess et al., 2016) from the deep groundwater, it was not included in this modeling study.

2.3. Model Calibration and Sensitivity Analysis

Daily simulations for the INCA-Cl model were performed for the Tioughnioga River watershed from January 1st, 2012 through December 31st, 2015 (n=1461 days). The INCA model was

calibrated manually to discharge data and stream Cl⁻ concentrations across spatial and temporal scales. Manual calibration has been proved as a robust method for obtaining acceptable simulations with the INCA family of models (Ledesma et al., 2012). Modeled stream flow was calibrated to mean daily discharge (USGS Station Number: 01509000). The model was calibrated to weekly/biweekly surface water Cl⁻ concentrations measured at reach 5 and reach 11 (sampling and analysis details in reference Gutchess et al., 2016) and daily Cl⁻ concentrations from a specific conductance probe installed at the bottom of reach 11 from 2012 to 2014. The probe recorded surface water conductivity at 30-minute increments from November 2013 to July 2014 and October 2014 to January 2015. Daily specific conductance values were then converted to daily concentrations of Cl⁻ based on a laboratory standard curve for model calibration. Bimonthly surface water samples were collected at several downstream locations along the East and West Branches of the Tioughnioga River in 2014. Sample sites were selected based on accessibility and confluences of major tributaries. Subcatchment boundaries were delineated to these downstream points. Cl⁻ data collected in 2014 at reach 2, 3, 4 and 7 were also used to assist calibration. Groundwater samples were collected from four locations from 2012-2014 (n=19) (Figure 1). Samples were analyzed for concentrations of Cl⁻ via ion chromatography (Dionex-ICS 2100) calibrated with five internal laboratory standards for anions. The average Cl⁻ concentrations in groundwater samples (35 and 70 mg/L, for East and West Branch respectively) were used as the groundwater Cl⁻ input for the model. INCA model fit was assessed based on values of R² coefficients and Nash-Sutcliffe (N-S) coefficients.

A simple “one-at-a-time” sensitivity analysis of INCA-Cl flow and Cl⁻ related parameters was performed to assess the effects of hydrological, catchment, and in-stream variability of concentrations of Cl⁻ in surface water. We adopted a previously employed approach in which

selected parameter values from the parameter set with the highest model efficiency coefficients (Nash-Sutcliffe (N-S) coefficients) were varied by 2x and 0.5x (Futter et al., 2011). The sensitivity of parameters was then defined as

$$N-S_{\text{Best}} - 0.5*(N-S_{2x} + N-S_{0.5x}) \quad [1]$$

2.4. Future Scenarios

Monthly mean values for average daily temperature and daily precipitation for two Global Climate Models (GCMs) (HADCM3 and CGCM2) and two Intergovernmental Panel on Climate Change (IPCC) emissions scenarios (A2 and B2) were obtained from the Canadian Climate Data and Scenarios (CCDS). Scenarios were selected to represent a range of emissions scenarios (moderate to extreme, with A2 representing higher CO₂ emissions). GCMs were selected because of their differences in projections for future precipitation, with CGCM2 producing more conservative outputs. We note that HADCM3 and CGCM2 perform well in northern catchments (Walsh et al., 2008). Monthly mean future temperature and precipitation series were bias corrected with local meteorological stations (NOAA CDC Station ID: GHCND: USC00301799) using the Δ change method (SI).

Future daily INCA inputs were generated using the PERSiST model by simulating scenarios spanning 1961-1990 and 2010-2039, 2040-2069, and 2070-2099 (Figure S1).

Using the application rates determined for the calibration period, daily road salt application was generated based on future meteorological projections for scenarios A2 and B2 for each GCM. During moderate to heavy snowfall rates of greater than 1.27 cm/hr characteristic of lake effect snow (LES), de-icing salt is often applied at higher rates (NYS Department of Transportation, 2006). To account for potential increases in increased winter precipitation in the form of LES

into the mid-21st century due to declining Great Lakes ice cover (Wright et al., 2013, Notaro et al., 2015), additional scenarios were run with daily application rates of 2x present day values.

Population in the U.S. is projected to increase rapidly (Colby and Ortman, 2014) and the associated changes in effluent discharge rates were calculated assuming population in Cortland County continues to increase at a rate equal to 1900-2010 increase (Forstall 1996). We determined potential future urban land use percentages in each sub-catchment from extrapolated future population data and current land use proportions, assuming that population density in urban areas in the Tioughnioga River watershed remains constant. Increases in urban land cover were accommodated by decreases in forest cover.

4. Results & Discussion

4.1. Model Calibration

To simulate concentrations of Cl⁻ in surface water, the INCA model was first calibrated to daily streamflow. Simulated values fit daily observations of flow at the main branch well with an R² of 0.72 and a N-S of 0.68 (Figure 2a). Maximum streamflow typically occurs following spring snowmelt during the month of April, whereas minimum streamflow occurs in summer months following prolonged dry periods. Modeled flow captured the seasonal variations and the timing of the rising and falling limbs. Peak flows were aligned and of similar magnitude with some overestimation. This may be due to the spatial variation of heavy rainfall events in the study area.

The INCA-Cl model simulations fit the observations well (Figure 2). While the model closely represented the mean conditions of the catchment, we found that the model often underestimated stream Cl⁻ during extremely low flow (flows less than approximately 5 m³/s). These conditions tended to occur during late summer to early fall when streamflow was likely sustained by

groundwater discharge. An overestimation of streamflow, and subsequent dilution, at the same time intervals may account for some of the differences between modeled and observed stream Cl⁻ concentrations (Figure 2). Simulated average daily Cl⁻ fluxes were approximately 13,000 kg/day and 19,000 kg/day at the mouths of East Branch and West Branch, respectively. There was generally a satisfactory fit of observed and simulated daily Cl⁻ fluxes throughout the catchments, with R² ranging from 0.70 to 0.90 and N-S values ranging from 0.12 to 0.77 (SI Table S8).

4.2. Uncertainty & Sensitivity

Uncertainty within the INCA family of models can generally be attributed to uncertainty in parameterization, structural uncertainty within the modeling framework, and the understanding of physical and chemical processes including model inputs (Jin et al., 2011, Crossman et al., 2013, Wade et al., 2002, Rankinen et al., 2006).

The most sensitive parameters for modeling streamflow were consistent with findings in previous studies in which a variation of the INCA model was used (Jin et al., 2012, McIntyre, et al., 2005). Flow velocity modifiers “a,” and “b,” along with the base flow index parameter were the most sensitive to perturbations (Table 2). These parameters are dimensionless and used to define flow velocity (as $V = a \times Q^b$, where V is equal to stream flow velocity, and Q is stream discharge). Flow velocity modifiers impact the simulated residence time of surface water and therefore shape flow flashiness. The base flow index parameter represents the fraction of water that is transferred from upper to lower model storage and alters the response time of subsurface water, contributing to stream flow from precipitation and snowmelt. Best-fit parameter values were determined from model calibration and are in similar ranges established in prior modeling

exercises (Wade et al., 2002, Whitehead et al., 2011, Miller et al., 1998, McIntyre et al., 2005, Jackson-Blake et al., 2016).

Model sensitivity to Cl⁻ varied across sub-catchments, likely due to differences in land use distribution and magnitude of in-stream concentrations of Cl⁻. Parameters relating to snowmelt and atmospheric deposition were insensitive. The initial concentration of Cl⁻ in groundwater was the most sensitive parameter in terms of in-stream concentrations of Cl⁻, followed by flow parameters (Table 2). In the model calibration, average measured Cl⁻ values were used as groundwater input (70 mg/L and 35 mg/L for West Branch and East Branch, respectively; see Methods). However, groundwater Cl⁻ concentrations varied across the catchment depending on location, depth and time of measurement (Gutchess et al., 2016, Miller et al., 1998, Buller 1978, Buller et al., 1978). For example, during dry periods, the amount of recharge to shallow aquifer decreases. Thus, the system may be more likely to exhibit influence from deeper, more saline groundwater. The complex groundwater sources could introduce the uncertainties that result in the underestimated Cl⁻ during extremely low flow condition.

Considering the high level of agreement between observed and modeled Cl⁻ for the INCA-Cl model of the Tioughnioga River catchment and the incorporation of observed data (e.g. streamflow, temperature, precipitation, surface water Cl⁻, groundwater Cl⁻), we believe our model to have reproduced the main processes operating at the catchment scale with relative accuracy. Thus, the calibrated model has potential for long-term and future scenario analysis.

System response to future changes

4.3. Baseline simulations

Under the 30-year baseline period (1961-1990), mean daily streamflow ranged, respectively, from 0.2 to 211.6 m³/s, with an average of 10.6 m³/s. Similar to the calibration period, maximum flows occur following spring snowmelt and high intensity rainfall events. Summer months are characterized by extended periods of low flow.

From 1961 to 1990 daily concentrations of stream Cl⁻ in reaches 5 and 11 ranged from 4.10 to 30.5 mg/l and 8.4 to 81.7 mg/l, respectively. Average Cl⁻ concentrations in reaches 5 and 11 during the baseline period were 17.9 and 35.7 mg/l, respectively. Annual maximum stream Cl⁻ for downstream reaches typically occurred during low flow periods as stream Cl⁻ concentrations approached that of groundwater. Peaks in stream Cl⁻ also accompanied spring snowmelt. For descriptive statistics of baseline and calibration periods refer to SI Table S2c.

4.4. Future climate-induced changes to stream Cl⁻ concentrations

Mean daily concentrations of Cl⁻ is projected to increase between the baseline period (1961-1990) and future simulation period 2010-2039 (Figure 3). Mean daily concentrations of Cl⁻ in all sub-catchments are highest for 2010-2039 in all sixteen scenarios, followed by markedly lower mean daily Cl⁻ concentrations into the latter half of the 21st century (Figure 3). Descriptive statistics for daily Cl⁻ for baseline and future simulation periods can be found in Supporting Information (SI) (SI Table S2).

In the latter half of the future simulation period (post 2040s), all GCM-IPCC combinations predicted a decrease in the frequency and occurrence of snowfall as winter temperatures crossed the freezing threshold of water. An increasing proportion of winter precipitation was projected to be rain (SI Table S6-7, Figure S2). Although rates will continue to be highly variable, all model scenarios consistently predicted declines in average annual snowfall totals through the end of the

twenty-first century. HADCM3 scenarios (A2, B2) predicted more winter precipitation for the catchment into the twenty-first century than CGCM2 scenarios (SI Table S6-S7). This is based on the GCM's projections for future precipitation (Wilby et al., 2006, Crossman et al., 2016). Higher precipitation rates yielded increased snowfall totals, and greater associated annual road salt loads, producing wider ranges in surface water Cl⁻ for HADCM3 scenarios compared to CGCM2 (Figure 3). Furthermore, A2 scenarios generally projected more elevated warming trends than B2 scenarios; which results in less road salt applied in the model (SI Table S3-S4, Figure S2). The variability of future climate dynamics was included intentionally to account for uncertainty within GCMs and to provide land use managers with a range of possible outcomes (SI Figure S2).

As a result of projected reductions in snowfall, the model applied less road salt across the reach network in 2040-2099 than in preceding decades (2010-2039 and baseline period) across all simulations (SI Table S3-S4). As winter snowfall transitions to rain, Cl⁻ stored in shallow groundwater from previous decades may serve as a continual source of stream Cl⁻, until reservoirs are depleted, leading to an overall net loss of Cl⁻. Without perturbations to daily road salt application rates, an overall decline in mean daily stream Cl⁻ concentrations by as much as to pre-baseline levels by the end of the current century is likely (Figure 3a-c), but not before reaching peak concentrations in decades preceding the 2040s.

Our findings are comparable to those observed in earlier investigations, while offering a dynamic approach to simulating future changes in surface water Cl⁻ as we incorporate variability in climate, land use, and snow management practices to our future estimates. Estimates vary from that of a previous study in the catchment in which a simplified mixing model was used to simulate future stream Cl⁻ concentrations (Gutchess et al., 2016). The 2016 study calculated

ranges of roughly 40-60 mg/l flow-weighted mean Cl⁻ in the West Branch (reach 11) given a variable increasing rate of road salt application from 2010 through 2050, while INCA-Cl outputs suggest more appropriate mean ranges of 55-66 mg/l Cl⁻ and 39-54 mg/l Cl⁻ from 2010-2039 and 2040-2069, respectively (SI Table S2). In this study, INCA model results reveal that an average of approximately 4,700-7,100 tons of Cl is exported annually from the East and West Branches of the Tioughnioga River, respectively. The 2016 study²⁰ estimated an overall annual export of 14,500-24,500 tons Cl⁻. Jin et al. (2011) predicted that under a 100% increase in application rate, stream Cl⁻ concentrations in a suburban Hudson River tributary could increase by up to 13%. Novotony and Stefan (2010) estimated that with no change to annual Cl⁻ loading surface water, Cl⁻ would continue to rise steadily for several decades in the Twin Cities Metropolitan Area of Minneapolis, Minnesota. Perera et al. (2013) projected an increase in baseflow Cl⁻ concentrations in the Highland Creek Watershed (Toronto) using a simplified mass balance approach. In general, our results are similar to simplified approaches into the early twenty-first century. However, the coupling of mass transfer with dynamic climate and hydrology inputs in our analysis leads to an overall decline in mean daily concentrations of Cl⁻ into the latter half of the twenty-first century (Figure 3), which is a novel finding compared to previous studies.

4.5. Future anthropogenic impacts on surface water Cl⁻

Coupled with urbanization, the impacts of deicing practices are prolonged into the latter half of the century, with mean monthly concentrations of Cl⁻ in surface water of urbanized catchments upwards of 40 mg/l above baseline concentrations (Figure 4).

Our model simulations suggest that future concentrations of Cl⁻ in surface water are sensitive to anthropogenic-induced changes alongside climatic factors. The greatest positive anomalies in

concentrations of Cl⁻ occurred in simulations subjected to urbanization, elevated application rates, or both (SI, Table S2).

The variation in response times between reaches 11 and 5 required for surface water Cl⁻ to return to baseline concentrations (Figure 3) may be explained by the difference in groundwater Cl⁻ concentrations. Higher groundwater Cl⁻ measured in the West Branch, attributed to long-term road salt application (Miller et al., 1998, Buller et al., 1978, Gutchess et al., 2016), may act as a high-Cl⁻ source for surface water Cl⁻. This subsequently enriches dilute rainfall and snowmelt relative to low-Cl⁻ groundwater in the East Branch, thereby moderating the overall decrease in stream Cl⁻ over time. Cl⁻ attenuation in groundwater has been observed extensively in mixed-land use and urban catchments and suggested as a buffer for stream Cl⁻ (Heisig 2000, Kincaid and Findlay 2009, Jin et al., 2011, Ledford et al., 2016).

The presence of the Interstate Highway in the West Branch may also contribute to the slow recovery of salinity despite future declines in salt application (Figure 3, 4), as it serves as a continual source of road salt that is absent in all reaches of the East Branch (Figure 1). Heisig (2000) noted a strong positive relationship between log Cl⁻ concentrations and annual application rate of de-icing salt in a small mixed land use catchment in southeastern NY, consistent with the elevated application rates of interstate highways. In Central Massachusetts, the greatest Cl⁻ concentrations observed in the Mill River Watershed coincided with runoff from interstate and state highways¹⁵.

We attribute the increase in surface water Cl⁻ from baseline concentrations projected for 2010-2039 to be predominantly controlled by greater annual Cl⁻ inputs to the system. Under all simulations mean daily streamflow underwent a steady decline throughout the twenty-first century. Thus, elevated concentrations of Cl⁻ cannot be explained by dilution processes (SI

Figure S3). Furthermore, land-use changes were assumed proportional to current land cover distributions. Although the same percent-increase was applied across all sub-catchments, those with higher urban land-cover at the beginning of the simulation period were subjected to greater urbanization, and thus higher road salt loads (see methods).

In general, sub-catchments in the West Branch were more sensitive to changes in land use and climate, likely due to the greater proportion of urban lands in the reach. In contrast, the East Branch did not respond as drastically to anthropogenic forcings, experiencing only minor changes in mean daily surface water Cl⁻ concentrations and with Cl⁻ concentrations falling below baseline conditions into the end of the century regardless of urbanization and salt application characteristics (Figure 3a,b). Rural catchments were projected to approach baseline levels of salinity by approximately mid-century despite anthropogenic factors (Figure 3a-b).

Whereas, simulations in the West Branch only declined to baseline levels of Cl⁻ by the end of the 21st century for one climate scenario (CGCM2, Scenario A2), with mean concentrations approaching, but continuing to exceed, baseline concentrations in all but one of the most extreme salting scenarios (Figure 3d). This suggests that densely paved catchments may not recover as readily as those that are more sparsely populated.

4.6. Implications and future work

The wide range of results projected by INCA-Cl simulations reflect inherent uncertainty in climate and population change studies. It is suggested that while simplified mass balance approaches do provide a suitable first-approximation for addressing water quality concerns, they are inherently unable to incorporate the intricacies of dynamic changes in climate and land cover components that may be imminent. The INCA-Cl process-based model generates a more realistic

range of responses to plausible future changes, and provides a useful tool in future management planning.

Increased urbanization may lead to a ubiquitous upward trend in surface water salinity from 2010-2039 as a direct result of de-icing practices. This continuation of present-day trends has the potential to further stress already-impaired water resources and aquatic ecosystems. However, our simulations suggest that these effects may be reversible over the next century as climate drivers shift winter precipitation type, thus lessening the need for de-icing measures and allowing concentrations of Cl⁻ to naturally return to baseline values. Catchments in regions where climate models predict an increase in snowfall may experience different changes, thus modeling approaches considering regional climate changes are necessary in order to accurately assess the response of these systems. Our simulations predict a cautiously optimistic outcome for drinking water resources contaminated by de-icing practices during the latter half of the 1900s.

Although the main goal of this study was to demonstrate the importance of long-term climate variability to salinity management, additional uncertainty (e.g. groundwater Cl⁻ concentrations) may require attention in future research to improve the accuracy of model predictions. Spatial and temporal groundwater heterogeneity is a common phenomenon and our catchment is no exception (Gutchess et al., 2016, Miller et al., 1998, Buller 1978, Buller et al., 1978)'. Our model underestimates stream water Cl⁻ concentration during some summer intervals at low flow conditions, which may be due to changes in groundwater Cl⁻ concentration. Available shallow groundwater data (Gutchess et al., 2016, Buller 1978) do not indicate temporal variations that may contradict our conclusion about the role of climate change. However, long-term groundwater monitoring data with improved spatial coverage may provide more insight into the role of groundwater in future studies.

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Tables.

Table 1. Watershed characteristics for Tioughnioga River. Reaches 1 through 5 correspond to East Branch Tioughnioga River, whereas reaches 6-7 and 8-11 are located within the Main Branch of the Tioughnioga River, and the West Branch, respectively.

| River Name | Reach Number | Reach Area (km ²) | Reach Length (m) | Land Use Class (%) | | | | |
|-------------------|--------------|-------------------------------|------------------|--------------------|---------|-------------|--------|---------|
| | | | | Urban | Highway | Agriculture | Forest | Wetland |
| East Branch | 1 | 219.22 | 26634 | 1.21 | 0.00 | 42.87 | 53.90 | 2.01 |
| East Branch | 2 | 93.66 | 10578 | 1.51 | 0.00 | 24.65 | 71.62 | 2.22 |
| East Branch | 3 | 147.84 | 13847 | 0.31 | 0.00 | 30.51 | 67.72 | 1.45 |
| East Branch | 4 | 10.74 | 2847 | 0.00 | 0.00 | 47.99 | 51.60 | 0.41 |
| East Branch | 5 | 24.32 | 7190 | 3.16 | 0.00 | 52.77 | 44.07 | 0.00 |
| Tioughnioga River | 6 | 3.17 | 947 | 25.96 | 6.71 | 2.02 | 65.31 | 0.00 |
| Tioughnioga River | 7 | 130.17 | 4956 | 3.72 | 0.87 | 37.44 | 57.70 | 0.28 |
| West Branch | 8 | 65.36 | 12166 | 2.61 | 3.33 | 42.27 | 45.80 | 5.98 |
| West Branch | 9 | 25.83 | 3293 | 1.07 | 4.42 | 42.41 | 46.01 | 6.09 |
| West Branch | 10 | 100.93 | 6274 | 2.79 | 1.79 | 42.02 | 51.83 | 1.56 |
| West Branch | 11 | 73.40 | 4918 | 17.45 | 1.58 | 52.11 | 28.86 | 0.00 |

Table 2. Results of sensitivity analysis obtained with best-fit model calibration. Results are shown as the average difference in N-S statistics of the perturbed simulations (2x-0.5x) and the best-fit model run. Higher values represent parameters more sensitive to changes. A value of zero signifies that the parameter exhibited no sensitivity to changes.

| Parameter | Reach 6 | Reach 5 | Reach 11 |
|---|----------------|----------------|-----------------|
| Baseflow index | 0.08 | 3.76 | 0.55 |
| Degree day melt-factor for snowmelt | 0.00 | 0.00 | 0.00 |
| Direct runoff residence time | 0.01 | 0.00 | 0.00 |
| Dry deposition Cl | 0.00 | 0.00 | 0.00 |
| Flow parameter 'a' | 0.13 | 0.24 | 0.06 |
| Flow parameter 'b' | 1.02 | 0.11 | 0.22 |
| Groundwater residence time | 0.00 | 0.55 | 0.00 |
| Initial concentration Cl ⁻ in groundwater | 0.00 | 7.43 | 2.41 |
| Initial concentration Cl ⁻ in soil water - highway | 0.00 | 0.00 | 0.00 |
| Initial concentration Cl ⁻ in soil water - urban | 0.00 | 0.00 | 0.00 |
| Soil water residence time | 0.04 | 0.02 | 0.01 |
| Threshold soil zone flow | 0.03 | 0.06 | 0.06 |
| Snow-water equivalent factor | 0.00 | 0.00 | 0.00 |
| Wet deposition Cl | 0.00 | 0.00 | 0.00 |

Figures.

Figure 1. INCA reach structure and land use classification (Anderson et al., 1976, U.S. Geological Survey 1980, U.S. Geological Survey 1990). Land use classification of the Tioughnioga river watershed is based on classification scheme developed by Anderson (1976). USGS flow station (USGS Station Number: 01509000) is located at the end of Reach 6. Daymet locations indicate geographic coordinate position of single-pixel extraction of daily temperature and precipitation outputs. Inset denotes location of study area relative to New York State (U.S. Census Bureau, 2016). Map generated using ArcGIS® software version 10.4 by Esri.

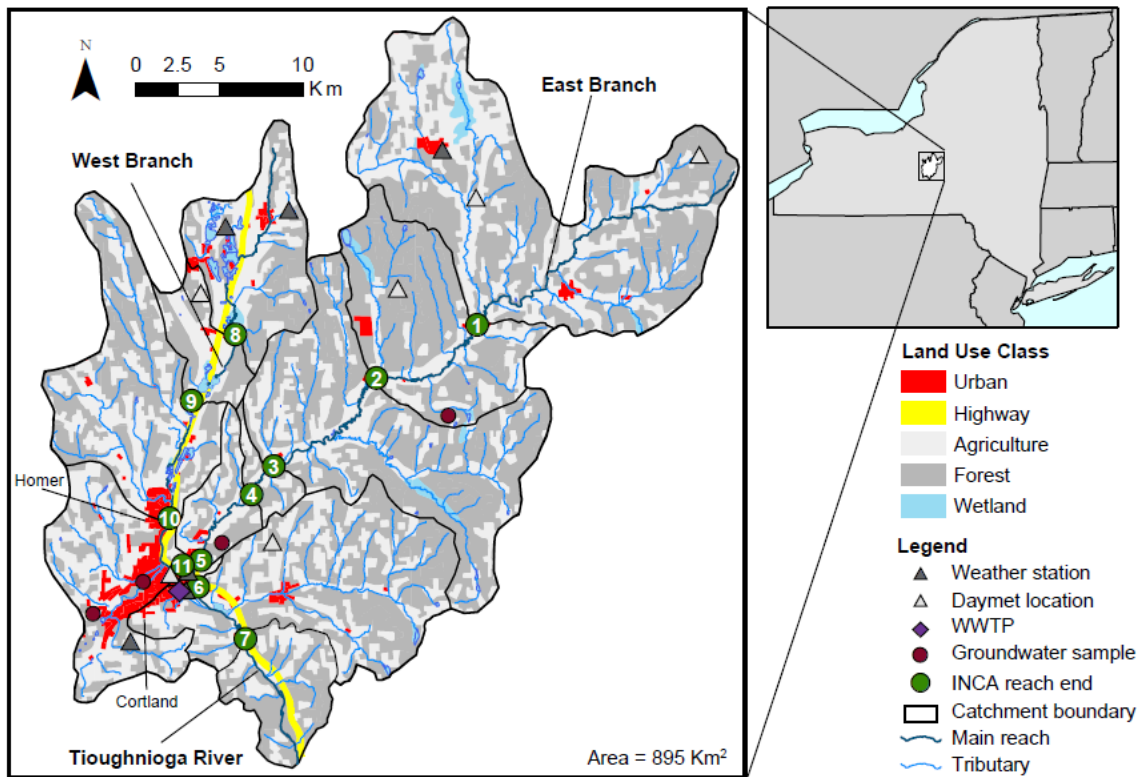


Figure 2. INCA calibration results from 2012 to 2015. a) simulated and observed daily stream flow at reach 6 (Main Branch Tioughnioga River at Cortland, USGS Gauging Station ID 01509000). b) simulated and observed Cl⁻ for reach 11 (West Branch). c) simulated and observed Cl⁻ for reach 5 (East Branch).

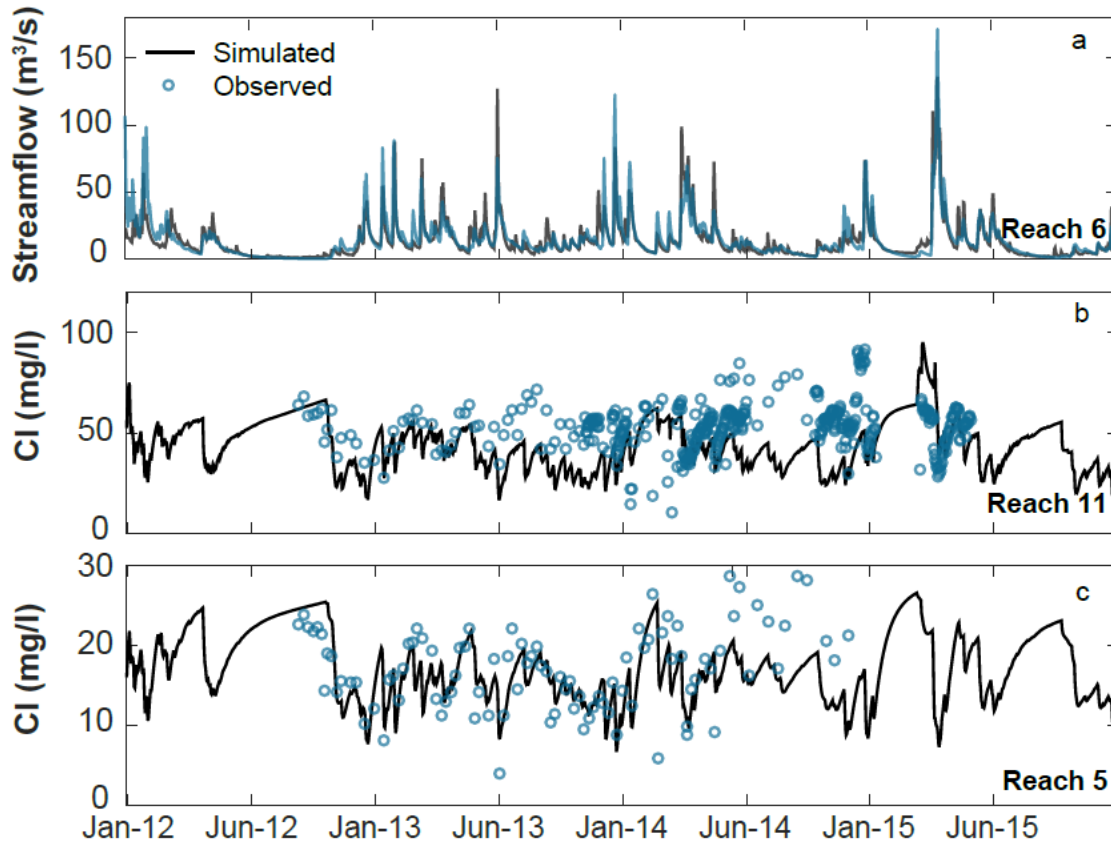


Figure 3. INCA-Cl model results for reaches 5 and 11. Simulated Cl⁻ in a) reach 5 assuming no change in land use or salting practices. b) reach 5 assuming 2x increase application rate of road salts and increased urbanization, c) reach 11 under current conditions, and d) reach 11 subjected to increased (2x current rate) de-icing salt application and urbanization. Gray line signifies mean daily Cl⁻ during baseline period. Open circles represent outliers. IPCC scenarios A2 (economics focused – higher CO₂ emissions translating to greater future temperature increases) and B2 (more environmentally focused – resulting in lesser increases in future temperature) were considered for this analysis.

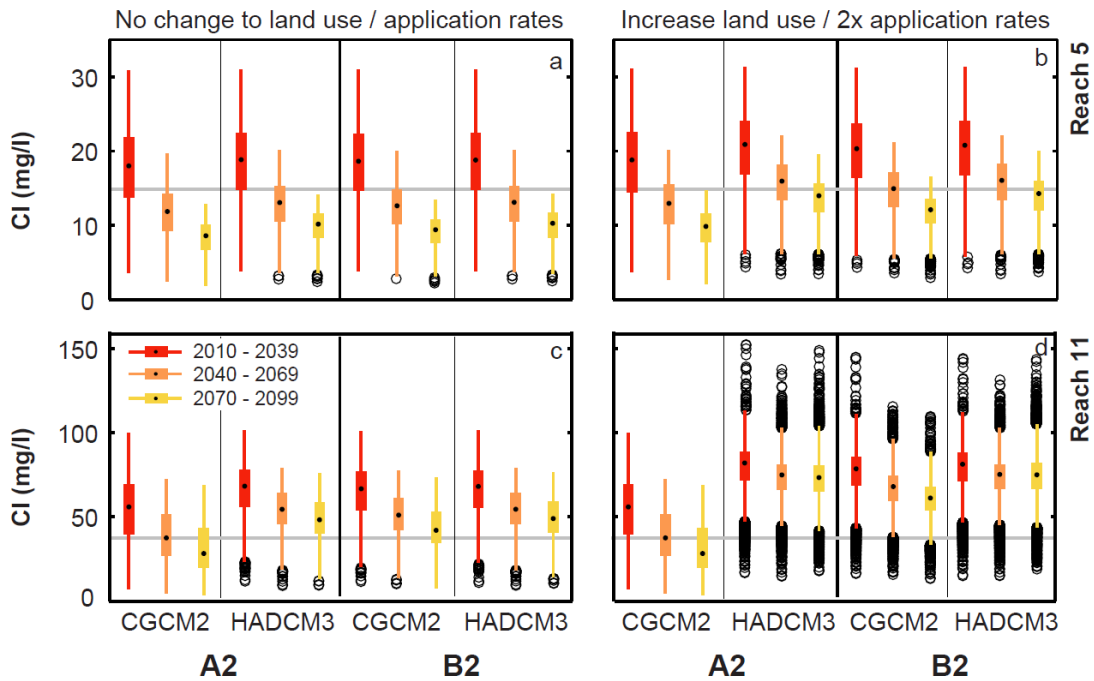
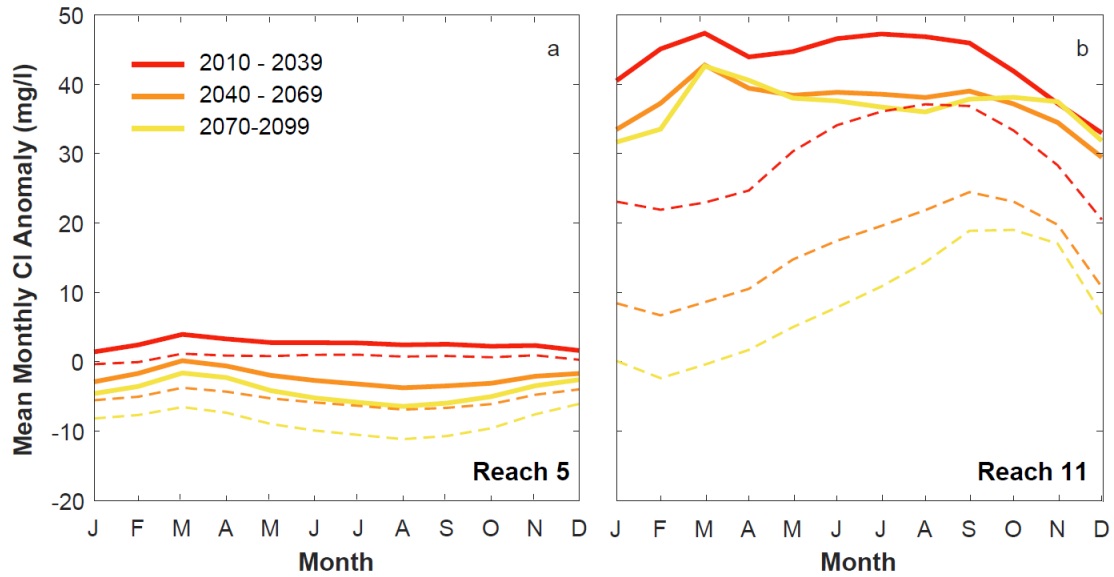


Figure 4. Mean monthly anomaly in surface water concentrations of Cl⁻ for reaches 5 and 11 (a and b, respectively) during future simulations. The lower limit of each future period is shown as a dashed line and represents the mean monthly anomaly in-stream Cl⁻ for the simulation period resulting from constant application rates and no change in land use, GCM CGCM2 and IPCC scenario A2. The upper bound is plotted as a solid line and represents surface water Cl⁻ concentrations under an increase in urbanization, 2x application rates, GCM HADCM3, and IPCC scenario B2.



Supporting Information

Delta Change Method Description

The Δ change method operates on the assumption that GCMs are better able to simulate relative change than absolute values for future scenarios and serves to calculate the difference between average monthly values of meteorological data between a baseline period (for this study 1961-1990) and future time spans of equal length (2010-2039, 2040-2069, and 2070-2099) (Aktar et al., 2008, Crossman et al., 2016, Hay et al., 2000). The monthly differences are then applied to observed baseline data (1961-1990). Equations S1 and S2 were used to calculate the future daily temperature ($T_{f,daily}$) and future daily precipitation ($P_{f,daily}$), respectively:

$$T_{f,daily} = T_{o,daily} + (T_{f,monthly} - T_{b,monthly}) \quad [S1]$$

$$P_{f,daily} = P_{o,daily} \times (P_{f,monthly} / P_{b,monthly}) \quad [S2]$$

Where $T_{o,daily}$ and $P_{o,daily}$ are the daily measured temperature and precipitation values, $T_{f,monthly}$ and $P_{f,monthly}$ represent the mean monthly temperature and precipitation for a future period (2010-2039, 2040-2069, or 2070-2099), and $T_{b,monthly}$ and $P_{b,monthly}$ are the mean monthly temperature and precipitation observed during a baseline period (1961-1990).

Figures.

Figure S1. INCA Inputs for calibration period (2012-2015) generated with the PERSiST model.

a) daily precipitation and hydrologically effective rainfall (HER), b) average daily temperature, and c) soil moisture deficit (SMD).

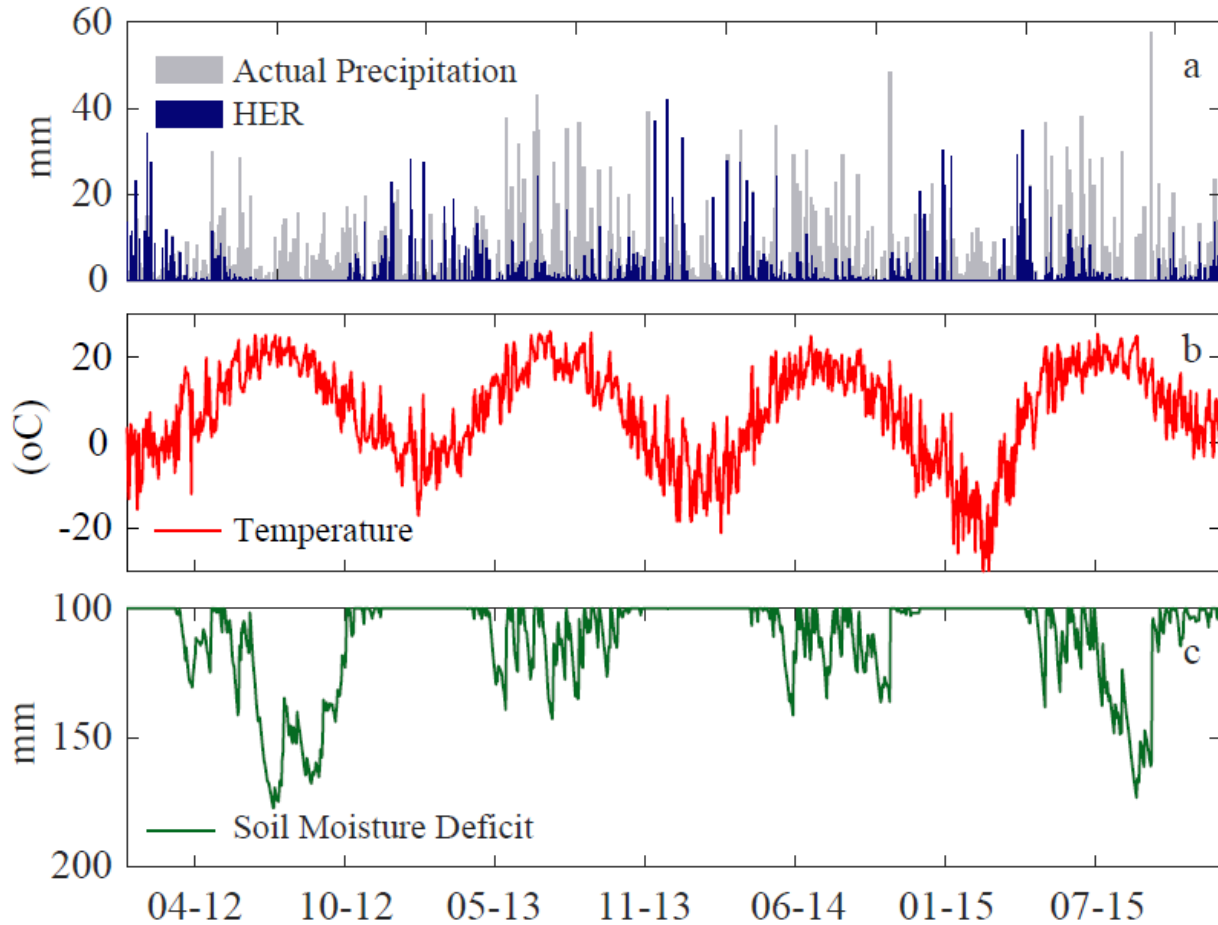
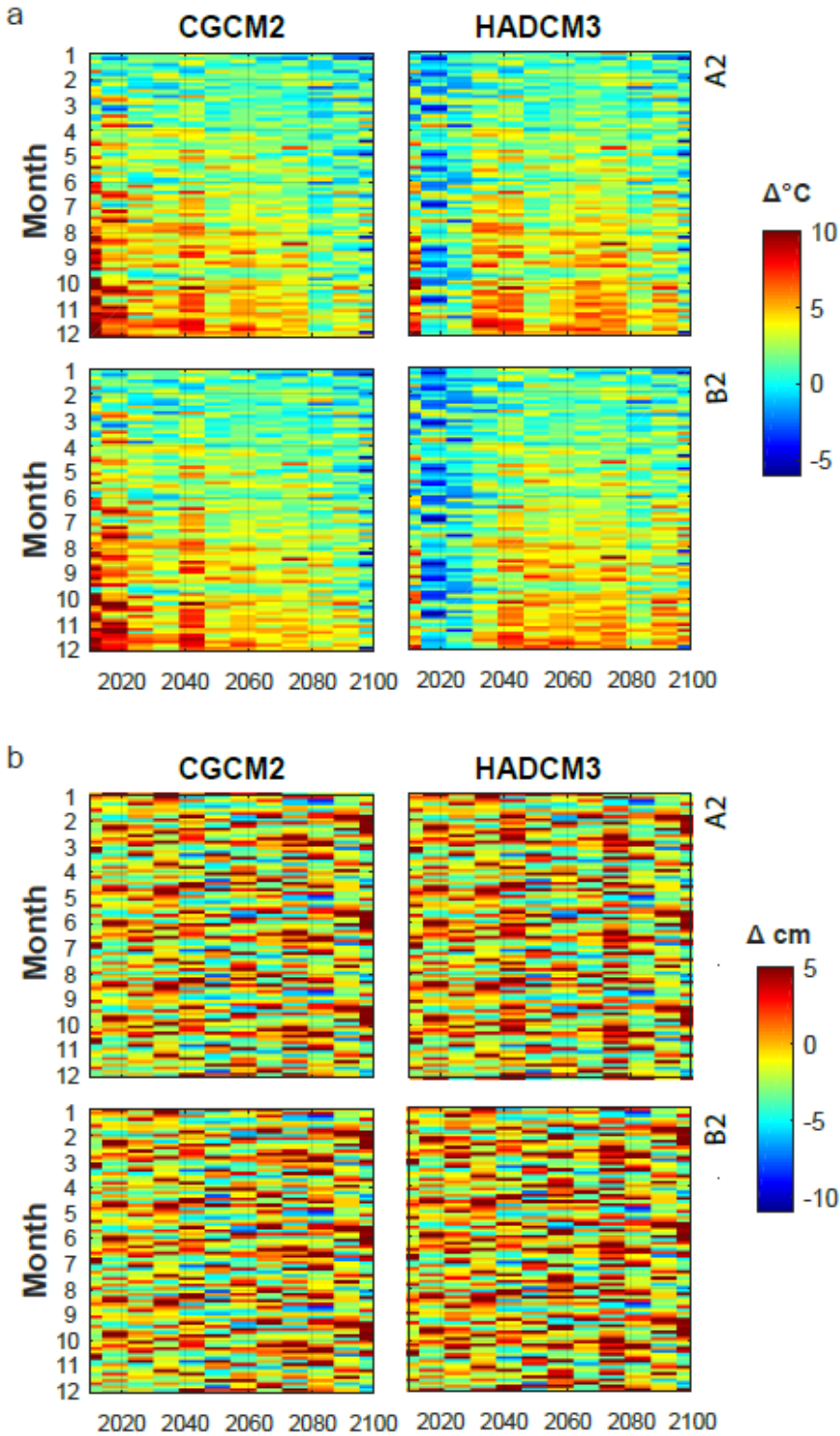


Figure S2. Downscaled and bias-corrected GCM temperature (a) and precipitation (b) monthly anomalies for IPCC scenarios A2 and B2.



Tables.

Table S1. Average annual Cl-loads during calibration period expressed as tons Cl/yr (left column) and percentage (right column) for 11 reaches in INCA-Cl model.

| Reach Number | Wet deposition | | Dry deposition | | Effluent discharge | | Road salt - urban | | Road salt - highway | | Total |
|--------------|----------------|-----|----------------|-----|--------------------|------|-------------------|------|---------------------|------|--------|
| | | | | | | | | | | | |
| 1 | 14.3 | 2.7 | 4.8 | 0.9 | 79.4 | 15.3 | 422.2 | 81.1 | 0.0 | 0.0 | 520.7 |
| 2 | 6.1 | 2.3 | 2.1 | 0.8 | 27.4 | 10.5 | 224.6 | 86.3 | 0.0 | 0.0 | 260.2 |
| 3 | 9.6 | 9.6 | 3.3 | 3.3 | 13.8 | 13.8 | 73.5 | 73.4 | 0.0 | 0.0 | 100.2 |
| 4 | 0.7 | 7.9 | 0.2 | 2.7 | 7.9 | 89.4 | 0.0 | 0.0 | 0.0 | 0.0 | 8.8 |
| 5 | 1.6 | 1.1 | 0.5 | 0.4 | 26.9 | 17.8 | 121.9 | 80.8 | 0.0 | 0.0 | 150.9 |
| 6 | 0.2 | 0.1 | 0.1 | 0.0 | 35.3 | 15.5 | 130.5 | 57.5 | 61.0 | 26.9 | 227.0 |
| 7 | 8.5 | 0.7 | 2.9 | 0.2 | 167.2 | 13.2 | 768.9 | 60.5 | 323.8 | 25.5 | 1271.2 |
| 8 | 4.3 | 0.4 | 1.4 | 0.2 | 56.2 | 5.9 | 270.9 | 28.3 | 625.3 | 65.3 | 958.1 |
| 9 | 1.7 | 0.4 | 0.6 | 0.1 | 30.1 | 7.5 | 43.7 | 10.8 | 327.7 | 81.2 | 403.8 |
| 10 | 6.6 | 0.6 | 2.2 | 0.2 | 78.1 | 7.4 | 447.0 | 42.5 | 519.1 | 49.3 | 1053.0 |
| 11 | 4.8 | 0.2 | 1.6 | 0.1 | 396.0 | 14.3 | 2032.0 | 73.5 | 332.0 | 12.0 | 2766.4 |
| Total | 58.2 | 0.8 | 19.7 | 0.3 | 918.3 | 11.9 | 4535.2 | 58.7 | 2188.8 | 28.4 | 7720.2 |

Table S2. Descriptive statistics (range, mean, and standard deviation) for daily Cl⁻ concentrations during future simulation periods for reach 5 for CGCM2 scenarios A2 (a) and B2 (b) and for HADCM3 scenarios A2 (a) and B2 (b).

a)

| Salt Application | Urbanization | 2010-2039 | | | 2040-2069 | | | 2070-2099 | | |
|------------------|--------------|-----------|------|-----|-----------|------|-----|-----------|------|-----|
| | | Range | Mean | SD | Range | Mean | SD | Range | Mean | SD |
| 2x | Increase | 3.8-31.1 | 18.6 | 5.3 | 2.7-20.1 | 12.8 | 3.4 | 2.2-14.7 | 9.7 | 2.4 |
| | No change | 3.7-31.0 | 18.5 | 5.3 | 2.6-20.0 | 12.5 | 3.4 | 2.0-13.8 | 9.2 | 2.3 |
| 1x | Increase | 3.6-30.9 | 18.0 | 5.3 | 2.5-19.7 | 11.9 | 3.3 | 2.0-13.0 | 8.7 | 2.2 |
| | No change | 3.6-30.9 | 17.9 | 5.3 | 2.5-19.6 | 11.8 | 3.2 | 1.9-12.9 | 8.4 | 2.1 |

b)

| Salt Application | Urbanization | 2010-2039 | | | 2040-2069 | | | 2070-2099 | | |
|------------------|--------------|-----------|------|-----|-----------|------|-----|-----------|------|-----|
| | | Range | Mean | SD | Range | Mean | SD | Range | Mean | SD |
| 2x | Increase | 4.4-31.2 | 20.1 | 5.0 | 3.6-21.1 | 14.7 | 3.2 | 3.0-16.6 | 11.8 | 2.3 |
| | No change | 4.2-31.1 | 19.8 | 5.0 | 3.3-20.8 | 14.0 | 3.2 | 2.6-15.1 | 10.7 | 2.2 |
| 1x | Increase | 3.9-31.- | 18.7 | 5.1 | 3.0-20.2 | 12.9 | 3.1 | 2.4-13.8 | 9.8 | 2.1 |
| | No change | 3.9-30.9 | 18.6 | 5.1 | 2.8-20.0 | 12.5 | 3.1 | 2.2-13.4 | 9.2 | 2.0 |

c)

| Salt Application | Urbanization | 2010-2039 | | | 2040-2069 | | | 2070-2099 | | |
|------------------|--------------|-----------|------|-----|-----------|------|-----|-----------|------|-----|
| | | | | | | | | | | |
| 2x | Increase | 4.4-31.4 | 20.4 | 4.9 | 3.4-22.1 | 15.7 | 3.3 | 3.5-19.6 | 13.9 | 2.7 |
| | No change | 4.3-31.3 | 20.2 | 5.0 | 3.2-21.3 | 14.8 | 3.2 | 3-17.0 | 12.1 | 2.5 |
| 1x | Increase | 3.9-31.0 | 18.9 | 5.1 | 2.9-20.3 | 13.3 | 3.1 | 2.7-15.0 | 10.7 | 2.2 |
| | No change | 3.9-31.0 | 18.7 | 5.1 | 2.8-20.1 | 12.9 | 3.1 | 2.4-14.1 | 9.9 | 2.1 |

d)

| Salt Application | Urbanization | 2010-2039 | | | 2040-2069 | | | 2070-2099 | | |
|------------------|--------------|-----------|------|-----|-----------|------|-----|-----------|------|-----|
| | | | | | | | | | | |
| 2x | Increase | 4.3-31.3 | 20.4 | 5.0 | 3.5-22.1 | 15.7 | 3.3 | 3.8-20.0 | 13.9 | 2.8 |
| | No change | 4.2-31.3 | 20.1 | 5.0 | 3.2-21.4 | 14.8 | 3.3 | 3.2-17.3 | 12.3 | 2.5 |
| 1x | Increase | 3.9-31.0 | 18.9 | 5.1 | 2.9-20.2 | 13.4 | 3.1 | 2.8-15.2 | 10.8 | 2.3 |
| | No change | 3.9-31.0 | 18.7 | 5.1 | 2.8-20.1 | 12.9 | 3.2 | 2.5-14.4 | 10.0 | 2.2 |

Table S3. Descriptive statistics (range, mean, and standard deviation) for daily Cl⁻ concentrations during future simulation periods for reach 11 for CGCM2 scenarios A2 (a) and B2 (b) and for HADCM3 scenarios A2 (a) and B2 (b).

a)

| Salt Application | Urbanization | 2010-2039 | | | 2040-2069 | | | 2070-2099 | | |
|------------------|--------------|----------------|------|------|---------------|------|------|---------------|------|------|
| | | | | | | | | | | |
| 2x | Increase | 7.3 - 100.1 | 54.5 | 18.1 | 4.8 - 72.5 | 39.2 | 15.1 | 3.7 - 68.6 | 31.1 | 15.2 |
| | No change | 7.3 - 100.1 | 54.5 | 18.1 | 4.8 - 72.5 | 39.2 | 15.1 | 3.7 - 68.6 | 31.1 | 15.2 |
| 1x | Increase | 7.3 - 100.1 | 54.5 | 18.1 | 4.8 - 72.5 | 39.2 | 15.1 | 3.7 - 68.6 | 31.1 | 15.2 |
| | No change | 7.3 - 100.1 | 54.5 | 18.1 | 4.8 - 72.5 | 39.2 | 15.1 | 3.7 - 68.6 | 31.1 | 15.2 |

b)

| Salt Application | Urbanization | 2010-2039 | | | 2040-2069 | | | 2070-2099 | | |
|------------------|-----------------|---------------|----------|-----------------|----------------|------|-----------------|----------------|------|-----------------|
| | | 2x | Increase | 16.3 - 145.0 | 76.2 | 14.2 | 15.8 - 115.6 | 66.2 | 11.8 | 13.4 - 109.7 |
| No change | 15.7 - 137.6 | | 75.1 | 14.3 | 15.0 - 102 | 63.2 | 11.9 | 11.5 - 92.7 | 55.8 | 11.3 |
| 1x | Increase | 12.0 - 101 | 65.3 | 15.0 | 11.1 - 77.7 | 52.7 | 12.1 | 8.5 - 74.2 | 46.3 | 11.9 |
| | No change | 11.6 - 101 | 64.8 | 15.2 | 10.2 - 77.4 | 51.2 | 12.5 | 7.6 - 73.6 | 44.0 | 12.6 |

c)

| Salt Application | Urbanization | 2010-2039 | | | 2040-2069 | | | 2070-2099 | | |
|------------------|--------------|-----------|------|------|-----------|------|------|-----------|------|------|
| | | 16.8 - | | | 14.8 - | | | 18.0 - | | |
| 2x | Increase | 152.4 | 79.0 | 14.3 | 137.7 | 72.9 | 12.8 | 149 | 72.5 | 13.2 |
| | No change | 148.8 | 77.8 | 14.3 | 121.2 | 69.2 | 12.4 | 118.5 | 65.9 | 12.4 |
| 1x | Increase | 101.4 | 66.7 | 14.7 | 79.3 | 56.0 | 11.9 | 81.3 | 52.3 | 11.7 |
| | No change | 101.4 | 66.2 | 14.9 | 78.9 | 54.2 | 12.3 | 76.1 | 49 | 12.2 |

d)

| Salt Application | Urbanization | 2010-2039 | | | 2040-2069 | | | 2070-2099 | | |
|------------------|--------------|-----------------|------|------|-----------------|------|------|-----------------|------|------|
| | | | | | | | | | | |
| 2x | Increase | 15.0 - 144.2 | 78.6 | 14.2 | 15.1 - 131.5 | 73 | 12.7 | 19.0 - 143.6 | 74.1 | 13.3 |
| | No change | 14.5 - 137 | 77.5 | 14.3 | 13.7 - 115.8 | 69.3 | 12.4 | 16.9 - 114.4 | 67.2 | 12.5 |
| 1x | Increase | 11.3 - 101.4 | 66.6 | 14.9 | 10.0 - 79.3 | 56.1 | 12.0 | 12.2 - 82.3 | 53.1 | 11.7 |
| | No change | 11.0 - 101.3 | 66.0 | 15.1 | 9.3 - 79.0 | 54.2 | 12.4 | 10.5 - 76.5 | 49.7 | 12.2 |

Table S5. Descriptive statistics (range, mean, and standard deviation) for daily Cl⁻ concentrations during the baseline simulation period for reach 5 and reach 11.

| Reach Number | Range (mg/l) | Mean (mg/l) | Standard Deviation (mg/l) |
|---------------------|-------------------------|------------------------|--------------------------------------|
| 5 | 4.1 - 30.5 | 17.9 | 5.2 |
| 11 | 8.4 - 81.7 | 35.7 | 7.5 |

Table S6. Number of days that baseline average annual precipitation as snowfall was exceeded for each model scenario.

| GCM | CGCM2 | | HADCM3 | |
|-----------------|--------------|-----------|---------------|-----------|
| Scenario | A2 | B2 | A2 | B2 |
| 2010-2039 | 8 | 8 | 7 | 8 |
| 2040-2069 | 4 | 5 | 6 | 7 |
| 2070-2099 | 2 | 2 | 5 | 5 |
| Total | 14 | 15 | 18 | 20 |

Table S7. Percent change from baseline in average annual total precipitation as snowfall and total precipitation for each model scenario. Negative numbers indicate decrease from baseline average.

| GCM | CGCM2 | | | | HADCM3 | | | |
|-----------------|----------------|--------------|----------------|--------------|----------------|--------------|----------------|--------------|
| Scenario | A2 | | B2 | | A2 | | B2 | |
| | as snow | total | as snow | total | as snow | total | as snow | total |
| 2010-2039 | -16.64 | -0.77 | -15.12 | -0.47 | -7.15 | 1.26 | -5.75 | 4.61 |
| 2040-2069 | -34.59 | -0.98 | -33.97 | -0.14 | -15.77 | 2.37 | -15.91 | 5.27 |
| 2070-2099 | -51.83 | -0.49 | -49.22 | -0.22 | -29.01 | 1.98 | -24.57 | 5.37 |

Table S8. INCA model calibration efficiencies (R^2 and N-S) for daily Cl^- flux (kg/d) of reaches with Cl^- observations spanning calibration period 2012-2014.

| Reach Number | No. Observations | Flux (kg/d) | |
|--------------|------------------|-------------|------|
| | | R^2 | N-S |
| 2 | 6 | 0.89 | 0.75 |
| 3 | 6 | 0.82 | 0.64 |
| 4 | 6 | 0.90 | 0.68 |
| 5 | 99 | 0.79 | 0.77 |
| 7 | 6 | 0.80 | 0.12 |
| 11 | 315 | 0.70 | 0.43 |

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Chapter 3:

Controls on iodine sources, storage, and transport in forested headwater catchments

Abstract

Iodine is a biophilic halogen that is concentrated in organic-rich sediments and soils. The natural baseline export of iodine from forested headwater catchments has yet to be rigorously investigated. We evaluate the controls on contributions of iodine to surface water from different sources under different hydrologic conditions across spatial and temporal scales in a mixed land use (primarily forested) headwater catchment in upstate New York State, USA. Iodine exhibits consistent seasonal trends, across all sample years, with enrichment occurring during warmer periods, and subsequent depletion during winter months. We attribute the observed seasonal trend to increases in the export of organically bound iodine during the same time interval. During hydrologic events, iodine peaks in the rising limb of the storm hydrograph, indicating that during dry periods iodine is likely stored and accumulates in the riparian zone, to be exported as riparian waters enter the main channel under high flow events. Like the export of organic carbon, event characteristics largely control the timing and response of stream iodine during storm flows, suggesting heterogeneous flow paths and variable flushing of accumulated iodine during repeat events. Groundwater likely contributes iodine to streams under base flow conditions. Spatial controls suggest local hydrogeology influences the spatial distribution of iodine in surface water, as elevated concentrations are observed downstream of wetlands and organic-rich rock outcrops. This suggests that controls on iodine in some catchments may be related to weathering of exposed organic-rich shale.

1. Introduction

Relatively few studies have examined the natural sources of iodine (^{127}I) to surface water systems in freshwater systems (Neal et al. 2007, Moran et al. 2002, Alvarez et al. 2015, Alvarez et al. 2016) in favor of focusing on the long-lived radioisotope (^{129}I) and subsequent ratios of $^{129}\text{I}/^{127}\text{I}$ as a tracer for water flow paths (Oktay et al. 2001, Moran et al., 2002, Santchi, Herod et al. 2013, Herod et al. 2016). Iodine is a biophilic element, primarily enriched in organic-rich material of marine origin (Muramatsu and Wedepohl 1998). Due to its large ionic radius and high mobility, iodine typically occurs at low concentrations in aquatic environments (Muramatsu and Wedepohl, 1998, Moran et al. 2002, Neal et al. 2007, Herod et al. 2015, Lu et al. 2015, Herod et al. 2016). Iodine enrichment in marine sedimentary strata may impact associated waters, and thus the terrestrial aquatic iodine cycle (Fuge and Johnson 1986, Lu et al. 2015). Therefore, understanding the controls on the cycling of ^{127}I in surface water settings may better inform the cycling of the radionuclide (^{129}I) in the environment and provide information related to the processing of organic matter released via weathering of organic-rich sedimentary rocks.

In addition to the chemical weathering of marine sedimentary rocks, iodine may also enter surface water systems via transport processes associated with atmospheric deposition, desorption from soils, and the natural migration of subsurface brines (Fuge and Johnson, 1986, Dissanayake et al., 1999, Oktay et al. 2001, Moran et al., 2002, Johnson et al., 2003, Neal et al. 2007, Ashworth, D. J., 2009, Lu et al., 2015). Human-derived wastewaters may be enriched in iodine as result of modern-iodized diets.

Concentrations of iodine in surface waters may covary with increased organic content, and land cover and soil characteristics (Fuge and Johnson 1986, Reiller et al. 2003, Dai et al. 2004, Keppler et al. 2004, Neal et al. 2007, Zeng et al. 2014). The concentration of available iodine in

soils is strongly correlated to the amount of organic matter, the concentration of iron and aluminum oxides and hydroxides, redox conditions, pH, particle size distribution, and contact time between soil and iodine (Ashworth and Shaw 2006, Bunzl and Schimmack 1988, Dissanayake et al. 1999, Dai et al. 2004, Fuge and Johnson, 1986, Fukui et al. 1996, Gil-Carcía et al. 2009, Keppler et al. 2004, Lieser and Steinkoff 1989, Muramatsu and Yoshida 1995, Sheppard et al. 1995, Sheppard and Hawkins 1995, Soderlund et al. 2011, Whitehead 1973, Whitehead 1981, Yuita et al. 2005, Yuita et al. 2006). Although numerous studies have effectively revealed the controls on specific components of the terrestrial aquatic iodine cycle (e.g. soil sorption and release, brine migration, atmospheric deposition) (Fuge and Johnson 1986, Muramatsu and Yoshia 1995, Sheppard and Hawkins 1995, Sheppard et al. 1995, Neal et al. 2007, Lu et al. 2015), few studies have attempted to examine the controls on the flux of terrestrial iodine in tandem.

In this study, we examine the hydrogeologic controls and the potential impacts of bedrock weathering on the fate and transport of iodine in the terrestrial aquatic environment in a headwater catchment to the Upper Susquehanna River Basin with mixed land cover located in Upstate New York State, USA. We employ a variety of different sampling regimes including sampling of surface waters from first to fourth order streams, ground water, and precipitation samples to elucidate the contributions of iodine resulting from both climatic-driven controls on iodine and those driven by differences in local hydrogeology. We supplement water quality data with measures of total iodine extractable by deionized water from Devonian-age rock outcrops. The combined sampling methodologies aim to capture the temporal and spatial dynamics of riverine iodine export, identify possible sources of iodine to surface water systems, and elucidate potential hydrogeologic controls on the transport of iodine at the catchment scale.

2. Methods

2.1. Sample Collection

From September 2012 through November 2014 groundwater and surface water in the Tioughnioga River watershed in Cortland County, New York was sampled. Samples from a single location at the mouth of both East and West Branches of the Tioughnioga River (n=205) and four groundwater wells were collected (n=28) (Figure 1). Surface water samples were collected weekly. Precipitation was sampled daily (n=91) pending a precipitation event. From May through November 2016 grab samples were collected monthly from approximately 50 locations along East and West Branches of the Tioughnioga River and their respective tributaries (n=261). In April and June 2016, an ISCO portable auto sampler collected surface water samples every two hours during a hydrologic event (snowmelt and rainfall, respectively).

Water samples were collected in prewashed bottles that were triple-rinsed with sample and filled to the mouth of the bottle to eliminate headspace. Samples were filtered with a 0.45- μm filter and split into three clean bottles for alternate analysis. Samples were stored between 0°C to 4°C depending on intended method of analysis. Samples analyzed for cations were acidified with a 5% HNO₃ solution before storage. Samples for anions were frozen and thawed immediately before analysis.

2.2. Data Acquisition

Mean daily discharge was recorded continually at a USGS gaging station (Station Number: 01509000) located 0.4 km downstream of the confluence of East and West branches. Individual daily streamflow estimates for East and West Branches were derived using a semi-distributed hydrologic model in an unrelated study (Gutchess et al. 2017). Maximum discharge values occur

following summer rain events or spring snowmelt. Precipitation measurements were acquired through the NOAA Climatic Data Center for appropriate stations within Cortland, Onondaga, and Madison counties.

2.3. Leaching experiments

Weathering of rocks may result in the removal of iodine from exposed rock, based primarily on climate and rock characteristics (Rankama and Sahama 1950, Goldschmidt 1954, Konovalov 1959, Fuge and Johnson 1986). Organic-rich sediments are particularly enriched in iodine, with the highest concentrations of iodine observed in marine sedimentary rocks, such as carbonates and shales (Fuge and Johnson 1986). These rocks subsequently release more iodine during weathering (Johnson 1980), leading to an enrichment in iodine in rivers draining marine sediments (Konovalov 1959).

We performed batch leaching experiments to determine the total amount of iodine available for release from rock outcrops in the study area through natural weathering processes. Nine bedrock samples corresponding to four separate geologic formation that intersect the Tioughnioga River catchment (e.g. members of the Sonyea Group, the Genesee Formation, and the Upper Hamilton Group including the Moscow Formation and the Upper Skaneateles Formation) were collected from exposed outcrops surrounding the catchment area (Spradlin 2015). Approximately 200 g of sample was collected at each location. Samples were excavated at greater than 10 cm into the exposed face to ensure the collection of un-weathered materials. Refer to Figure S2 for location of sample collection relative to study area and stratigraphic information.

We followed the USGS Field Leach Test (FLT) protocol to create a with a 20:1 water to rock ratio (Hageman 2007). Leaching experiments were performed by combining 50 mL of deionized

water to 2.5 g of crushed rock sample (20:1). Rock-water mixtures were then agitated for 1 hour using a Burrell wrist-action shaker. After the agitation processes, the solutions were centrifuged for 15 minutes at 6,000 rpm. The centrifuged rock-water solutions were extracted, filtered through 0.45 μM Polyvinylidene difluoride (PVDF) membrane filters, and refrigerated until analysis.

2.4. Analytical Methods

Major cations and anions (Ca^{2+} , Na^+ , Mg^{2+} , K^+ , Cl^- , SO_4^{2-} , and NO_3^-) were measured on an ion chromatograph (IC) at the State University of New York College at Cortland 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. Total dissolved iodine and bromine (Br) concentrations were measured on a Bruker Aurora M90 ICP-MS at Syracuse University. Iodine and bromine calibration standards were prepared prior to analysis and diluted by a matrix containing cesium as the internal standards. Blanks were monitored every three samples. Calibration standards were run every six samples. Instrument precision is typically less than 1%, and was not reported individually.

3. Setting

Two tributaries originating in central New York, converge in Cortland County to form the Tioughnioga River (East and West Branches, respectively). The West Branch begins in Onondaga County, New York, and flows south through a series of lakes before converging with the East Branch to become the Tioughnioga River in the southern extent of Cortland County, New York. The headwaters of the East Branch flow southwest, emerging as outlets of wetlands located in southwest Madison County. The watershed area in this study is roughly 936 km^2 . The

catchment is located within the glaciated region of the Appalachian Plateau physiographic province. The Tioughnioga River is a main headwater watershed to the Upper Susquehanna River Basin and the largest estuary in the United States, Chesapeake Bay, where the decline of water quality related to water treatment and agriculture practices has been the focus of numerous investigations (Buda 2008, Hetcher-Aguila and Eckhardt 2006). As a headwater watershed, the Tioughnioga River provides a unique opportunity to understand the transport of solutes downstream to the Susquehanna River Basin.

Watershed Characteristics

3.1. Land Use Classification

Land use in the Tioughnioga River watershed is predominantly forest and agriculture (U.S. Geological Survey 2001) (Table 1). Dairies, typically situated in valleys adjacent to the river channel, are the dominant agricultural practice (U.S. Department of Agriculture). Forest cover is dominated by mixed-growth vegetation, distributed roughly evenly across the two branches. Urban lands make up a larger proportion of the West Branch, is located adjacent to a major interstate highway (Interstate I-81) for the entirety of its reach and flows through the cities of Cortland and Homer in downstream reaches. The city of Cortland wastewater treatment plant (WWTP) discharges treated effluent to the Tioughnioga River in downstream of all sampling locations.

Wetlands account for approximately 4% of the total watershed area (Tiner, R.W. 2006), with the East Branch containing roughly double that of the West Branch (U.S. Fish and Wildlife Service National Wetlands Inventory). Wetlands in the East Branch catchment are generally concentrated to the upstream reaches and classified as emergent or forested wetlands (U.S. Fish and Wildlife

Service National Wetlands Inventory). Wetlands in the catchment are primarily throughflow wetlands, thus having a high potential for surface water detentions, sediment retention and nutrient transformation (Tiner, R.W. 2003, 2006).

3.2. Hydrogeology

In north-south trending valleys, the river is underlain by a two-aquifer valley-fill system comprised of a surficial unconfined sand and gravel aquifer (12-24 m thick) and a confined basal sand and gravel aquifer (0-52 m thick) (Hammer et al. 1986, Reynolds 1987, Muller and Calkin, 1993, Miller et al., 1998, Kappel et al. 2001, Kappel and Miller 2003, Miller 2004). The aquifers are separated by a relatively thick glaciolacustrine fine sand, silt, and clay confining unit (0-47 m thick) (Reynolds 1987, Kappel and Miller 2003). The upper unconfined aquifer is absent from the upstream reaches of the East Branch. The entire aquifer system rests on bedrock of Upper to Middle Devonian age and consisting predominantly of organic-rich shale interbedded with repeating sequences of siltstone, sandstone, and limestone (Miller et al., 1998, Kappel and Miller 2003, Miller 2004). Depth to bedrock in the catchment can range from 0 (outcrops) - 194 m (Reynolds 1987, Miller et al. 1998). Valley walls are comprised of bedrock covered by a thin veneer of low permeability glacial till (Cosner and Harsh 1978, Reynolds 1987). Black shales deposited in the Appalachian Basin are enriched in organic matter and iodine (Lu et al. 2015). The glacial aquifer system underlying the catchment provides drinking water to its approximately 47,000 inhabitants (U.S. Census Bureau, 2010), and has been designated as a “Primary Aquifer” by the New York State Department of Environmental Conservation (NYS DEC) and as a “Sole Source Aquifer” by the U.S. Environmental Protection Agency (US EPA) under the Safe Drinking Water Act (Miller 2004). Thus, processes that impact local water are inherently linked to human health.

Previous studies have illustrated that groundwater discharges into the Tioughnioga River and its tributaries (Miller 1998, Reynolds 1987, Buller 1978, Gutchess et al. 2016). Groundwater in the unconfined aquifer flows predominantly south through the river valleys and is recharged at various locations throughout the study area (Buller et al., 1978, Cosner and Harsh 1978, Reynolds 1978, Miller et al. 1998, Kappel et al. 2001). Soils in the Tioughnioga River watershed are comprised of silty loams classified as alfisols, entisols, histosols, and inceptisols soil orders. The majority of surface land is covered by soils with high organic content (histosols) dominate in the river valleys (Soil Survey Staff, 1999). Soil orders with markedly higher organic content (e.g. histosols) are concentrated

4. Results

4.1. Water samples

Iodine concentrations measured weekly in downstream reaches range from 0.90 – 5.42 and 0.80 – 3.78 $\mu\text{g/L}$ in East and West branches, respectively (Table 2). Concentrations of iodine measured in surface waters were generally highest in samples collected in the East Branch, in contrast to all other dissolved ions which tend to be elevated in West Branch waters (SI, Figure S1). The greatest iodine concentrations measured in downstream reaches were not systematically linked to flow, with higher concentrations typically occurring during or immediately succeeding high flow events (Figure 2, 3). Iodine concentrations exhibit seasonal variations, with an increasing trend in stream iodine into the warmer months, and subsequent decreases in surface water concentrations into colder (fall and winter) periods (Figure 2, 4). Timing of annual maximum and minimum concentrations of iodine varied from year to year, although seasonal trends were consistent across sampling years (SI Figure S2). The greatest variability in surface water iodine concentrations occurred during summer months (JJA), and in the East Branch.

Moran et al. (2002) examined spatial distributions of iodine concentrations in precipitation and surface water across the United States, Canada and Europe. Average iodine concentrations measured in the Tioughnioga River catchment are comparable to those of other rivers sampled along the Northeast Coast of the U.S. (average = 5.74 $\mu\text{g/L}$) but markedly lower than those affected by nuclear fuel reprocessing facilities such as the Savannah River Plant (Moran et al. 2002, Santchia, Oktay).

Relative to surface waters, concentrations of iodine in groundwater and precipitation (as rain and snow) were depleted. Concentrations of iodine in groundwater ranged from 1.95 to 3.33 and 1.20 to 2.28 $\mu\text{g/L}$ for East and West Branches respectively. Iodine concentrations in precipitation did not vary seasonally, with no significant difference between mean values of iodine measured in snowfall vs. rain. This observation is consistent with prior studies (Fuge and Johnson 1986). Average iodine concentrations in precipitation collected for this study ranged from 0.17-1.81 $\mu\text{g/L}$ with average concentrations of 0.68 $\mu\text{g/L}$. The minimum concentration of iodine in precipitation coincides with the timing of the maximum observed iodine concentration in surface water (June 2013). Descriptive statistics for concentrations of iodine measured in different water types are provided in Table 1.

4.2. Iodine Leaching

The results of USGS FLT are shown in Table 3. The greatest mass of leachable iodine resulted from experiments with organic rich rock units, such as the Renwick Shale Member of the Genesee Formation in NYS, and units contained within the Moscow Formation and Upper Skaneateles Formation, the latter two of which comprise several large outcrops in the upstream reaches of the East Branch of the Tioughnioga River (Figure 6, Table 3). Weathering of the Renwick Shale likely does not contribute iodine to the upstream reaches of the Tioughnioga

River, as it outcrops stratigraphically downstream of Tioughnioga headwater tributaries. (SI, Figure S2). However, within the same formation (Genesee Formation), the bulk of exposed rock in the Tioughnioga catchment area is described as shale interbedded with limestone (Dickens et al., 2005), with notably lower leachable iodine (Table 3). The Moscow and Skaneateles Formations demonstrated the greatest amount of total leachable iodine. Both Moscow and Upper Skaneateles Formations outcrop in the upstream reach of the East Branch Tioughnioga River.

4.3. Mass Balance

Annual atmospheric inputs of iodine were calculated based on weather data (NOAA CDC GHCND: USC00301799). Average iodine concentrations were measured in precipitation from 2013 and 2014 (most complete sample years). Annual mass balance indicates an average excess flux of approximately 163 - 291 kg iodine per year (for West and East Branches, respectively), suggesting an additional source of iodine may be present beyond that of atmospheric deposition and evapoconcentration to account for the greater export. The larger excess in annual iodine loads in the East Branch may suggest a prominence or stronger additional source of iodine to the catchment, reflective of local hydrogeology (see discussion for more details regarding local hydrogeologic influences). Annual iodine flux in the West Branch is largely controlled by atmospheric processes. Contributions from groundwater likely do not account for these inputs, as groundwater iodine concentrations in the catchment are lower than those measured in surface water.

5. Discussion – Hydrogeologic Controls on total dissolved in-stream iodine dynamics

5.1. Sources of iodine

Iodine concentrations measured in the downstream reaches (East and West Branches) varied seasonally, with the greatest concentrations occurring during warmer months (May through September) and notably lower concentrations observed during fall and winter months (October through March) (Figure 2a, SI Figure 2). Concentrations of iodine measured in the East Branch generally exceeded those of the West Branch during warm periods. This divergence is less pronounced during winter months, as concentration profiles are indistinguishable across the two branches.

Atmospheric inputs

The seasonal variation in iodine concentrations in the Tioughnioga River is comparable to patterns observed in headwater areas of the River Severn in mid-Wales in the Plynlimon experimental catchments (Neal et al. 2007), although the seasonal peak in our study precedes that of the 2007 study (SI Figure S2), likely due to temperature variations across the different catchments (Wales vs. NYS). In addition to elevated stream iodine during warm periods, Neal et al. (2007) also observed an increase in dissolved organic carbon (DOC) during the same time interval, suggesting a systematic link in the transport processes of iodine and DOC. Neal et al. (2007) further discuss the mechanisms linking DOC and iodine transport, suggesting atmospheric inputs as the main driver for the relationship. However, we suggest that the seasonal amplitude in stream iodine concentrations in this setting varies from that of the experimental forest in mid-Wales, as unlike the 2007 study, iodine concentrations in the Tioughnioga River catchment are not enriched in precipitation relative to stream water (Table 2), and were lower than those of precipitation collected in mid-Wales (Neal et al. 2007). Thus, precipitation does not account for the seasonal patterns observed in stream iodine concentrations in this inland setting.

Additionally, mass balance approximations further suggest that atmospheric processes alone cannot account for the patterns in iodine observed in the East Branch Tioughnioga River.

Groundwater contributions to streamflow

Groundwater iodine concentrations were less variable seasonally than those measured in surface waters (Table 2). During baseflow and winter months, surface water iodine concentrations approached those of groundwater in the study area (Figure 2a). In a prior study (Gutchess et al., 2016), surface water chemistry during low flow was largely controlled by groundwater discharge to the stream. Multivariate statistical analysis suggests that surface water collected during periods of low flow reflects the mixing of groundwater influenced by minor contributions (<0.1%) of basinal brines (Gutchess et al., 2016). Thus, shallow groundwater that has undergone natural mixing (albeit volumetrically minor contributions) with deep, saline brines (e.g. Appalachian Basin brines), likely serves as the main source of iodine to surface water during winter base flow conditions (Figure 2a, Figure 8a-b). This is further supported by seemingly indistinguishable concentrations among surface water and groundwater collected during these intervals.

Elevated concentrations of iodine have been observed in NYS in relatively deep groundwater associated with organic-rich marine sedimentary rocks (Lu et al. 2015). High I/Cl and low Br/Cl ratios of waters from the Atacama Desert of Northern Chile indicate a mixture of relatively fresh (meteoric) groundwaters with more saline waters impacted by weathering of organic-rich sedimentary rocks of marine origin (Alvarez et al. 2015, 2016). In the Tioughnioga River catchment however, thick glacial outwash deposits (~100-250 m) which typically have low iodine concentrations (Goldschmidt 1954, Fuge and Johnson 1986) overly Devonian age marine sedimentary rocks. Potential contributions from high iodine deep waters to shallow groundwater

are low (typically <0.1%, Gutchess et al. 2016) and thus could not have contributed the necessary concentrations iodine to raise surface water iodine concentrations from those observed during base flow conditions over winter months. Concentrations of other ions (Ca, Mg, Na, Cl, and SO₄) that tend to be enriched in shallow groundwaters do not increase with temperature as does iodine in either Branch (Figure 4, Figure S1). Rather, geochemistry of surface waters approaches that of groundwater during low flow measured in winter months (December through February), as groundwater contributions dominate streamflow (Figure 3 SI, Figure S1). Recharge during summer storms results in a dilution response of all major ions, with the exclusion of iodine (Figure 3, SI Figure S1). In contrast to all other measured solutes, iodine does not exhibit a significant dilution effect (significant negative linear trend, $\alpha = 0.05$) during high flows (Figure 3). The absence of any significant dilution effect during hydrologic events suggests that the source of iodine to surface water during snowmelt and rainfall events does not originate from groundwater - in contrast to geochemistry surface waters during of low flow, where groundwater likely accounts for the majority of iodine contributions (Figure 2a, Figure S1, Figure 8b). Additionally, the observed iodine enrichment in surface waters relative to groundwaters during warm periods (Figure 2a) further suggests that groundwater contributions alone do not control the trends observed in surface during summer months.

Organic matter processing

DOC increases seasonally, with elevated concentrations accompanying warmer temperatures (Raymond and Saiers 2010, Vidon et al. 2010, Roig-Planasdemunt et al. 2017). The covariance between temperature and DOC has been linked to increased size of DOC pools during warmer periods (Raymond and Saiers 2010). In soils, the association of iodine with organic matter (OM) has been extensively documented (Fuge and Johnson 1986, Santchi, Yuita, etc.), thus it is likely

that iodine dynamics in surface water systems are largely controlled by OM associated processes. Total organic carbon (TOC) was not measured for this study, but existing data collected in the catchment during 2007 and 2013 suggest that East Branch surface waters have higher TOC than West Branch, with markedly higher concentrations observed in surface waters than in groundwater of either branch and generally elevated TOC in samples collected in August relative to May of the same year (EPA Storage and Retrieval (STORET) database).

The temperature association (Figure 4) presented by our data suggest that riverine iodine flux may be governed by the same processes that control DOC export (e.g. primary production). Iodine stored in the riparian zone is likely mobilized during wet and warm conditions present in the summer months (changing oxygen conditions) (Figure 8b-c). The contrast across Branches is likely due to differences in 1) local hydrogeology that favor iodine transport (e.g. organic content, soil composition, etc.), and 2) an additional source of iodine to the East Branch catchment. The additional source will be discussed further in later sections.

The East to West contrast (iodine enrichment observed in East relative to West Branch waters) was notably more pronounced during warmer periods, with the two branches converging to indistinguishable iodine concentrations during winter (D-F) months. Atmospheric processes alone cannot account for the inter-catchment contrast, as it is unlikely that precipitation regimes would vary substantially over the study area for a given event. Furthermore, the mass of iodine concentrated in near-channel soils resulting from the evapoconcentration of atmospheric inputs should be comparable across both branches if inputs to either catchment were equal. The maximum surface water iodine concentration measured in weekly surface water samples coincides with the minimum iodine concentration measured in precipitation (0.18 $\mu\text{g/L}$ on July 2nd, 2013).

5.2. *Event-based iodine flux*

Unlike other ions, iodine concentrations measured during storm events (snowfall and summer rainfall event) do not exhibit a dilution response (e.g. Cl), but instead either peak within the rising limb of the hydrograph or remain relatively stable throughout the event (Figure 5).

Furthermore, conditions leading up to a storm event, and those of the event itself (hydrologic flow paths/runoff sources) may produce unique responses in stream iodine concentrations (Figure 5). These observations suggest that iodine export during hydrologic events may be inherently linked to DOC transport processes.

Dissolved organic carbon (DOC) typically increases during the rising limb of the storm hydrograph, exhibiting hysteretic effects, as concentrations begin to decline during the receding limb of the hydrograph (McClain et al. 2003, McGlynn et al. 2003, Hood et al. 2006, Inamdar et al. 2004, Inamdar et al. 2006, Raymond and Saiers 2010, Andrews et al. 2011). This phenomenon has been the focus of numerous studies as interpreted to represent “hot moments,” of terrestrial DOC transport. Similar to DOC event flux (Hood et al. 2006, Raymond and Saiers 2010, Andrews et al 2011), we interpret the rapid flushing response of in-stream iodine concentrations to be indicative of a near channel source of stream iodine (Figure 5). Analysis of waters collected during different stages of hydrologic events has indicated that during the rising limb of the storm hydrograph, waters are dominated by inputs from riparian areas, whereas contributions from catchment hillslopes dominate the latter half (receding limb) of the hydrograph (McGlynn et al. 2003). Thus, we propose that iodine stored in riparian soils during periods of relative dryness is mobilized during storm events and flushed into adjacent surface water bodies (Figure 8b-c). This “pulse” of initial iodine is eventually depleted, and latter concentrations measured during events reflect hillslope contributions of iodine. The unique

responses observed across catchments (East vs. West) and events (e.g. snowmelt vs. rainfall) highlights the variability of flow paths and/or distinct source areas of iodine that may be mobilized during different hydrologic events and across the two catchments. Different iodine profiles between snowmelt and rainfall events may also reflect the specific conditions leading up to the events (e.g. antecedent wetness and temperature). DOC dynamics during hydrologic events have been shown to be largely dependent on antecedent conditions and catchment characteristics (Hood et al. 2006, Raymond and Saiers 2010, Vidon et al. 2010, Andrews et al. 2011).

5.3. Surface-subsurface hydrogeologic controls on in-stream iodine

The results of longitudinal sampling of Tioughnioga River reaches reveal that the East-West contrast observed in downstream reaches (Figure 2a) is not exclusive to the weekly sites. Iodine concentrations measured in tributaries of East and West Branches were generally elevated relative to those of measured at the mouth of either branch (Figure 7), suggesting that tributaries contribute much of the iodine measured in downstream reaches of East and West branches. Elevated I/Cl ratios suggest that the levels of iodine observed in upstream tributaries likely do not result from variable groundwater contributions across the catchment. This further suggests that spatial variability in iodine concentrations cannot be attributed to atmospheric inputs alone, but rather is more likely due to differences in local hydrogeology (e.g. channel morphology, rock outcrops, soil characteristics). Tributaries exhibit a seasonal clockwise hysteresis with iodine (Figure 7) that is preserved in individual points from the main channel and consistent with observations in downstream reaches (Figure 2a). In the following paragraphs, we discuss the potential sources of iodine to upstream tributaries in further detail.

Channel morphology, wetlands, and soil orders

Channel morphology varied distinctly from East to West Branches (Figure 1, Figure 6), with a lower gradient and more sinuous stream profile present in the East Branch (Table 1). The latter has been documented to be conducive to DOC export and riparian development (Vidon et al. 2010), and thus likely has a role in the flux of dissolved iodine.

Although wetland type did not vary substantially across branches or across their individual tributaries (SI, Table 1), a greater proportion of catchment area was comprised of wetlands in upstream tributaries, particularly those that drain to the East Branch (0.71-8.32% East vs. 0.81-3.83% West tributaries) (Figure 6). Subsequently, upstream tributaries tend to exhibit iodine (and I/Cl) enrichment (Figure 7), suggesting that iodine is introduced to the catchment through these interchanges, from a source other than saline groundwater (would result in lower I/Cl due to the presence of Cl). Wetlands are associated with the production of peat, where humification leads to the formation of organoiodine (Keppler et al. 2003, Biester et al. 2006 Maillant et al. 2007, Levy et al. 2017). Fluctuating water levels in wetland environments may lead to variations in oxygen conditions, and thus the mobility of solutes (Grunth et al. 2008, Kao et al. 2013, Borken et al. 2009). This allows the organic-rich soils that exist in wetlands (e.g. histosols, peats) to accumulate iodine during oxic conditions, and release iodine during anoxic (saturation) conditions (Denham et al, 2009), with organoiodine increases of up to 2.5x those of oxic conditions within the saturated zone (Yuita 1992). Fuge and Johnson (1986) suggest that iodine uptake by Fe and Al-oxides in soils and sediments is governed by pH, and thus oxygen conditions. Experiments performed by Dai et al. (2004) confirmed that soils rich in iron oxide more readily sorbed iodate.

Consistent with present-day wetland classification in the catchment (Tiner et al. 2003, Tiner et al. 2006), the U.S. Department of Agriculture Natural Resources Conservation Service (USDA

NRSCS) National Cooperative Soil Survey identified a prevalence of organic-rich histosols and Fe and Al rich alfisols in upstream reaches of the East Branch. Thus, it is likely that during dry periods, iodine accumulates in organic-rich sediments in the floodplains of upstream tributaries (Figure 8b). Under saturation conditions (most likely during heavy summer storms), iodine is mobilized and flushed into pore waters (Figure 8c). Much of the contrast in surficial deposits (e.g. wetland and soil cover) across the two branches resulted from the varying location of the Laurentide Ice Sheet during the advance and retreat of the Laurentide Ice sheet during the Valley Heads Advance of the Wisconsinian glaciation (117,000-10,800 ya) (Hammer et al. 1986, Reynolds 1987, Muller and Calkin, 1993, Miller et al., 1998, Kappel et al. 2001, Kappel and Miller 2003, Miller 2004). The position of the ice sheet effectively altered the development of the surficial geology of the West Branch (lower affinity for alfisols formation, in favor of entisols, inceptisols). Thus, we propose that the combined influence of connectivity of different taxonomic soil orders and present-day wetland locations in the East Branch are favorable for the transport of iodine, and thus may account for a portion of the seasonal and spatial variability observed in early sections.

Shale outcrop weathering

Rivers that drain marine sedimentary basins (including the Susquehanna River) have $\Delta^{14}\text{C}$ depleted waters (thus, ancient carbon sources) relative to catchments that drain igneous basins, suggesting that OM-rich sedimentary rocks make significant contributions to riverine DOC export (Kao and Lui et al. 1996, Leithoid and Blair 2001, Masiello and Duffel 2001, Raymond 2004). Runoff from black shale outcrops does contribute to surface water major ion geochemistry, with less pronounced effects during base flow (Cox et al. 2007). Rivers that drain marine sedimentary basins have higher iodine concentrations (Fuge and Johnson 1986). Given

this distinction, and the relative enrichment of iodine measured in organic-rich rocks relative to other rock types (Fuge and Johnson 1986), sedimentary rock outcrops containing black shales may serve as an additional source of iodine to adjacent catchments (Figure 8a). Several of such outcrops exist within the Tioughnioga River catchment (Figure 6).

Additionally, bedrock outcrops located in the upstream reaches of the East Branch are comprised of formations containing geologic units that contain black shale (e.g. Moscow and Skaneateles Formations). Samples collected from Moscow and Upper Skaneateles Formations in NYS released the greatest amount of total iodine during leaching experiments compared to other, less organic rich units (Table 3). Black shales typically have a higher organic content than other marine sedimentary rock types, and consequently contain greater levels of iodine relative to other rocks. Across the entirety of the West Branch catchment, there is a notable absence of bedrock outcrops that intersect organic-rich rock units (Figure 6), including the Moscow and Skaneateles Formations. This distinction has important implications for the contrast in iodine concentrations observed at downstream reaches (Figure 2a), as well as the dynamics of iodine transport across variable spatial (Figure 6, Figure 7) and temporal scales (Figure 2a, Figure 5) at the catchment level. It's likely that more iodine is released through weathering processes at rock outcrops located in the upstream reaches of the East Branch, thus introducing an additional iodine source to the catchment to be transported downstream. The iodine released from surficial weathering processes may account for the elevated concentrations observed during downstream sampling of the East Branch (Figure 6, Figure 7), and the differences in mass balance calculated for the two catchments. Our findings suggest that rock outcrop weathering, particularly black shale weathering, may contribute to global riverine iodine export.

The variation between branches in concentrations of iodine is likely due to the presence of an organic-rich source in the East Branch, and absence thereof in the West Branch. An additional source of iodine is required to account for the iodine enrichment observed in the East Branch (relative to the West). Concentration processes alone do not account for the preferential enrichment of iodine over and chloride (and other major ions, see SI Figure S1) observed in the East Branch catchment. We instead propose that local hydrogeologic characteristics, including the prevalence of organic-rich bedrock outcrops, soil composition, and riparian wetlands concentrated in and along upstream reaches of the East Branch may more readily facilitate the transport of iodine in the East Branch catchment.

5.4. Broader impacts

Iodinated disinfection by-products (I-DBPs) are an emerging group of DBPs that are highly toxic (genotoxic and/or cytotoxic, teratogenic, and potentially carcinogenic) (Hunter et al 1995, Plewa et al. 2004, Richardson et al. 2007, Richardson et al. 2008, Guo et al. 2014). I-DBPs form when source waters containing halogens and organic matter are disinfected via chloramination during traditional wastewater treatment processes (Hunter et al 1995, Plewa et al. 2004, Richardson et al. 2007, Richardson et al. 2008, Guo et al. 2014). Iodine containing source waters are believed to be the major source of iodide to I-DBP formation in waters treated with chloramination (Plewa et al. 2004, Guo et al. 2014, Hanigan et al. 2017), with source waters containing elevated concentrations of iodide leading to generally increased formation of I-DBPs (Bischel et al. 1999, Richardson et al. 2008, Ye et al. 2013). Anthropogenic sources of I-DBPs have been linked to compounds used in medical imaging and wastewater associated with sanitation practices at dairies (Duirk et al. 2011, Hladik et al. 2016). As source water iodine is a major source of iodine in the formation of I-DBPs (Hannigan et al. 2017), developing a thorough understanding of the

controls on the natural cycling of iodine in paired surface water-groundwater systems is essential to providing accurate assessments for the potential of adverse environmental and health effects following modern wastewater treatment practices.

6. Conclusions

This work provides the first comprehensive assessment of transport and storage of iodine in temperate forested catchments in the United States. The results of our study are relevant to improving the understanding of the cycling of the radionuclide (^{129}I) in the environment, and its use as a tracer for hydrologic flow paths and also provide insights to the processing of organic matter released via weathering of organic-rich sedimentary rocks.

Our findings reveal that iodine varies seasonally with temperature, suggesting a linkage to DOC export. Future studies should incorporate analysis of organic carbon and/or organic matter characterization to supplement our current understanding of iodine cycling and its connection to the carbon cycle. Iodine may be elevated temporarily during high flow events, resulting from near-stream subsurface storage during dry periods. Under base flow conditions, concentrations of iodine measured in stream flow closely resemble that of groundwater. Additionally, our findings illustrate that iodine varies significantly ($p < 0.05$) across a catchment, suggesting influence from local hydrologic controls. In addition to atmospheric deposition of iodine in rainwater, additional controls on transport may be linked to weathering of exposed rocks. Thus, we propose that terrestrial iodine fluxes in temperate forested catchments are closely tied to surface sources and local hydrogeology. Due to the high variability of in-stream iodine concentrations resulting from seasonal enrichment (Figure 2a, Figure 5, Figure SI), episodic flushing during hydrologic events (Figure 3a-b), and association with spatial variations in geology and soil organic content (Figure

4, Figure 5) we suggest that WWTPs closely monitor source water iodine concentrations and adjust treatment practices accordingly.

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Tables.

Table 1. Hydrogeologic characteristics of East and West Branches of the Tioughnioga River for this study. Characteristics were calculated via ArcGIS Version 10.4.1. Land cover determined using the method proposed by Anderson (1976).

| Characteristic | West | East |
|---------------------------------------|-------------|-------------|
| <i>Channel Characteristics</i> | | |
| Main channel length (km) | 26.65 | 61.10 |
| Channel slope | 650.04 | 247.35 |
| Total area (km ²) | 264 | 502 |
| Land Cover (km²) | | |
| <i>Outcrops</i> | | |
| Total outcrop area | 28.50 | 32.36 |
| Black shale units | 0.12 | 8.30 |
| Soils | | |
| Inceptisol area (Fe, Al rich) | 173.43 | 406.01 |
| Histosol area (OM rich) | 3.33 | 5.14 |
| <i>Land Use</i> | | |
| Forested | 172.51 | 288.91 |
| Agriculture | 178.82 | 198.8 |
| Urban | 35.05 | 6.20 |
| Wetlands area | 7.29 | 19.25 |

Table 2. Descriptive statistics (mean, minimum, maximum, standard deviation and sample count) for iodine concentrations measured in groundwater, rain water and surface water collected in the Tioughnioga River catchment from 2012 through 2014. Surface water reflects downstream East and West Branches of the Tioughnioga River.

| | Groundwater | | Precipitation | Surface Water | |
|--------------------|-------------|------|---------------|---------------|------|
| | East | West | - | East | West |
| Mean | 2.52 | 1.55 | 0.68 | 2.31 | 2 |
| Minimum | 1.95 | 1.20 | 0.18 | 0.90 | 0.80 |
| Maximum | 3.33 | 2.28 | 1.81 | 5.42 | 3.79 |
| Standard deviation | 0.72 | 0.34 | 0.35 | 0.98 | 0.56 |
| Number of samples | 4 | 15 | 53 | 98 | 100 |

Table 3. Results of cold-water extractable iodine leaching experiments and associated bedrock characteristics. See SI Figure S2 for location of rock sample collection sites relative to Tioughnioga River catchment. * Primary rock type reflects descriptions in Dicken et al. (2005) for formations as identified by Spradlin (2015).

| Formation | Group | Primary Rock Type* | Br (µg/L) | I (µg/L) |
|-----------------------------|--------------|-----------------------------|----------------------|---------------------|
| Moscow Formation | Hamilton | Shale (sandstone interbeds) | 150 | 44 |
| Upper Skaneateles Formation | Hamilton | Shale - black shale unit | 214 | 42 |
| Upper Skaneateles Formation | Hamilton | Shale (limestone interbeds) | 172 | 16 |
| Renwick Shale Member | Genesee | Black Shale | 104 | 34 |
| (Genesee Formation) | | | 0 | 24 |
| Genesee Formation | Genesee | Shale (limestone interbeds) | 64 | 18 |
| | | Shale (siltstone interbeds) | 302 | 26 |
| Enfield & Kattel Formation | Sonyea | Shale (siltstone interbeds) | 568 | 18 |
| | | Shale (siltstone interbeds) | 96 | 8 |

Figures.

Figure 1. a) Site map of study area showing location and type of sample sites and relative relief of catchment. Solid lines indicate catchment boundaries. b) inset map showing location of study area (green) relative to Chesapeake Bay catchment (gray) and northeast United States (U.S. Department of Agriculture 2014). Solid gray lines indicate county boundaries.

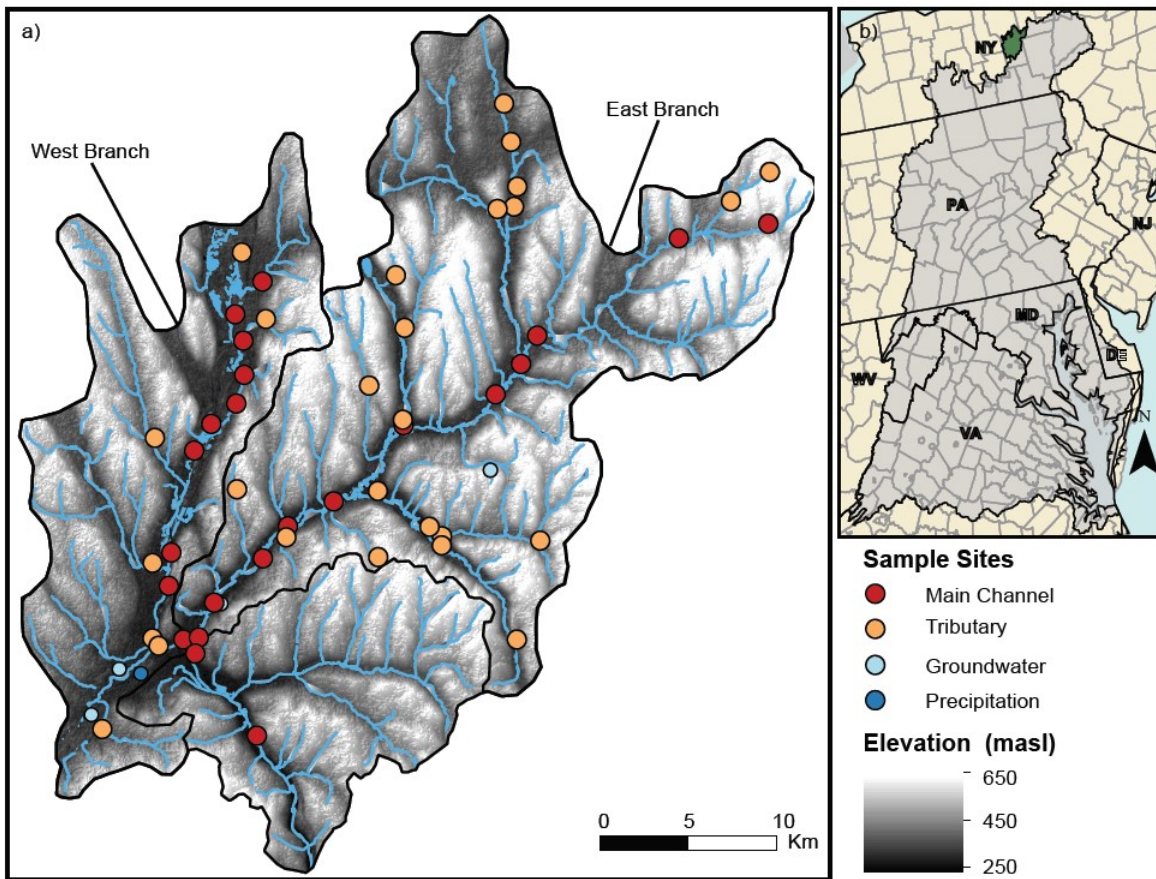


Figure 2. a) Concentrations of iodine measured weekly in East and West Branches of the Tioughnioga River, Cortland, NY. Thicker solid lines indicates smoothed data using LOESS smoothing. b) daily precipitation, temperature, and soil moisture deficit (SMD) for the Tioughnioga River catchment and streamflow measured at the main Branch of the Tioughnioga River (Main Branch Tioughnioga River at Cortland, USGS Gauging Station ID 01509000). Daily SMD was calculated for the catchment using the Precipitation, Evapotranspiration and Runoff Simulator for Solute Transport (PERSiST) model for a previous study (Gutchess et al. 2017).

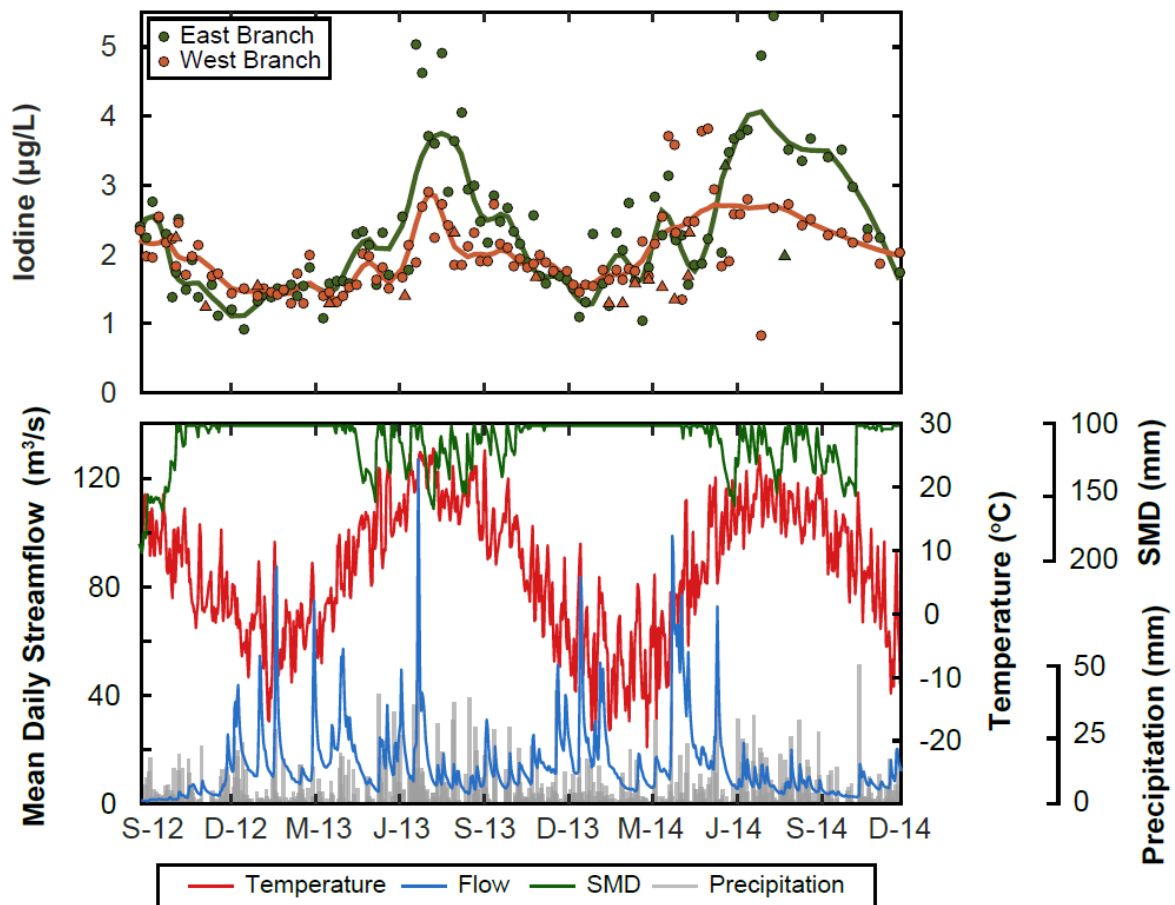


Figure 3. Log concentration-discharge (CQ) plots for downstream reaches of a) East Branch and b) West Branch Tioughnioga River samples collected from September 2012 through November 2014. Discharge values were determined using the INtegrated CAtchment model in a previous study (Gutchess et al. 2017). All trends were significant at $\alpha=0.05$ significance level ($p < 0.05$), with the exclusion of iodine ($p = 0.262$ and 0.264 , for East and West Branch, respectively).

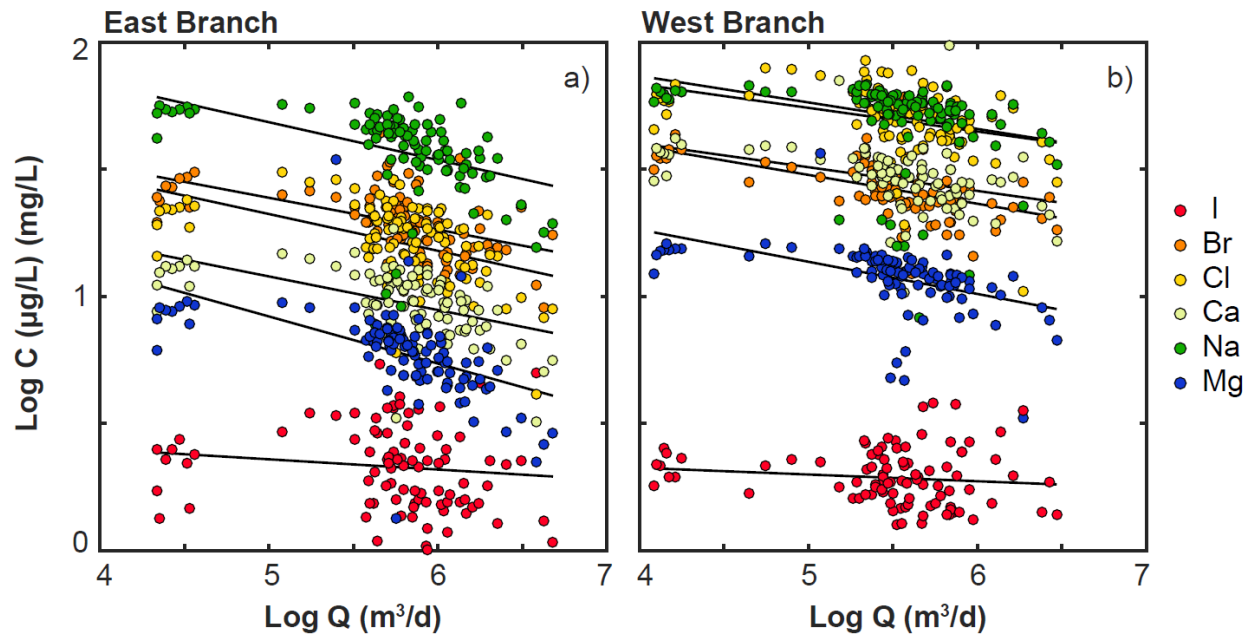


Figure 4. Concentrations of iodine and corresponding a) stream temperature measured in East and West Branches of the Tioughnioga River and b) average monthly (solid lines) concentrations of iodine measured in East and West Branches from 2012-2016. Colored bands indicate 95% confidence intervals for monthly concentration data.

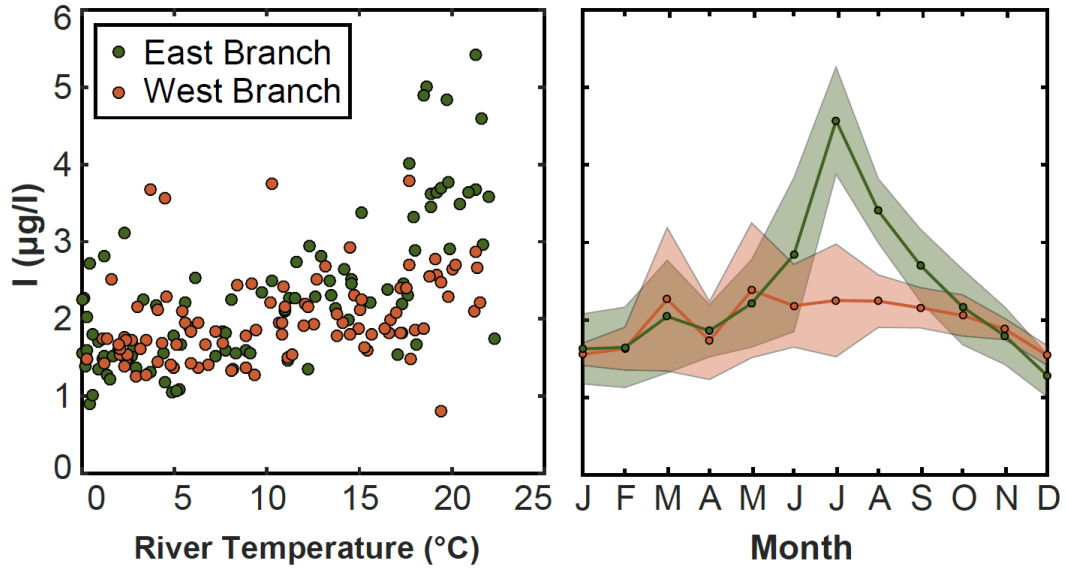


Figure 5. Event-based dissolved ion concentrations of iodine and chloride measured in East (a-b) and West (c-d) branches of the Tioughnioga River during snowmelt (a, c, and e) and rainfall (b, d, and f) events. Corresponding streamflow measured at USGS stream gauge (e-f).

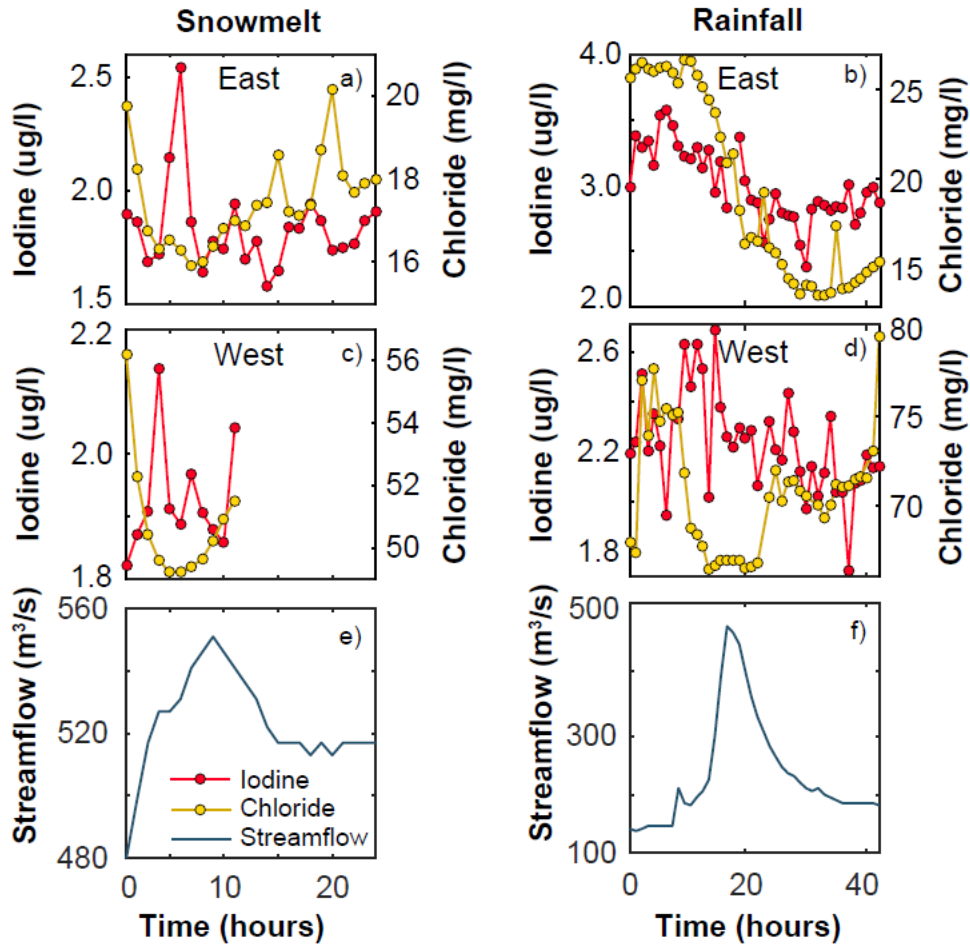


Figure 6. Site-map of Tioughnioga River catchment in this study and corresponding average iodine concentrations measured monthly during downstream sampling from May through November 2016. Locations of bedrock outcrops and emergent and forested wetlands are shown. Corresponding downstream distances labelled accordingly.

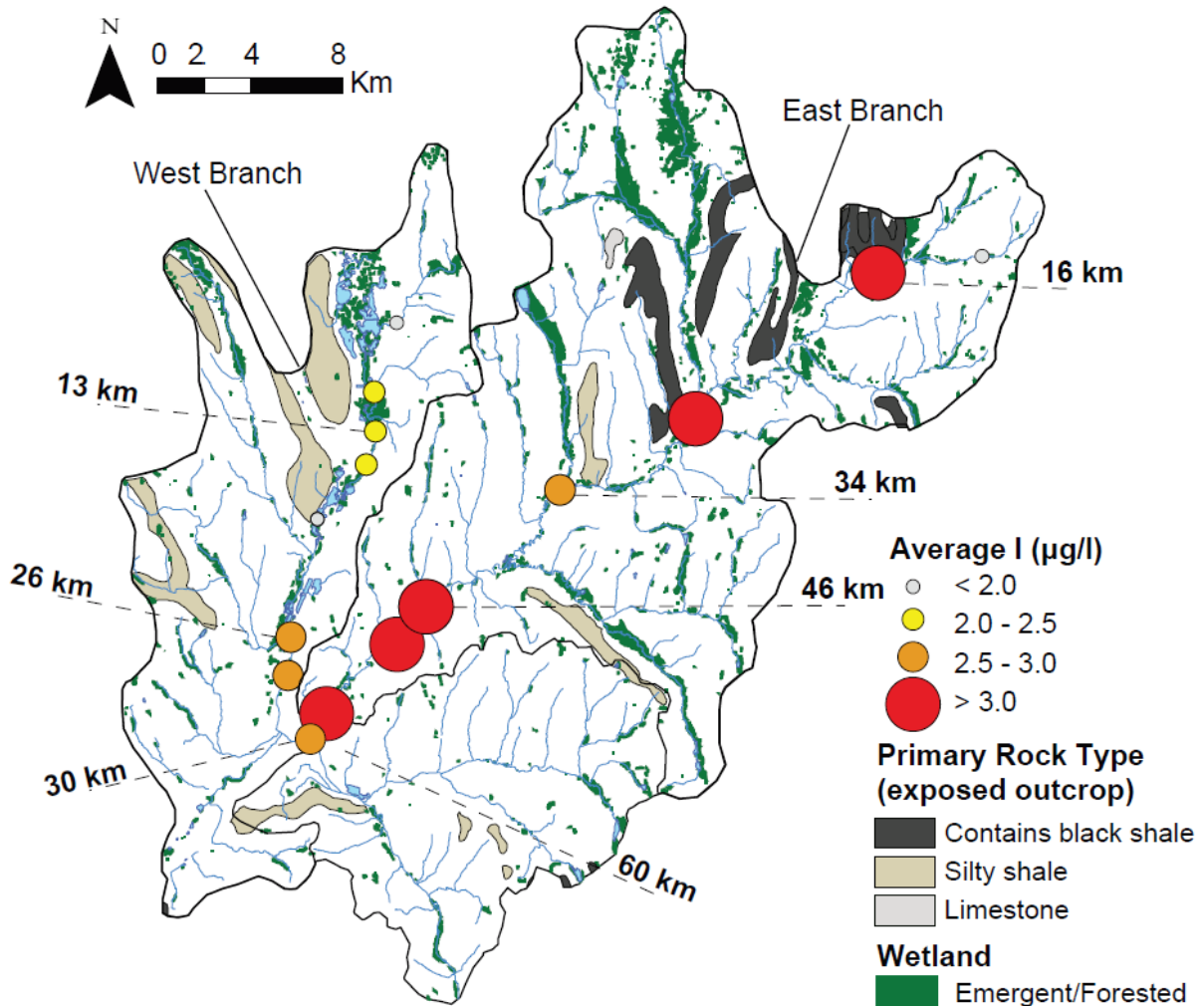


Figure 7. Iodine concentrations in upstream reaches of East (top) and West (bottom) Branches of the Tioughnioga River from May 2016 through October 2016.

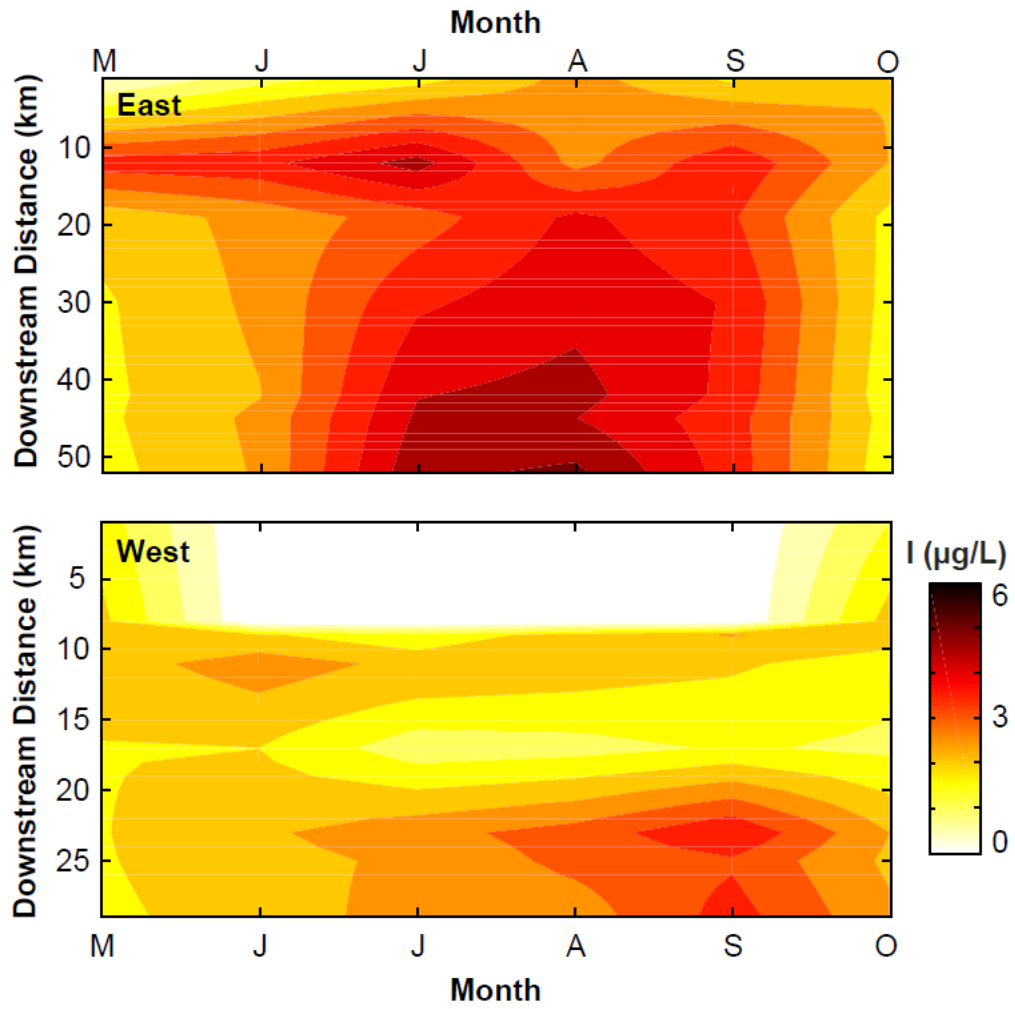
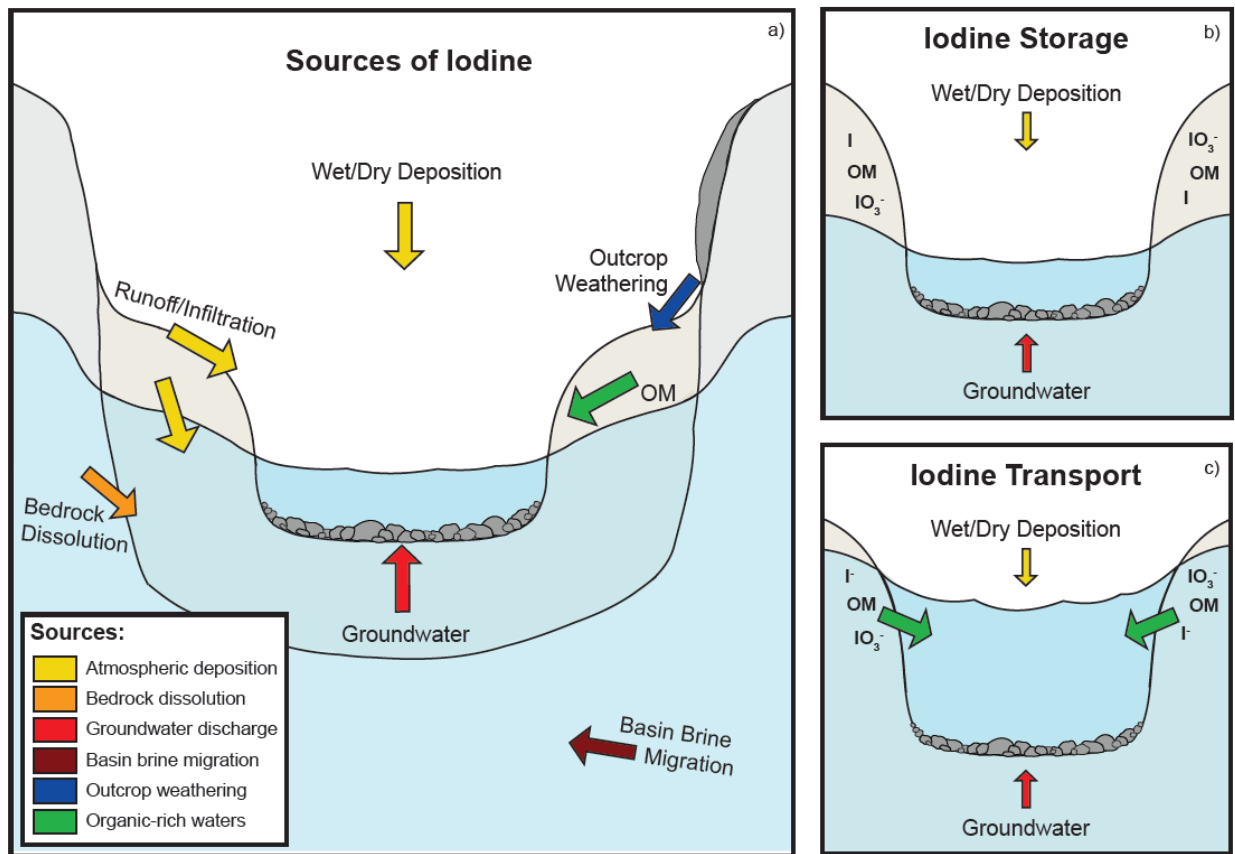


Figure 8. Conceptual model of terrestrial aquatic iodine cycle showing a) sources of iodine to surface water, soils water, and shallow groundwater, b) iodine storage and hydrogeologic controls on in-stream iodine dynamics during low flow conditions, and c) subsequent release of iodine from soil pore waters during high flow events and relative contributions of atmospheric and groundwater sources. Shaded areas represent bedrock hills (gray), valley aquifer (beige), and saturated zone (blue).



Supporting Information.

Figure S1. Time series for major ions measured in this study in East and West Branches of the Tioughnioga River (a and b, respectively). Concentrations of Br are reported in ug/L. All other ion concentrations are in mg/L.

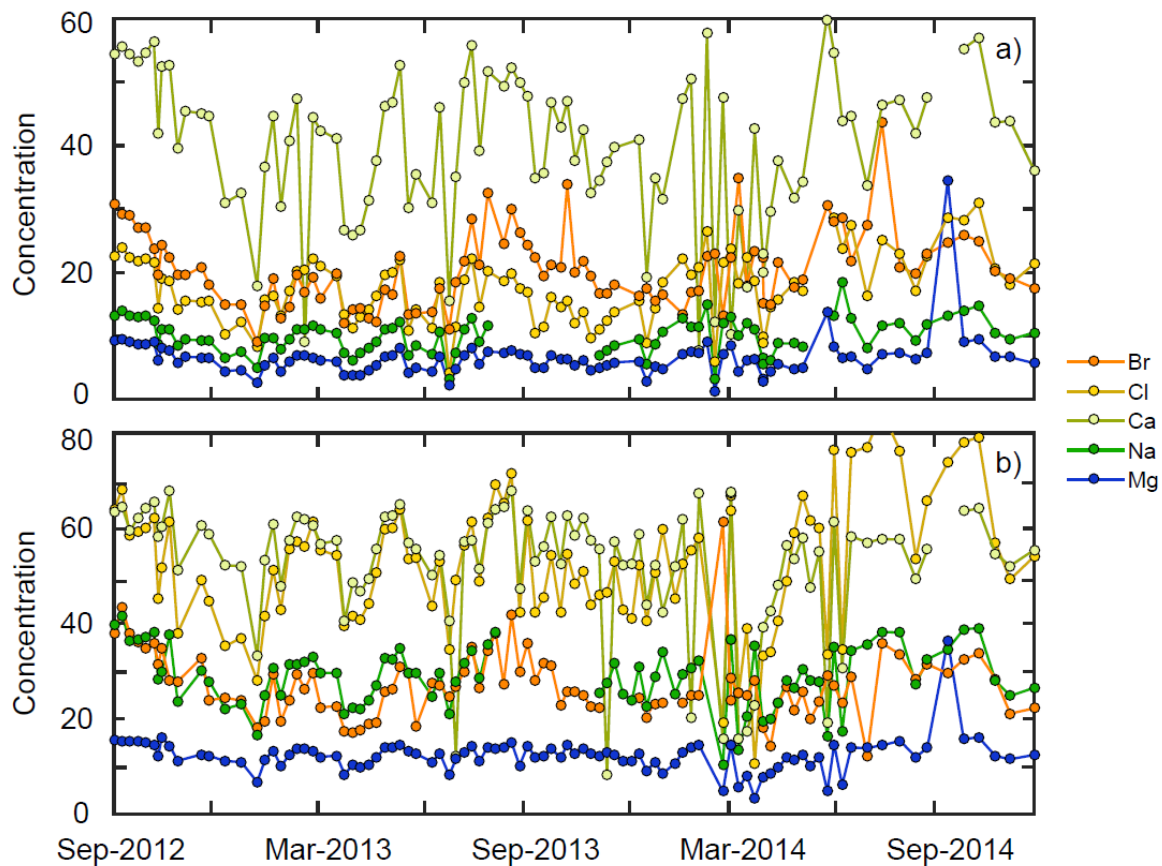
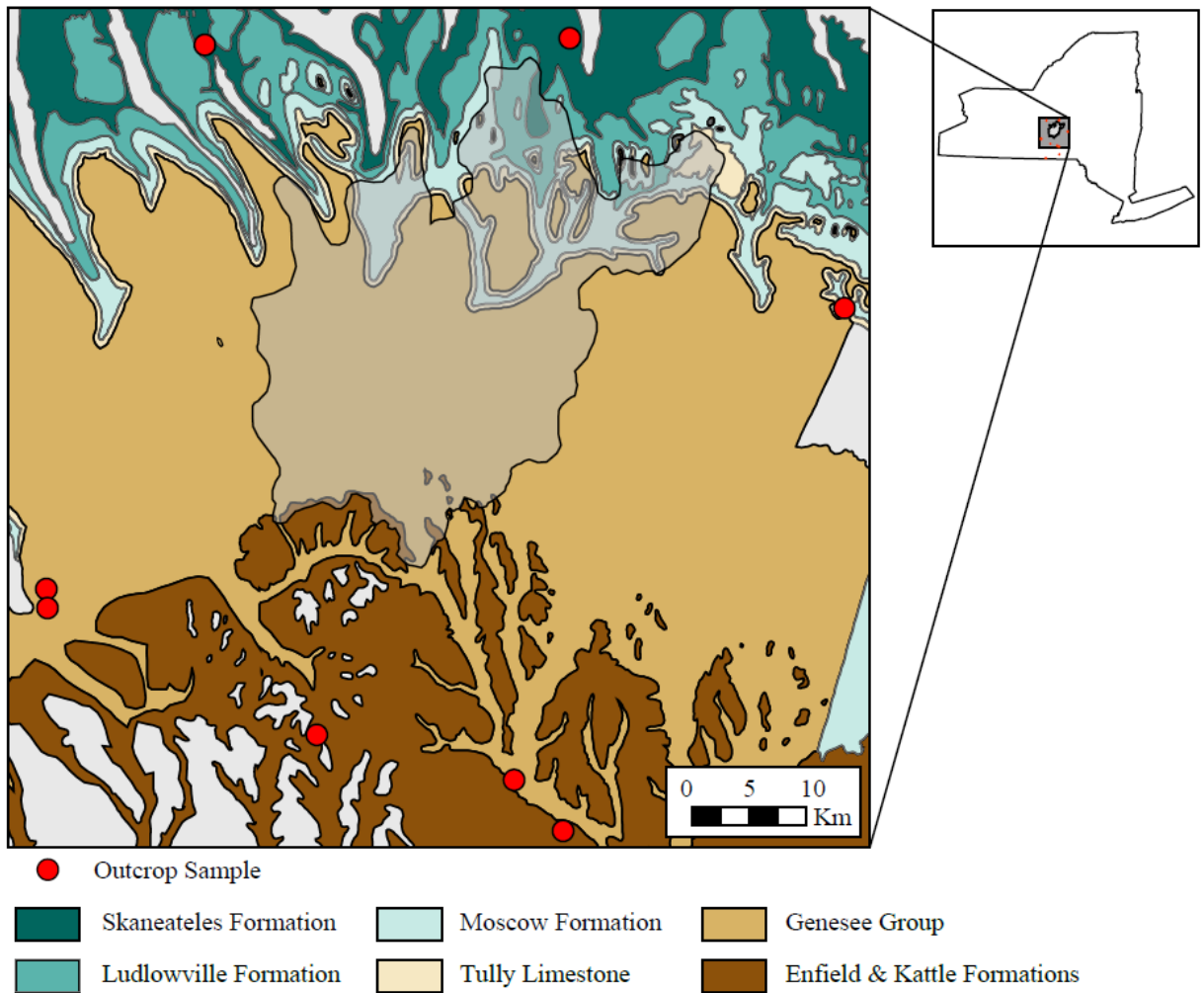


Figure S2. Geologic map of the area surrounding the Tioughnioga River watershed (shaded gray outline) in which bedrock samples were collected from exposed outcrops (Spradlin 2015). Units signify uppermost geologic unit (Dicken et al., 2005). Inset map shows location of geologic map area relative to New York State. Note: 8 of 9 collected samples are shown, refer to Table 3 for coordinates of samples.



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trihalomethanes during UV / chloramination with iodate as the iodine source. *Water
Research*, 98, 199–205. <http://doi.org/10.1016/j.watres.2016.04.012f>

Biographical Data

Kristina M. Gutchess

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Education

2018, Ph.D., Earth Sciences, Certificate in University Teaching, Syracuse University, Syracuse, NY

Dissertation: Evaluating the effects of hydrogeologic processes on the fate of salinity and halogens in headwater catchments

2013, B.S., Geology, State University of New York at Cortland, Cortland, NY

2011, A.A.S. Adolescent Education, Tompkins Cortland Community College, Dryden, NY

Research Grants & Proposals

Evaluating hydrogeologic controls on the transport of iodine in headwater catchments, Geological Society of America Graduate Student Research Grant, January 2017, PI: Kristina Gutchess, Co-PI: Zunli Lu Award: \$2,500

Tracing the influence of weather patterns on runoff and de-icing salt: Campus Adaptations to Climate Disruption, Syracuse University Campus as a Laboratory for Sustainability Call for Proposals, January 2017 – January 2018, PI: Kristina Gutchess, Co-PI: Zunli Lu, Award: \$6,530

Understanding the dynamics of terrestrial aquatic iodine, Syracuse University Department of Earth Sciences Graduate Research Funding, May 2016, PI: Kristina Gutchess, Co-PI: Zunli Lu, Award: \$2,500

Research Interests

My research interests focus on fundamental questions regarding solute transport and the movement of water in catchments. I am particularly interested in understanding how both natural and anthropogenic processes can impact water quality in paired surface water – groundwater systems. To do so, I utilize geochemical tracers combined with stochastic modeling approaches to elucidate solute transport pathways and surface water – groundwater interactions. My research is highly interdisciplinary and has a strong computational component to complement direct field observations.

Research Skills

Technical: YSI ProPlus multiparameter water quality probe, current meter, Solinst level logger, Lietz automatic level, Dionex ICS-1100 and ICS-2100 Ion Chromatograph, Picarro L2130-i Water Isotope Analyzer, High-resolution surface water sampling with Teledyne ISCO 6712 full-size portable sampler, groundwater sampling with Geotech Geopump™ Peristaltic Pumps, LTC Levellogger Edge installation, management, and monitoring, piezometer installation, and stream flow measurements via current meter

Analytical: Analysis on Bruker Aurora ICP-MS, Dionex ICS-1100 and ICS-2100 Ion Chromatograph, Picarro L2130-i Water Isotope Analyzer, Horiba Aqualog Benchtop Fluorometer, Phoenix 8000 Carbon Analyzer

Software: ArcGIS, Chromeleon 7, Microsoft Word, Excel, PowerPoint, Adobe Illustrator, Photoshop, InDesign, Level Logger, PHREEQC, R, Matlab, INCA, SAS, AQTESOLV, Geochemist's Workbench, TopoDrive

Pedagogical Preparation

Lecturer:

Natural Hazards and Disasters, State University of New York at Cortland, 2016

1 section / 50 students / Lecture / non-majors

Course focus on the interaction between present and past societies and natural hazards. Special emphasis on current events and/or recent natural disasters. Topics range from the physical operation and impacts of these phenomena to how humans evaluate and respond to these threats.

Physical Geology Laboratory, State University of New York at Cortland, 2016

2 sections / 25 students each / Laboratory / majors and non-majors / Field Trips

Laboratory sections of introductory physical geology course. Topics include: Topographic and Geologic maps, mineral and rock identification, introductory hydrogeologic principles.

Teaching Assistant:

Oceanography, Syracuse University, 2014, 2015

Hydrogeology, State University of New York at Cortland, 2012, 2013

Teaching Assistant Coordinator:

Climate Change, Past and Present, Syracuse University, 2014, 2018

Honors & Awards

Director's Citation of Excellence Award, EMPOWER NRT Program, Syracuse University, 2017

Department of Earth Sciences Student Publication Award, Syracuse University, 2016

Newton Chute Award for Professional Promise in the Earth Sciences, Syracuse University, 2016

3rd Place Student Poster Competition Syracuse Center of Excellence Symposium, 2016

Syracuse University Water Fellow, 2015 – 2016

W. Maxwell Hawkins Award for the Most Outstanding Senior, SUNY Cortland, 2013

Merit Scholarship, SUNY Cortland, 2013

Dean's List, SUNY Cortland, 2013

W. Graham Heaslip Award for the Most Outstanding Junior, SUNY Cortland, 2012

Merit Scholarship, SUNY Cortland, 2012

Dean's List, SUNY Cortland, 2012

Merit Scholarship, SUNY Cortland, 2011

Dean's List, SUNY Cortland, 2011

Dean's List, Tompkins-Cortland Community College, 2011

Dean's List Tompkins-Cortland Community College, 2010

Publications

Gutchess, Kristina, Jin, Li, Ledesma, José L. J., Crossman, Jill, Kelleher, Christa, Ledford, Sarah, Lautz, Laura, Lu, Zunli. 2018. Modeling future nitrogen dynamics in Chesapeake Bay Headwaters: INCA insights. In prep, Target Journal: Water Resources Research.

Gutchess, Kristina, Moran, Jean, Zeng, Teng, Lu, Wanyi, Jin, Li, Levy, Zeno, Lautz, Laura, Lu, Zunli. 2018. Shale weathering controls on in-stream iodine dynamics in headwater catchments. In prep, Target Journal: Environmental Science & Technology.

Lautz, Laura, McCay, Deanna, Driscoll, Charles, Glas, Robin, Gutchess, Kristina, Johnson, Alexander, Millard, Geoffrey. 2018. Designing student-centered STEM graduate programs for a multitude of career pathways. EoS, in review.

Lu, Wanyi, Ridgwell, Andy, Thomas, Ellen, Hardisty, Dalton S., Luo, Genming, Algeo, Thomas J., Saltzman, Matthew R., Gill, Benjamin C., Shen, Yanan, Ling, Hong-Fei, Edwards, Cole T., Whalen, Michael T., Zhou, Xiaoli, Gutchess, Kristina, Jin, Li, Rickaby, Rosalind E. M., Jenkyns, Hugh C., Lyons, Timothy W., Lenton, Timothy M., Kump, Lee, Lu, Zunli. 2018. Late inception of a resiliently oxygenated upper ocean. Science, in review.

Gutchess, Kristina, Jin, Li, Ledesma, José L. J., Crossman, Jill, Kelleher, Christa, Lautz, Laura, Lu, Zunli. 2017. Long-term climatic and anthropogenic impact on stream water salinity in New York State: INCA simulations offer cautious optimism. Environmental Science & Technology, 52 (3), pp 1339–1347.

Lu, Zunli, Hoogakker, Babette A.A., Hillenbrand, Claus-Dieter, Zhou, Xiaoli, Thomas, Ellen, Gutchess, Kristina M., Lu, Wanyi, Jones, Luke, and Rickaby, Rosalind E. M. 2016. Oxygen depletion recorded in upper waters of the glacial Southern Ocean. Nature Communications, 7.

Gutchess, Kristina, Jin, Li, Lautz, Laura, Shaw, Stephen B., Zhou, Xiaoli, Lu, Zunli. 2016. Chloride sources in urban and rural headwater catchments, central New York. *Science of the Total Environment*, 565, 462-472.

Conference Abstracts

Invited Oral Presentations

Gutchess, Kristina, Jin, Li, Crossman, Jill, Kelleher, Christa, Lautz, Laura K., Lu, Zunli. 2018. A case of cautious optimism: INCA simulations suggest climate change drives future reductions in surface water chloride in New York State. Canadian Geophysical Union Annual Meeting, Niagara Falls, CA.

Gutchess, Kristina, Jin, Li, Crossman, Jill, Kelleher, Christa, Lautz, Laura K., Lu, Zunli. 2017. Back to the Future: INCA Simulations Suggest Climate May Drive Decreases in Future Stream Salinity in New York State. 17th annual Syracuse Center of Excellence for Environmental and Energy Systems Symposium.

Oral Presentations

Gutchess, Kristina, Jin, Li, Crossman, Jill, Kelleher, Christa, Lautz, Laura K., Lu, Zunli. 2017. Long-term INCA simulations favor climatic over anthropogenic impacts on a reduction of stream water salinity in New York State. *Geological Society of America Abstracts with Programs*, 49(6). doi: 10.1130/abs/2017AM-301266

Gutchess, Kristina, Garvin, Shannon, Jin, Li, Lu, Wanyi, Levy, Zeno, Lautz, Laura, Lu, Zunli. 2017. Evaluating the Natural Transport Pathways of Iodine in Headwater Catchments.

Geological Society of America Abstracts with Programs, 49(2). doi: 10.1130/abs/2017NE-291044

Gutchess, Kristina, Jin, Li, Lautz, Laura, Zhou, Xiaoli, Lu, Zunli. 2016. Detection of Appalachian Basin Brines in the Tioughnioga River, central New York. Geological Society of America Abstracts with Programs, 48(2). doi: 10.1130/abs/2016NE-272803

Gutchess, Kristina, Jin, Li, Lautz, Laura, Zhou, Xiaoli, Lu, Zunli. 2015. Using halogens and discriminant analysis to distinguish among sources of salinity in the Tioughnioga River, Central New York. Geological Society of America Abstracts with Programs, 47(7), p.55.

Gutchess, Kristina, Jin, Li, Zhou, Xiaoli, Lu, Zunli. 2015. Identifying sources of salinity in the Tioughnioga River using halogens as a sensitive tracer. Geological Society of America Abstracts with Programs, 47(3), p.66.

Jin, Li, Gutchess, Kristina, Whitehead, Paul, Findlay, Stuart, Siegel, Don. 2013. How much more can we take? – Road salt as an emerging contaminant in streams. Geological Society of America Abstracts with Programs, 45(1), p.132.

Poster Presentations

Gutchess, Kristina, Jin, Li, Kelleher, Christa, Lautz, Ledford, Sarah, Laura K., Lu, Zunli. 2018. Modeling future nitrogen dynamics in Chesapeake Bay headwaters. Geological Society of America Abstracts with Programs, 50(2).

May, Amanda, Smith, Rebecca, Parody, Brittany, Gutchess, Kristina, Jin, Li. 2018.

Hydrogeologic controls on spatial and temporal variations in groundwater chemistry in a glacial-

aquifer system in Cortland, New York. Geological Society of America Abstracts with Programs, 50(2).

Gutchess, Kristina, Lu, Wanyi., Lu, Zunli. 2017. Potential shale weathering controls on surface water iodine dynamics in headwater catchments. American Geophysical Fall Meeting, New Orleans, Louisiana.

Garvin, Shannon, Gutchess, Kristina, Lu, Wanyi, Kappel, William M., Lautz, Laura K., Lu, Zunli. 2017. Groundwater iodine across New York State: Potential linkage to methane? Geological Society of America Abstracts with Programs, 49(6). doi: 10.1130/abs/2017AM-306257

Jin, Li, Gutchess, Kristina, Lu, Zunli. 2017. Modeling Nitrogen Dynamics in the Tioughnioga River, New York. Geological Society of America Abstracts with Programs, 49(2). doi: 10.1130/abs/2017NE-291527

Gutchess, Kristina, Garvin, Shannon R., Jin, Li, Zhou, Xiaoli, Lu, Zunli. 2016. Increased salinity in central New York headwater catchments associated with long-term road salt application. Syracuse University Center of Excellence Symposium, Syracuse, New York.

Gutchess, Kristina, Fisher, Eric, Hall, Jared, Jin, Li. 2014. Integrating research into teaching: an 11-week chemical analysis of east and west branches of the Tioughnioga River, New York. Geological Society of America Abstracts with Programs, 47(3), p.66.

Gutchess, Kristina, Nowalk, Collin, Jin, Li, Whitlock, Amy, June, Jamie, Barclay, David. 2013. Understanding spatial and temporal patterns of water chemistry in Otter Creek, New York. Geological Society of America Abstracts with Programs, 45(1), p.121.

Nowalk, Collin, Gutchess, Kristina, Barclay, David, Whitlock, J.R. June, L. Jin. 2013.
Fingerprinting of water sources to Otter Creek in Cortland County, New York, using in situ
measurement. Geological Society of America Abstracts with Programs, 45(1), p.122.

Workshops & Training

2017

Workshop with WRR Publishing Process, AGU Fall Meeting, New Orleans, LA

Multivariate Statistical Analysis in Water Quality, NWQMC Webinar Series

What's Your Problem, What's Your Point? Publishing Workshop, GSA Annual Meeting,
Seattle, WA

2016

EMPOWER Peer Mentoring Workshop, Syracuse University

AAAS Science Communication Workshop, Syracuse University

Reactive Transport Modeling with The Geochemist's Workbench, Temple University

Excellence in Communicating Science: Scientific Writing Workshop, Syracuse University

Service

Department and University

M.S. Thesis co-advising: Shannon Garvin, M.S. 2018 (expected), 2016 – 2018

Department of Earth Sciences Graduate Student Faculty Representative, 2017 – 2018

Environmental Challenge Science Fair Judge, SUNY ESF, 2017

Geology Graduate Seminar Coordinator, 2015 – 2016

High School outreach activities, 2015

Professional community

Peer Reviewer for: Science of the Total Environment, Water Resources Research

Memberships

American Geophysical Union (AGU)

Canadian Geophysical Union (CGU)

Education Model Program on Water-Energy Research Program (Syracuse University)

Future Professoriate Program (Syracuse University)

The Geological Society of America (GSA)

Geology Club (State University of New York at Cortland / Syracuse University)

Graduate Student Organization (Syracuse University)

Phi Theta Kappa Honor Society

United University Professions (UUP) Union

Women in Science and Engineering (Syracuse University)