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

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HIGHLIGHTS

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

GRAPHICAL ABSTRACT
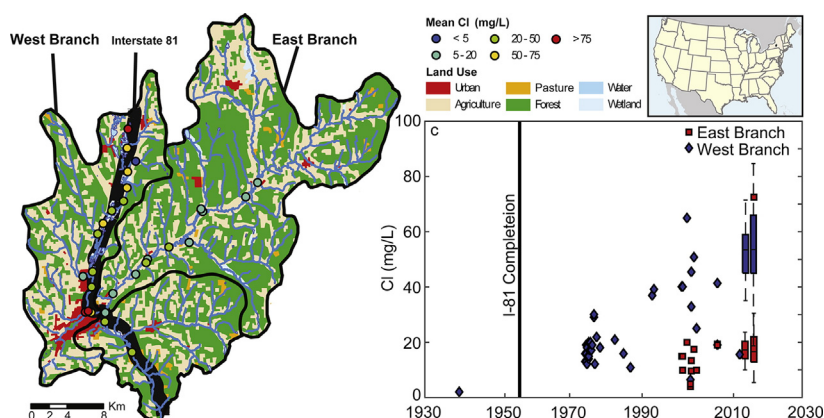
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ABSTRACT

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.

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1. Introduction

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

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

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

The primary objective of our study is to characterize the sources of salinity in two branches, with contrasting land use, of the Tioughnioga River, in central New York. Previous studies have attributed the increase in Cl in the Tioughnioga River, as well as groundwater in central New York, to the application of road salts, agricultural runoff from dairy farming, and effluent discharge from septic systems (Buller, 1978; Buller et al., 1978; Waller and Finch, 1982; Miller et al., 1998). However, prior work in the study area does not attempt to distinguish the impacts of road salt from different sources of salinity. We use both Cl/Br ratios and LDA as two independent means to differentiate among sources. We apply a previously developed LDA modeling approach (Lautz et al., 2014) to identify the most probable sources of salinity from ABB, road salts, and animal waste. In addition, we also examine annual and decadal scale temporal variations in longitudinal Cl concentration profiles, which sheds light on spatial distribution of Cl sources and residence time of Cl in the watershed.

2. Background

2.1. Study area

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

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

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

Table 1
Concentrations of Cl, Br, and ratios of Cl/Br in various sources of salinity. First line for each source of salinity includes the range of concentration values. The second line contains the mean value for each (Adapted from Lautz et al., 2014).

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