

Stream chloride concentrations as a function of land use: a comparison of an agricultural watershed to an urban agricultural watershed

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Abstract The concentration of chloride (Cl^-) in streams in northern regions has increased as a result of applications of deicers. This study focused on quantifying the relationship between land use and stream Cl^- concentrations. The study area comprises two adjacent watersheds in central Illinois, with similar geology and climate but different land uses (agricultural and urban). GIS analysis delineated watershed land use and calculated road surface areas. Stream water samples were collected and analyzed for anionic composition. During the winter months, streams dominated with urban land use experienced a 20-fold increase in Cl^- concentrations (range between 36 and 1350 mg L^{-1}); Cl^- concentrations in agricultural dominated streams also increased, but the increase was smaller (3X) and concentrations remained low (between 11 and 58 mg L^{-1}). As road salts are not the sole source of Cl^- in a stream, Cl^- and bromide (Br^-) mass ratios (Cl/Br) and Cl^- and sodium (Na) molar ratios ($[\text{Cl}]/[\text{Na}]$) were used to identify potential sources of Cl^- . The ratios indicate urbanized watersheds were impacted by road salts; agricultural watersheds ratios indicate other anthropogenic sources. A nonlinear relationship between urban land use and stream Cl^- concentrations indicates urban land use as low as 23% results in elevated Cl^- concentrations (greater than 150 mg L^{-1}) in stream waters.

Keywords GIS · Land use · Road salts · Chloride · Deicers

Introduction

Chloride (Cl^-) is highly soluble and does not biodegrade, volatilize, precipitate, or significantly adsorb onto mineral surfaces (Environment Canada 2001; Meriano et al. 2009). Thus, Cl^- is mobile and easily transported within surface water or infiltrated into the subsurface. Natural sources of Cl^- include atmospheric deposition, rock weathering, and basin brines (Gardner and Royer 2010; Kelly et al. 2008; Panno et al. 2006); the contribution of these sources is a function of geologic materials and geographic location. Humans have altered the natural cycle of Cl^- in systems through changes associated with urbanization (Kelly et al. 2008; Ramakrishna and Viraraghavan 2005; Schlesinger 2004) and agriculture (Gardner and Royer 2010; Kelly 2008). During winter months in northern latitudes, deicers, primarily sodium chloride (NaCl) or potassium chloride (KCl), are often applied to impervious surfaces such as roads, walkways, and parking lots to keep these areas clear of snow and ice (Environment Canada 2001; Locat and Gélinas 1989; Marsalek 2003). In watersheds where deicers have been employed, natural inputs contribute less than 1% to the total Cl^- load (Meriano et al. 2009; Novotny et al. 2009; Pajak et al. 2015). In rural watersheds, Cl^- inputs from agriculture and septic sewer systems only contribute an additional 1–3% to the total Cl^- load (David et al. 2016; Kelly et al. 2008). The remaining load is attributed to deicers, which as a non-point source of Cl^- accounts for 87–97% of the Cl^- entering a system (Kelly et al. 2008; Meriano et al. 2009). In urban watersheds, wastewater treatment plants contribute more Cl^- than road salts, but roads salts still contribute over 35% (Novotny et al. 2009).

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The application of deicers for removal of ice and snow from roads is essential to wintertime road maintenance in countries of high latitude where snowfall is significant (Joutti et al. 2003). Road salt application has saved countless lives but not without a cost (Keummel 1992; Salt Institute 2013). The Federal Highway Administration identifies the following potential impacts of road salts: (1) contamination of drinking water supplies; (2) corrosion of automobiles; (3) corrosion of bridges and other infrastructure; (4) damage to vegetation within 15.2 m (50 ft.) of roadside; (5) temporary reduction in soil microbes, followed by summer recovery; (6) sensitivity of various deciduous trees; (7) attraction of deer to salts on roadways, increasing the risk of accidents; (8) stratification of small lakes, hindering seasonal turnover; (9) secondary components (3–5% of road salt composition) include nitrogen, phosphorus, and metals in concentrations exceeding those in natural waters (Shoemaker et al. 2002). The use of road deicers on soils and groundwater has raised many concerns among environmentalists, scientists, and regulatory bodies (Joutti et al. 2003). In surface waters, the impact of deicing salts can change the density gradient in lakes, deplete oxygen, reduce diversity, and shift population species (Allert et al. 2012; Thunqvist 2003).

The level of contamination to local hydrology from road salts is controlled by many factors. Site-specific characteristics, like topography, hydrogeology, road density, and climate, determine the fate of deicers (Foos 2003). Annual rock salt use for road deicing in the US increased from 163,000 tons in 1940 to over 23 million tons in 2005 (Jackson and Jobbágy 2005), with most of the deicer applied to roads in northeastern and Midwestern states.

Once applied, excess road salt is transported to ditches and near-road soils through snow plowing, vehicle spray, wind, and snowmelt runoff (Labadia and Buttle 1996). Between 35 and 55% of the applied salt will be transported via runoff to surface water bodies (Church and Friesz 1993). The direct runoff often has Cl^- concentrations in excess of 1000 mg L^{-1} (Kelly et al. 2009), which elevates Cl^- concentrations in streams during the winter. In the northeastern USA, surface waters have Cl^- concentrations that are up to 25% of the concentration of seawater (Kaushal et al. 2005). Following runoff, streams exhibit acute, 20–30 fold increases in Cl^- concentrations (Bäckström et al. 2003; Godwin et al. 2003; Howard and Beck 1993; Koryak et al. 2001; Ruth 2003; Scott 1976). The long-term use of deicers has had a chronic impact on streams (Corsi et al. 2015) and lakes (Dugan et al. 2017), with reported Cl^- concentrations increasing 1.5 mg L^{-1} per year (Bowen and Hinton 1998; Warren and Zimmerman 1994). Urban areas are not the only areas experiencing

elevated concentrations of Cl^- ; baseline Cl^- concentrations in rural watersheds with low density of roadways in Maryland, New York, and New Hampshire have increased over the past 30 years as a result of deicing applications (Kaushal et al. 2005). However, Peterson and Benning (2013) found that Cl^- concentrations in streams were negatively related with agricultural land use and positively linked to urban land use.

With only 35–55% of the applied deicers transported out of a system by surface water, the remaining 45–65% accumulates in the soils and waters of the vadose zone (Environment Canada 2001; Foos 2003; Howard and Haynes 1993; Labadia and Buttle 1996; Löfgren 2001; Novotny et al. 2009; Ruth 2003). Infiltration prolongs the presence of the Cl^- in the hydrologic system (Lax and Peterson 2009; Mikkelsen et al. 1997). Once in groundwater, Cl^- can persist for many years (Watson et al. 2002), and even if deicing applications stopped, it would be decades before the Cl^- concentrations returned to pre-1960 levels in shallow groundwater (Howard and Beck 1993).

Land-use- Cl^- concentration relationships are not new. Herlihy et al. (1998) concluded that land use/land cover correlated to stream Cl^- concentrations. While they suggested that Cl^- concentrations can serve as a proxy for anthropogenic influences, the mathematical relationship was not directly reported. Poor et al. (2008) reported a relationship between surface elevation and Cl^- concentration but suggested that within agricultural settings, Cl^- are not an appropriate proxy for human influences. Cunningham et al. (2009) reported a linear relationship between percentage of impervious surface, parking lots, roadways, buildings, etc. that restrict infiltration, to Cl^- concentrations in streams. Their work was limited to an upper percentage of impervious cover of 34%.

This study approaches concerns of Cl^- through an investigation of two neighboring watersheds with differing land use (urban and agriculture), developing a relationship between urban land use (up to 94%) and Cl^- concentration in streams (Herlihy et al. 1998; Poor et al. 2008). The two adjacent watersheds have similar geology and climate but distinctive land use: one urbanized in the headwaters and transitions into agriculture and the second watershed is primarily agricultural. A geographic information system (GIS) was used to subdivide two watersheds into several sub-watersheds and for each, the land use totals and percentages (agricultural, urban, and road areas) were calculated. Average Cl^- concentrations for biweekly collected samples were compared to the respective sub-watershed land-use characteristics. Results allowed for the creation of a regression model to estimate average in-stream Cl^- concentrations as function of land use.

Materials and methods

The study site

The study site incorporates the Upper Kickapoo Creek watershed (UKCW), and the Upper Little Kickapoo Creek watershed (ULKCW) in the northeastern part of the Sangamon River Basin in central Illinois (Fig. 1). The watershed boundaries, delineated using digital

topographical maps, represent only the headwater portions of the entire Kickapoo Creek and Little Kickapoo Creek watersheds within McLean County. The region has a temperate, humid, and continental climate. Historical climate data, from 1971 to 2000, provide an average annual precipitation of 95.1 cm, an average annual snowfall of 55.6 cm, and mean annual temperature of 10.4 °C.

A perennial fourth-order stream, Kickapoo Creek (KC) is a tributary of Salt Creek, which in turn is a tributary of

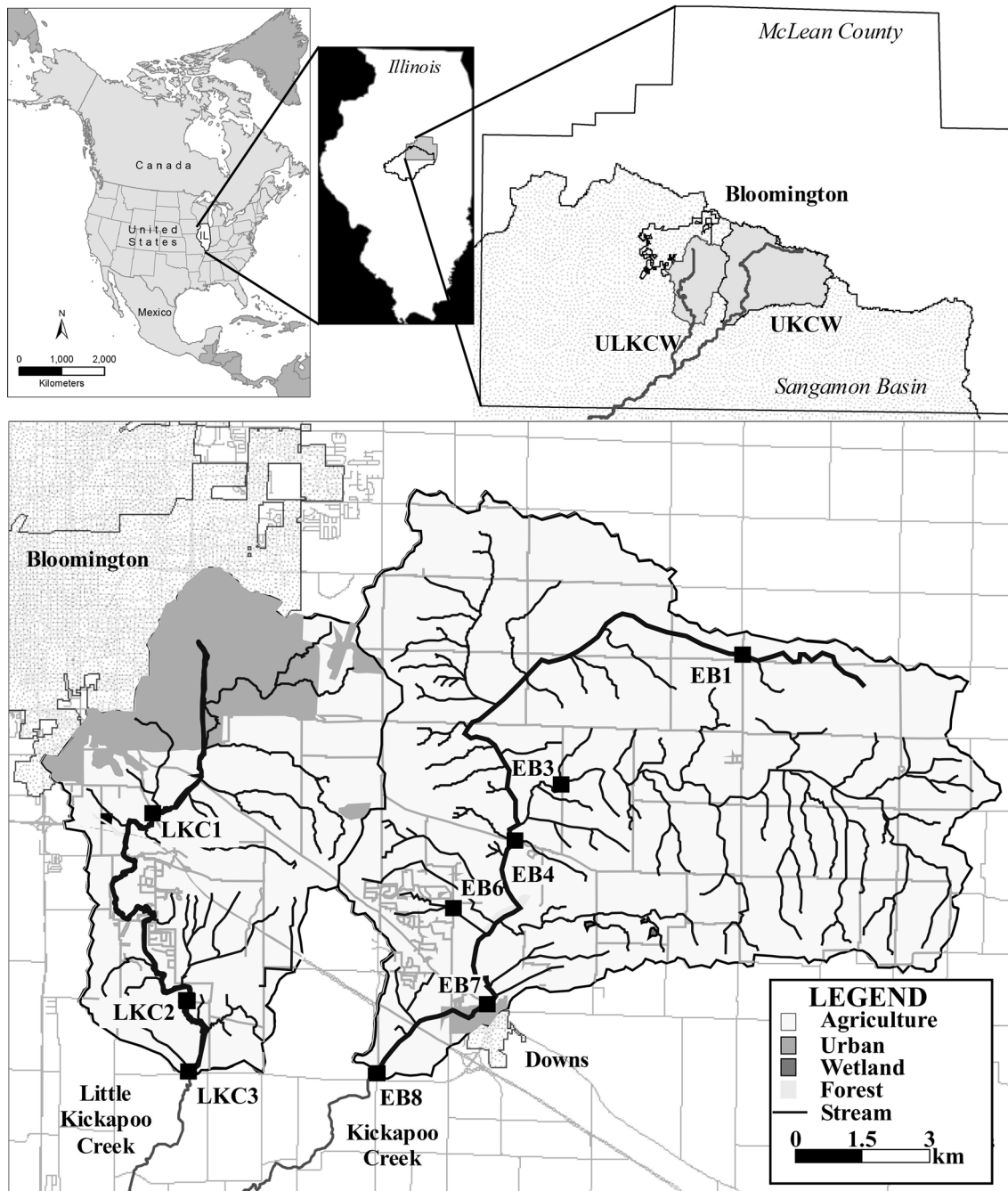


Fig. 1 Map of the study area showing the UKCW, the ULKCW and sampling locations within McLean County, Illinois

the Sangamon River. The Sangamon River discharges to the Illinois River, which discharges to the Mississippi River. Little Kickapoo Creek (LKC) is a tributary of KC. The two watersheds are adjacent to each other and differ considerably in terms of size and urbanization levels but have similar geology and climate.

Quaternary materials in McLean County consist of a sequence of tills, sands, and gravels generated from three major glaciation events (Beach and Peterson 2013; Peterson and Benning 2013; Peterson and Sickbert 2006; Van der Hoven et al. 2008). Thickness of the Quaternary deposits vary from around 15 m on the northeast part of the county to over 122 m found within large bedrock valleys in the northwest, southwest, and southeast portions of the county. Exposed material near the surface in the Bloomington/Normal area consists mainly of clay-rich tills, with very little or no sand or gravel. Glacial outwash deposits range in grain size from sand to cobble (Soller et al. 1998). Panno et al. (2006) report groundwater background Cl^- concentrations ranging between < 1 and 15 mg L^{-1} for glacially deposited sand and gravel aquifers in northern Illinois. Panno et al. (2006) stated that 90% of farmers in Illinois apply potassium chloride (KCl) to the croplands at an annual rate of 111 kg/acre.

The Upper Little Kickapoo Creek watershed

The ULKC starts in southeast Bloomington and runs south (Fig. 1). Although 76% of the watershed, as a whole, is used for agriculture, the headwaters originate in a 13 km^2 sub-watershed (represented by sampling site LKC1) dominated by urban land use (92.9%) (Table 1). After the stream leaves Bloomington, the stream flows through a low-density urban setting (LKC2) and then into agricultural areas (LKC3). The entire ULKCW study area covers a total area of approximately 56 km^2 , of which 1.7 km^2 is road surface, representing 3% of the watershed area. Less

than 1% of the watershed is composed of forested or wetlands land uses; removal of forest and wetlands is consistent with drainage modifications that have been conducted in the area (Mattingly et al. 1993).

The Upper Kickapoo Creek watershed

The UKCW covers an area of approximately 120 km^2 . The headwaters of KC are located east, southeast of Bloomington, Illinois in a rural setting (Fig. 1). The stream runs southwest toward the village of Downs for approximately 19.2 km. The UKCW is 96.6% (116.2 km^2) agricultural (row-crop, mostly corn and soybeans) and 3.4% (3.8 km^2) urban. Within the watershed, there are 17.4 km of highways and 178.8 km of smaller county and secondary roads. All the roads cover an area of 1.4 km^2 , representing 1.1% of the total watershed area. As with the LKC watershed, the land use comprised of forest and wetlands is less than 1%.

Downs, the largest community within the UKCW, with a population of 760, is located approximately 15 km southeast of the city of Bloomington. Residents of Downs and smaller, but growing, suburban areas in UKCW are on private septic systems. Sampling site EB6 is located at the discharge of a man-made reservoir that drains one of the subdivisions.

Field data

Water collection

Water samples from four stations along the KC (EB1, EB4, EB7, and EB8) and two stations from KC tributaries (EB3 and EB6) were collected every 2 weeks from December 2006 to July 2007. Three stations along LKC (LKC1, LKC2, and LKC3) were sampled during the same period following the same schedule. KC had a thick ice cap between January 21 and February 22, 2007, which made

Table 1 Land-use percentages and summary of chemical composition, chloride (Cl^-) and sodium (Na^+), for selected sub-watersheds

Station	Land use		Cl^- (mg L^{-1})			Na^- (mg L^{-1})		
	Agricultural (%)	Urban (%)	Mean	Max	Min	Mean	Max	Min
EB1	98.5	1.5	20.7	25.1	11.0	20.7	25.1	11.0
EB3	98.3	1.7	25.0	31.1	16.5	25.0	31.1	16.5
EB4	98.2	1.8	28.0	38.0	23.7	28.0	38.0	23.7
EB7	97.6	2.4	34.5	56.1	27.7	34.5	56.1	27.7
EB6	16.1	83.9	156.8	206.3	104.6	87.6	131.3	69.4
EB8	96.6	3.4	37.6	58.1	27.3	37.6	58.1	27.3
Agricultural tile			63.5	95.2	36.2	18.9	27.9	18.1
LKC1	7.1	93.9	258	1344	36.2	141.9	372.8	79.8
LKC2	71.5	28.5	104.1	1301	58.5	104.1	230.7	63.9
LKC3	76.2	23.8	87.0	787	46.6	85.6	168.1	46.6

daily sampling impossible during that period. During sampling, pH, specific conductance, and temperature were measured in the field. Samples were collected in acid-washed polyethylene bottles following a triple rinse with the stream water. Bottles were kept in a cooler for the duration of the sampling. In the laboratory, samples were split into two smaller samples, one used for major anion analysis and the other for major cation analysis. The anion splits were stored at 4 °C and analyzed within 2 days of sampling. Cation splits were filtered using a 0.45-micron Millipore membrane, acidified with nitric acid, and stored at 4 °C until analysis.

Laboratory analysis

Concentrations of major anions (NO_3^- , Cl^- , F^- , and SO_4^{2-}) were determined through ion chromatography using a Dionex DX-120 ion chromatograph (IC). Concentrations of NO_3^- are reported as nitrate as nitrogen ($\text{NO}_3\text{-N}$). Major cation concentrations (Ca^{2+} , Mg^{2+} , and Na^+) were determined through inductively coupled plasma emission spectrometry (ICP). Duplicates were used for quality control of chemical analyses. Bromide concentrations were below the method detection limit of the IC and analyzed by neutron activation analysis (NAA) at the University of Wisconsin Nuclear Reactor Lab. Cost constraints limited the number of bromide samples analyzed, with the EB4 and EB7 samples not analyzed. Cl^- sources have characteristic conservative ionic ratios that can be employed to differentiate sources of Cl^- (Davis et al. 1998; Panno et al. 2006). Plotting $[\text{Cl}]/[\text{Na}]$ versus Cl^- or Cl^- versus Cl/Br ratios can help identify the influence of road salts and other sources of Cl^- .

Data analysis

Digital elevation models (DEM) (30 by 30 m cells) were used to define watershed boundaries. Due to reduced accuracy of the raster in the low relief of the area, streams had to be digitized manually using USGS DLGs (digital line graphs) and aerial photos. The data from the 2000 LU/LC (land use/land cover) with a resolution of 30 m by 30 m show the following classes: agricultural, urban, wetland, forested, and others (cloud cover, bare land, water surfaces, etc.). Land use was reclassified as urban (including areas related to buffered roads) or agricultural (including wetlands, forested, and others, which accounted for less than 1%). Street data from topologically integrated geographic encoding and referencing (TIGER) shape files were used to determine road density for each sub-watershed as well as area of roads for each sub-watershed. All digital data analysis was done in ArcGIS 9.2.

Results

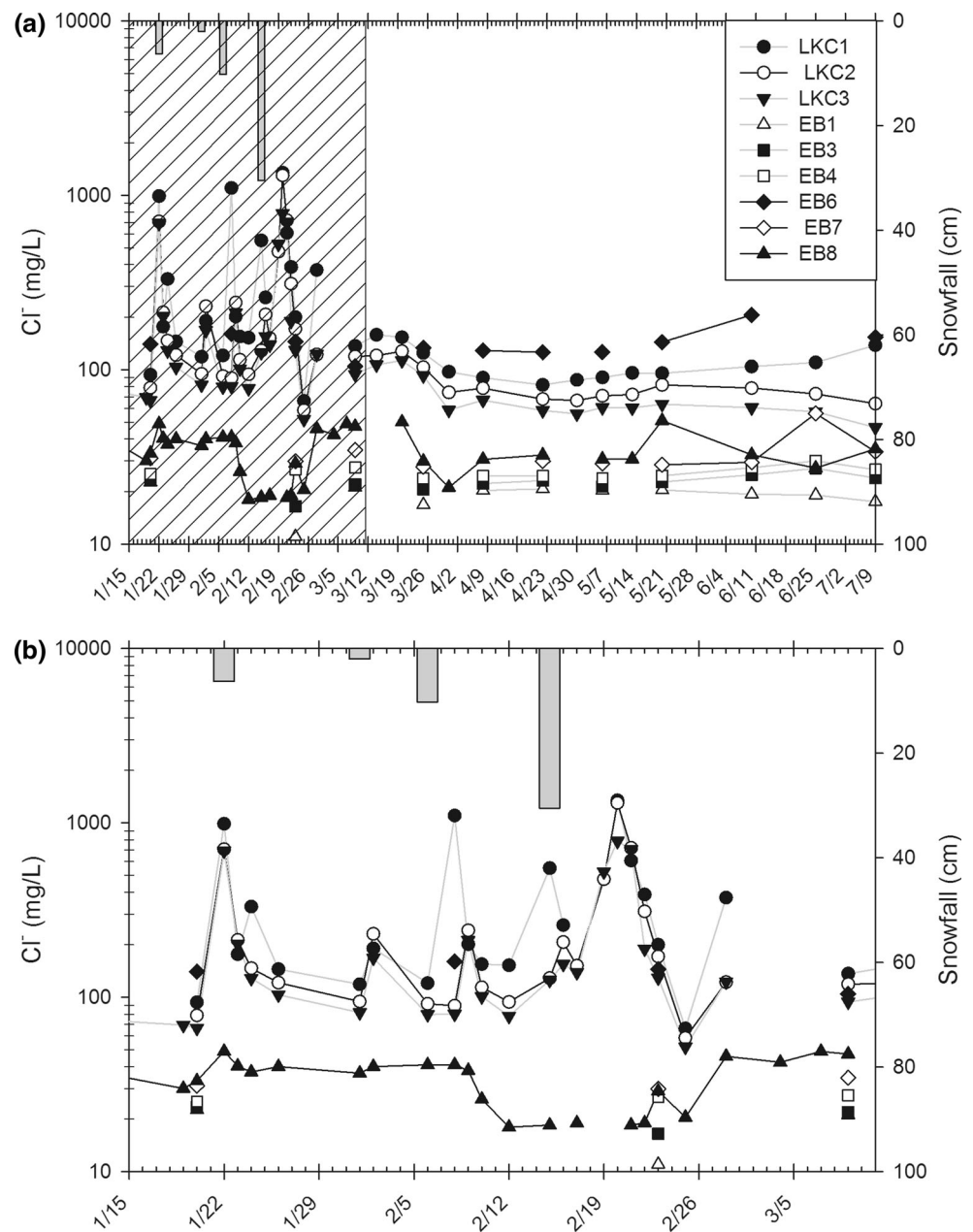
Chemistry

Cl^- is present in waters from all of the sampling locations, representing the different land uses (Fig. 2). Stream waters collected within agricultural areas show Cl^- concentrations between 11 and 58 mg L^{-1} (Table 1), while areas with greater urban land use (EB6 and the LKCs) show much higher Cl^- values, between 36 and 1344 mg L^{-1} . The range of concentrations seen in agricultural streams is much smaller than the urbanized streams. Mean Cl^- concentrations for agricultural watersheds are lower than 40 mg L^{-1} , while the urban watersheds had mean Cl^- concentrations greater than 80 mg L^{-1} . The peak Cl^- concentrations measured in the most urbanized stream segments are above 800 mg L^{-1} for a short duration, around 4 days for the LKC, which is due to the influx of salts following the application of road salts and snow melting events.

As the proportion of urban land use decreases traversing downstream on LKC, the concentration of Cl^- decreases due to the dilution from agricultural waters with significantly smaller concentrations of Cl^- . LKC1 represents the most urbanized area and shows the larger variability of Cl^- concentrations (mean of 258, maximum of 1344 and minimum of 66 mg L^{-1}). Unlike other urbanized areas (Novotny et al. 2009), the LKC locations receive no input from wastewater treatment plants. Located 10.6 km downstream of LKC1 and having a higher area devoted to agriculture (from 7 to 76% agricultural), samples collected at LKC3 had less variability in terms of Cl^- concentrations (mean of 87, maximum of 787 and minimum of 47 mg L^{-1}). The lower concentrations imply the dilution of Cl^- -rich waters originating in urban areas by waters from less urban areas. As LKC is a gaining stream, dilution of Cl^- concentrations in waters at downgradient locations is expected and is consistent with reporting by Peterson and Benning (2013).

Waters from the sampling locations exhibit variation in Cl^- concentration following snowfall events (Fig. 1 and 2), especially the LKC locations, which had the most influence from road salts. With the exception of EB6, the EB locations represent agricultural land use (Figs. 2 and 3). The EB waters have low and constant Cl^- concentrations as compared to the urban stream during and after salting events. Deicing application occurred during the first hours of snowfall. Following the snowfall events, the LKC location experiences magnitude increases in Cl^- , indicating acute spikes associated with surface runoff. In the days following the storm, Cl^- concentrations decrease due to the stream dilution from the snowmelt runoff. During March,

Fig. 2 **a** Time plot illustrating the large variation of Cl^- due to the use of road salts on the urban stream (LKC3) and no impact on the agricultural stream (KC EB8), and **b** an enlargement of the winter variation in stream Cl^- concentrations



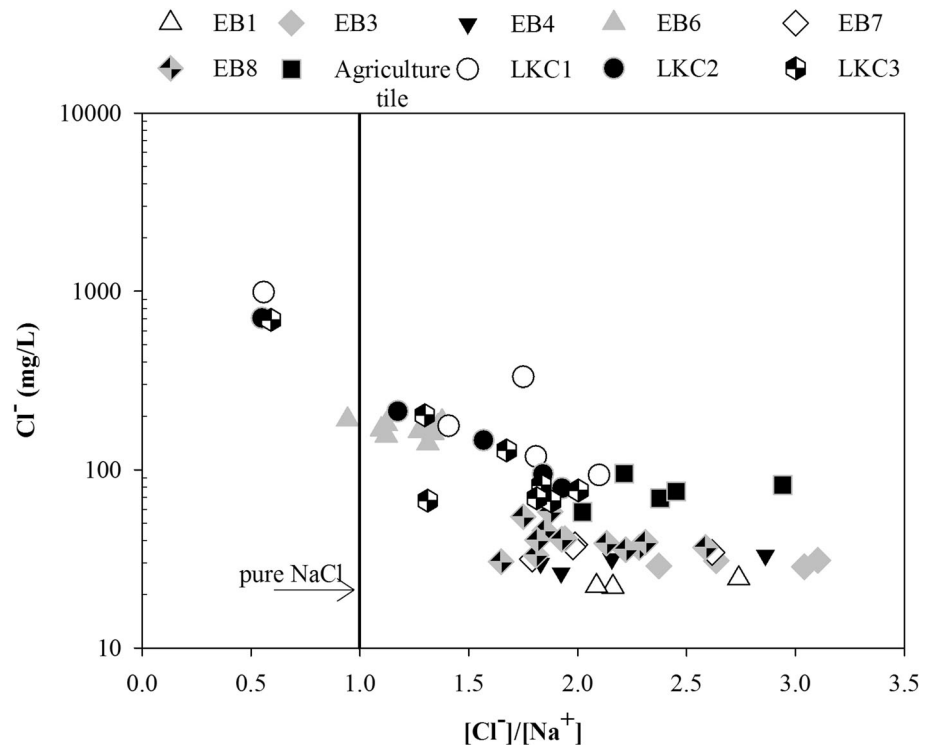
values were close to mean values and by early April, they had dropped considerably and remained low for the rest of the sampling period year. EB6, representing a suburban area with septic systems, has a more constant concentration between 105 and 206 mg L^{-1} .

Cl^- and Na^+

The relationship between Cl^- and Na^+ concentrations can be used to identify if deicers are a Cl^- source. In a plot of $[\text{Cl}]/[\text{Na}]$ versus Cl^- concentrations (Fig. 3), samples plotting closer to the $[\text{Cl}]/[\text{Na}]$ value of 1 (molar ratio for NaCl) with high Cl^- concentrations characterize road salts.

Within Fig. 3, sample locations produce different clusters. The tile drain samples possess $[\text{Cl}]/[\text{Na}]$ ratios between 2.2 and 2.9 with Cl^- concentrations (between 36 and 95 mg L^{-1}) above background levels, a signature consistent with KCl fertilizers. Waters from EB1 (98.5% agricultural) and EB3 (98.3% agricultural) have the same range of $[\text{Cl}]/[\text{Na}]$ as the agricultural tile drain, but lower concentrations of Cl^- as a result of dilution. Downgradient agricultural samples in KC (EB7, and EB8) show maximum Cl^- concentration of 58 mg L^{-1} and $[\text{Cl}]/[\text{Na}]$ ratio above 1.6. While still representing an agricultural area, the higher Cl^- concentrations, as compared to EB1 and EB3, are reflective of the input from EB6 and from the village of

Fig. 3 [Cl⁻]/[Na⁺] ratios compared to Cl⁻ concentration for selected sampling locations. The vertical line presents a [Cl⁻]/[Na⁺] ratio of 1



Downs. The lowest [Cl⁻]/[Na⁺] ratios correspond with the highest Cl⁻ concentrations for LKC1 (0.6, 989 mg L⁻¹), LKC2 (0.6, 706 mg L⁻¹) and LKC3 (0.6, 691 mg L⁻¹) were taken immediately following the snowstorm in January 21, 2007. Note that samples from EB6 (83.9% urban, direct runoff from a subdivision) show smaller range of both variables with Cl⁻ concentrations between 105 and 206 mg L⁻¹ and [Cl⁻]/[Na⁺] ratios between 0.9 and 1.4.

Samples from station of the LKC locations clearly reveal some influence from road salts. As Cl⁻ concentrations increase the [Cl⁻]/[Na⁺] ratios decrease, suggesting the added Cl⁻ is associated with deicers. During base flow, the chemical signatures for the LKC locations are similar to waters for KC, reflecting the influence of agriculture in LKC. While waters from EB1, EB3, and the tile have elevated Cl⁻ concentrations, the [Cl⁻]/[Na⁺] ratios are higher and not representative of road salts. The Upper LKC watershed samples show a large range of Cl⁻ concentrations and [Cl⁻]/[Na⁺] ratios, which indicates the control of road salts due to [Cl⁻]/[Na⁺] ratios being closer to 1. The large range of Cl⁻ concentrations is a reflection of the acute impact of snowmelt runoff. For sample site EB6, the influence of water softener salts explains the low [Cl⁻]/[Na⁺] ratios.

Cl/Br ratios

The relationship between Cl⁻ concentrations and Cl/Br ratios varies spatially and temporally (Fig. 4 and Table 2).

The labeled areas (Fig. 4) are taken from Panno et al. (2006) and indicate the potential sources of Cl⁻. The general trend depicted in Fig. 4 indicates that locations with higher Cl⁻ concentrations exhibit higher Cl/Br ratios. During the winter, the Cl/Br ratios were elevated compared to sampling events in April and June. For the agricultural samples EB8 and EB3, the variability in Cl/Br ratio as well as the Cl⁻ concentrations is quite small and they plot on the same general region (field tile) as EB1. The variability of the data for the urban stream is quite large, and both the ratios and concentrations increase during winter and decrease afterward to lower values closer to the agricultural stream samples. Panno et al. (2006) reported Cl/Br ratios above 13,000 represented deicing applications, while Davis et al. (1998) suggest that septic effluent is represented with a Cl/Br ratio in the range between 300 and 600. While the Cl/Br ratios for EB6 are above 600, the lack of response to deicing events supports that the source is septic effluent from the subdivision.

Land use versus Cl⁻

Land-use percentages for each sub-watershed were plotted against mean Cl⁻ concentrations for all stations within the Upper KC watershed and LKC watershed (Fig. 5). Stations included on the model represent those located in the main streams and the tributaries. Initially, small changes in percent urbanization raise the average Cl⁻ concentration rapidly. However, above 10% urbanization, average Cl⁻

Fig. 4 Plot of Cl/Br ratios and Cl^- concentration (mg L^{-1}) showing the variability of Cl/Br ratios for stations during winter, spring, and summer. The categorized areas in the graph are defined by Panno et al. (2006) and indicate the most likely source of Cl^- to the streams. Note samples from EB4 and EB7 were not analyzed for bromide

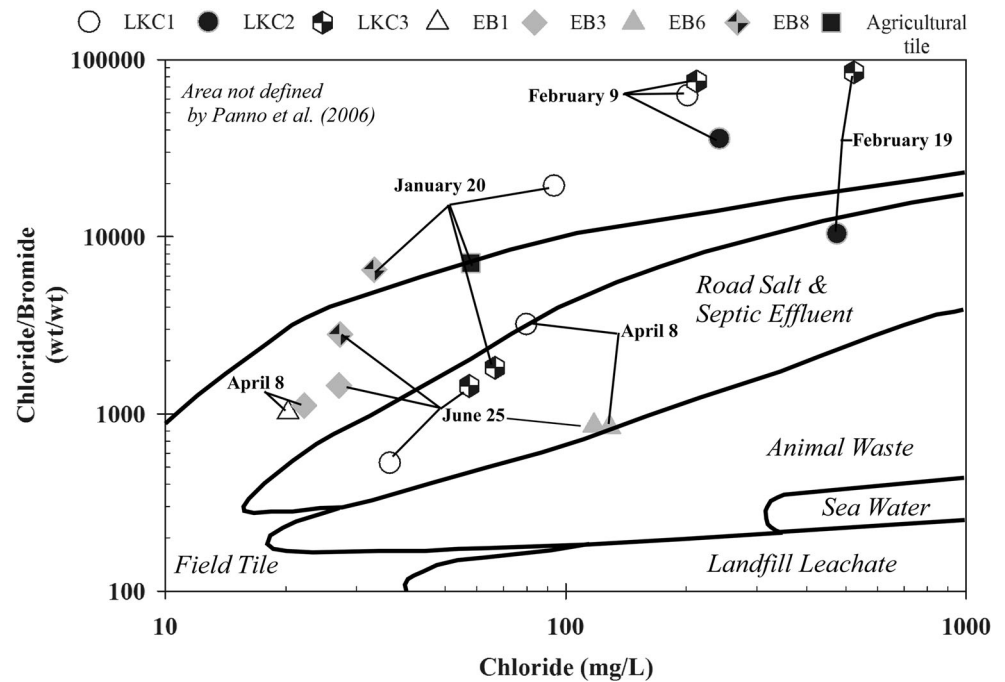


Table 2 Cl^- ($\mu\text{g L}^{-1}$) and Br^- ($\mu\text{g L}^{-1}$) concentrations and Cl/Br ratios

Station	Date	Cl, $\mu\text{g L}^{-1}$ (IC)	Br, $\mu\text{g L}^{-1}$ (NAA)	Cl/Br
LKC1	1/20/2007	93,470	4.8	19,412
	2/9/2007	201,400	3.2	62,849
	4/8/2007	79,750	24.8	3212
	6/25/2007	36,380	68.8	529
LKC2	2/9/2007	241,905	6.8	35,813
	2/19/2007	475,800	45.7	10,406
LKC3	1/20/2007	66,607	36.5	1822
	2/9/2007	212,193	2.8	75,351
	2/19/2007	524,670	6.2	84,763
	6/25/2007	57,430	39.9	1438
EB1	4/8/2007	20,269	20.0	1015
EB3	4/8/2007	22,220	20.0	1112
	6/25/2007	27,152	18.7	1450
EB6	4/8/2007	128,740	153.0	841
	6/25/2007	117,635	137.1	858
EB8	1/20/2007	33,240	5.1	6501
	6/25/2007	27,330	9.7	2808
Tile	1/20/2007	57,970	8.2	7095

concentration increases are much smaller per percent increase in urbanization. The best-fit line (R^2 of 0.90) for the data is represented with the logarithmic function:

$$\text{Cl}^- \text{ concentration} = 50.9 \times \ln(\text{Urban}\%) - 5.6 \quad (1)$$

where Urban% is the percentage of land classified as urban. Although the downstream sample locations are not

independent of the upstream locations, the use of downstream locations in the regression analysis is consistent with that used by Cunningham et al. (2009). However, to evaluate how the removal of the locations influenced by the upstream locations controls the nonlinear relationship, a second regression analysis was conducted in which only the two headwater locations, EB1 and LKC1, and the two tributaries, EB3 and EB6, were employed in the analysis. These sample locations are independent of each other and include the end members of urban land use. Subsequently, the resulting best-fit equation, Eq. (2), generated a curve similar to Eq. (1), but with a slightly poorer R^2 of 0.87.

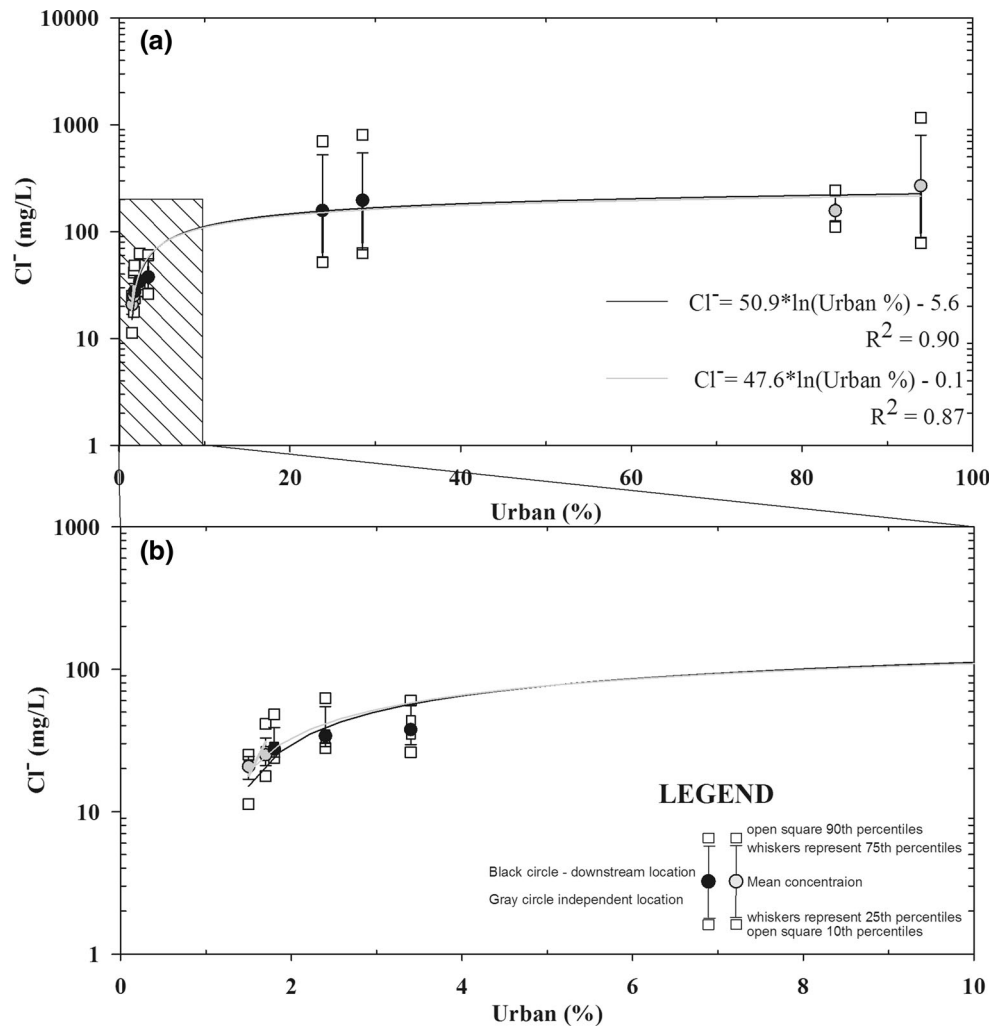
$$\text{Cl}^- \text{ concentration} = 47.6 \times \ln(\text{Urban}\%) - 0.1 \quad (2)$$

Unlike the linear relationship reported by Cunningham et al. (2009), the best-fit relationship for these watersheds is logarithmic. Both Eqs. (1) and (2) produce steep increases in Cl^- concentrations with small increases in urban land use up to approximately 3%. By an urban land use of 5%, the change in Cl^- concentrations associated with an increase in urban land use has stabilized at a lower rate of increase.

Discussion

All sub-watersheds show elevated Cl^- concentrations as compared to the background Cl^- concentrations of 15 mg L^{-1} reported by Panno et al. (2006), indicating negative effects associated with anthropogenic activities even in areas with only 1.5% designated as urban land use.

Fig. 5 **a** Relationship between urban land use and measured Cl^- concentrations. The black line is the curve generated using all of the sample locations; the gray line is the curve generated using only the four independent locations. **b** Enlargement of the cluster of points for urbanization less than 10%, hatched area in **a**. Circles represent mean, whiskers represent 25th and 75th percentiles, open squares represent 10th and 90th percentiles



The negative impact of modified land use is not new (Herlihy et al. 1998; Peterson and Benning 2013); Cunningham et al. (2009) reported increases in Cl^- concentrations in watersheds with less than 5% impervious surface, noting a linear relationship for impervious land surface up to 40% and concentrations of 200 mg L^{-1} . However, the impacts associated with urban land use less than 10% suggest that headwaters are a critical area of concern. The location of urban areas within the watershed is another controlling factor of the Cl^- concentrations seen in the watershed streams. Streams that have the headwaters in urban areas (LKC1) have a much higher Cl^- concentration than those streams fed by agricultural drained waters (EB1). Although agricultural areas do contribute to total Cl^- in streams, fertilizer and septic effluent sources (Peterson and Benning 2013), the lower Cl^- concentration agricultural waters dilute the impact from urban-originated surface waters. Not all suburban areas indicate road salt impact. At EB6, the $[\text{Cl}]/[\text{Na}]$ ratios suggest a halite source, but Cl/Br ratios are consistent with septic effluent, indicating water softeners contribute the halite.

The results of the regression analyses show that the average estimated Cl^- concentrations for a small, urban watershed with no wastewater input (LKC1) is an order of magnitude larger than an agricultural watershed (EB1). Because the sources and proportions of Cl^- for these two land uses are quite different, urban streams that run into agricultural areas have concentrations diluted over distance to concentrations seen in agricultural areas. Streams that drain areas comprised by at least 96% agriculture show anthropogenic Cl^- input, as illustrated by elevated Cl^- concentrations, but do not possess signatures indicating the Cl^- is from road salt application. The areas with greater urban land use exhibit impact from road salts, high peak, short duration pulses with $[\text{Cl}]/[\text{Na}]$ and Cl/Br ratios consistent with halite. While this work did not examine the role of drainage area, the property cannot be ignored. As the area of a watershed grows, dilution by waters less impacted will result. Along LKC, Peterson and Benning (2013) reported dilution decreased Cl^- concentrations. The gradual decrease in concentration associated with lower urban land use defined by the LKC locations in Eqs. (1) and (2) is believed to reflect the role of dilution.

Once applied, excess road salt is transported to ditches and near-road soils through snow plowing, vehicle spray, wind, and snowmelt runoff (Labadia and Buttle 1996). Between 35 and 55% of the applied salt will be transported away via runoff to surface water bodies (Church and Friesz 1993). The direct runoff often has Cl^- concentrations in excess of 1000 mg L^{-1} (Kelly et al. 2009), which elevates Cl^- concentrations in streams during the winter, as witnessed in waters from LKC stations. While LKC waters had measured peak Cl^- concentrations 10–100 times larger than baseline concentrations, the mean the increase was smaller than the 20- to 30-fold increases in Cl^- concentrations observed in other higher latitude study areas (Bäckström et al. 2003; Godwin et al. 2003; Howard and Beck 1993; Koryak et al. 2001; Ruth 2003; Scott 1976). Pre-deicer application concentrations are not known in KC and LKC, but employing locations EB 1 and 3 as proxies for pre-deicer conditions suggest Cl^- concentrations have increased in the LKC (impacted) watersheds by seven times, which is consistent with observations in rural watersheds with low density of roadways in Maryland, New York, and New Hampshire (Kaushal et al. 2005).

Although Cl^- has typically been viewed as a benign ion in the environment, exposure to acute and chronic Cl^- concentrations can have deleterious effects on aquatic flora (Panno et al. 1999) and fauna (Bollinger et al. 2005; Fraser and Thomas 1982). Along the impacted segments, Cl^- concentrations are consistently above the 210 mg L^{-1} threshold (Fig. 2). Concentrations above this threshold have been linked to a decrease in diversity of benthic communities and an increase benthic drift (Crowther and Hynes 1977; Demers 1992; Molles 1980) and a decrease in both diversity and populations of aquatic biota (Birge et al. 1985; Evans and Frick 2001; Fay and Shi 2012; Hart et al. 1991; Karraker et al. 2008; Sanzo and Hecnar 2006; Seilheimer et al. 2007).

As a result of prolonged Cl^- concentrations above 210 mg L^{-1} in streams, sensitive life stages can be exposed to concentrations long after the winter period of application has occurred (Findlay and Kelly 2011). For post-snowfall (March) to the end of the study, the most downstream locations, LKC3 and EB8, still have consistent Cl^- concentrations above 50 and 30 mg L^{-1} , respectively. These concentrations are below the threshold of 210 mg L^{-1} for chronic concentrations, Chadwick and Feminella (2001) report that the minimum tolerance to Cl^- by organisms decreases with increasing temperature. If Cl^- is stored within the groundwater system and concentrations continue to increase in streams, understanding the summer base flow Cl^- contribution is critical to ensuring stability of aquatic ecosystems.

Conclusions

Like other studies, streams that receive waters drained from urban areas are many times more susceptible to road salt contamination compared to agricultural areas. Urbanization increases impervious surfaces and runoff waters containing elevated Cl^- is quickly discharged into streams. Agricultural areas, on the other hand, have a more pervious land surface and lower road density. However, streams within watersheds with both agricultural and urban land uses are susceptible to sustained high Cl^- concentrations in the spring and summer. Cl^- trapped within snow banks and grass patches infiltrates into the subsurface, eventually reaching the water table. In urban areas, higher salinity waters that flow into storm-water retention basins infiltrate the soil, contaminating the groundwater. The groundwater fed streams receive a constant supply of Cl^- from the slow release of Cl^- -rich base flow throughout the year.

This research examined how deicing applications and land use within a watershed influenced Cl^- concentrations in streams. Impacts of deicing practices are observed in watersheds with as little as 23% urban land use. Additionally, streams are impacted by anthropogenic activities; agricultural land use has resulted in the elevation of Cl^- concentrations in streams devoted to agriculture (1.5% urban land use). These results indicate Cl^- , regardless of source, is accumulating within watersheds. Subsequently, attempts to decrease Cl^- concentrations that focus solely on road salts may not lead to the desired outcome.

Using land use as the controlling variable, a nonlinear regression model can be adapted for any area being studied and can be used along with the understanding of the potential sources of Cl^- for the watershed. While areas with different geology, topography, watershed area, and different land-use characteristics will yield different equations, land-use classification and average Cl^- concentrations can be gathered for any area. If care is taken when adapting this model for different areas, it could be effectively used as a tool to estimating average stream Cl^- and the model can then be modified to represent stream chemistry for the respective area.

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