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River chloride trends in snow-affected urban watersheds: increasing concentrations outpace urban growth rate and are common among all seasons

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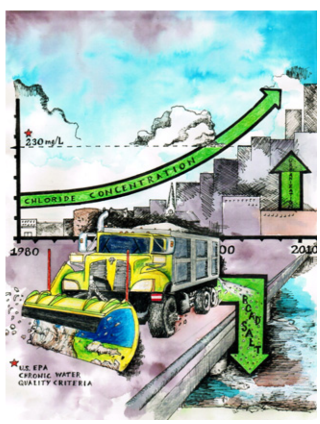
HIGHLIGHTS

- Chloride trends in northern U.S. urban streams are computed.
- The rate of chloride concentration increase outpaced urbanization from 1990 to 2011.
- The greatest chloride concentration increase was during the winter.
- Increasing chloride concentration trends were observed in all seasons.
- Chronic water quality criteria for chloride were exceeded for extended durations.

GRAPHICAL ABSTRACT



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ABSTRACT

Chloride concentrations in northern U.S. included in this study have increased substantially over time with average concentrations approximately doubling from 1990 to 2011, outpacing the rate of urbanization in the northern U.S. Historical data were examined for 30 monitoring sites on 19 streams that had chloride concentration and flow records of 18 to 49 years. Chloride concentrations in most studied streams increased in all seasons (13 of 19 in all seasons; 16 of 19 during winter); maximum concentrations occurred during winter. Increasing concentrations during non-deicing periods suggest that chloride was stored in hydrologic reservoirs, such as the shallow groundwater system, during the winter and slowly released in baseflow throughout the year. Streamflow dependency was also observed with chloride concentrations increasing as streamflow decreased, a result of dilution during rainfall- and snowmelt-induced high-flow periods. The influence of chloride on aquatic life increased with time; 29% of sites studied exceeded the concentration for the USEPA chronic water quality criteria of 230 mg/L by an average of more than 100 individual days per year during 2006–2011. The rapid rate of chloride concentration increase in these streams is likely due to a combination of possible increased road salt application rates, increased baseline concentrations, and greater snowfall in the Midwestern U.S. during the latter portion of the study period.

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1. Introduction

The impact of road salt on aquatic ecosystems continues to increase as urban development and subsequent road salt applications increase with time. Substantial application of road salt in the U.S. began in the 1940s increasing to an annual average of 9.6 million metric tons/yr of NaCl-based road salt in the 1980s and 19.5 million metric tons/yr in the last 5 years reported, ending in 2011 (Kelly and Matos, 2013). Increasing trends in chloride concentrations have been observed in water bodies of the U.S. and attributed, at least in part, to road salt influence. These trends have included rivers (Godwin et al., 2003; Interlandi and Crockett, 2003; Thunqvist, 2004; Kaushal et al., 2005; Kelly et al., 2012a), groundwater (Reisch and Toran, 2013; Kelly, 2008; Perera et al., 2009; Cassanelli and Robbins, 2013), inland lakes (Ramstack et al., 2004; Novotny and Stefan, 2010; Müller and Gächter, 2012), and even water bodies as large as the Laurentian Great Lakes (Chapra et al., 2009, 2012).

Elevated salt concentrations in surface waters can exert an adverse effect on aquatic organisms (Cañedo-Argüelles et al., 2013). The U.S. Environmental Protection Agency (USEPA) ambient water quality criteria for chloride (when associated with sodium) defines the chronic criterion as a 4-day average concentration exceeding 230 mg/L and the acute criterion as a 1-h average concentration exceeding 860 mg/L (U.S. Environmental Protection Agency, 1988). Given the sensitivity of freshwater organisms to chloride, exceedances of these criteria have the potential to affect a substantial number of species (U.S. Environmental Protection Agency, 1988). In a thorough assessment of the environmental impacts of road salt, Environment Canada estimated that 5% of aquatic species would be affected at chloride concentrations of 210 mg/L and 10% of aquatic species would be affected at chloride concentrations of 240 mg/L for chronic exposures (Environment Canada, 2001). Multiple studies have observed chloride concentrations greater than these benchmark concentrations in streams as a result of road salt runoff. These studies have included local (Ruth, 2003; Trowbridge et al., 2010; Allert et al., 2012; Morgan et al., 2012), regional (Kelly et al., 2012b), and national geographic scopes (Corsi et al., 2010).

Urban land cover in the U.S. has also increased over time from an estimated 61,000 km^2 in 1945 to 247,000 km^2 in 2007 (Nickerson et al., 2011). With urban land cover projected to continue increasing (Alig et al., 2004), applications of road salt for deicing impervious surfaces are also likely to increase. Adding to the current and past water quality issues resulting from the salinization of streams, including road salt runoff, an analysis of water quality in the northeastern U.S. predicted that many surface waters in that area of the country would not be potable for human consumption and would become toxic to freshwater life within the next century (Kaushal et al., 2005).

The primary objectives of this study were to define temporal trends in chloride concentrations in the context of chloride dependency on streamflow rates, compare temporal chloride trends among seasons, and compare these trends to changes in urban land cover, aquatic life criteria, and road salt sales patterns. Trend analysis was done using the modern water quality trend modeling technique that controlled for streamflow rate and season to help avoid confounding results due to natural variability (Hirsch et al., 2010).

2. Methods

2.1. Site selection

An initial focus for 14 sites on 3 streams in the Milwaukee metropolitan area was conducted. To assess the broader geographic impact, 11 additional streams in urban areas of the northern U.S. were studied, 4 streams in northern areas with little urban impact were studied, and one stream in an urban area of the southern U.S. was studied as a warm-climate reference.

Sites were initially chosen based on proximity to areas of urban influence in the northern U.S. (Fig. 1, Table 1). Three sites with a low degree of urbanization in northeast Wisconsin and one site in Oregon were included to evaluate non-urban influence, and the Trinity River in Texas was also examined as a non-deicing reference site in an urban area. Second, adequate data availability for modeling was necessary. Most sites had 200 or more chloride observations and 20 or more years of record with no significant gaps in data collection (i.e., larger than 5 years), and sample representation during all seasons throughout the water quality record (Table S1). The exceptions include five sites that had between 151 and 194 observations, and one site that had a 6-yr gap. These sites were included to maintain adequate geographic representation of sites (Table S1). Sites located within or just downstream from large lakes or impoundments were omitted. A continuous record of streamflow data concurrent with the chloride record was required at the selected site or at a nearby site on the same stream. Sites selected in the Milwaukee metropolitan area were chosen from a dense network of available sites in an effort to adequately represent changes in the Milwaukee, Menomonee, and Kinnickinnic Rivers.

2.2. Data sources

Chloride data were obtained from the Milwaukee Metropolitan Sewerage District (MMSD), the Wisconsin Department of Natural Resources (WDNR), and the Water Quality Portal (WQ portal; http://www.waterqualitydata.us/), which includes data from the USGS National Water Information System (NWIS) and EPA STOrage and RETrieval Data Warehouse (STORET). Coordinate bounding boxes were used to query the WQ Portal to locate streams in metropolitan areas of primarily the northern U.S. with sufficient data (Fig. 1). Where data from different sources overlapped at common sites, data were combined except for one site where data from one of the sources were not considered valuable due to many duplicate data points and data differences that called into question analytical results.

If available, streamflow data from the USGS National Water Information System (http://waterdata.usgs.gov/nwis) were retrieved from the same location where chloride samples were collected; otherwise, data from a nearby location(s) on the same stream were scaled by drainage area to estimate streamflow at the chloride sampling location. In two cases, there were data gaps in streamflow that were estimated using an ordinary least squares regression with streamflow data from a nearby site (Meno 70th, $R^2 = 0.65$; Milw Cedarburg, $R^2 = 0.95$).

Road salt sales data were compiled from an annual reporting of Historical Statistics for Mineral and Material Commodities in the United States (Kelly and Matos, 2013) and used as a proxy for assessing overall road salt applications in the studied watersheds. Road salt sales were used in place of actual application numbers due to the complicated nature of gathering road salt application data from all municipalities and private applicators on the scale of this study.

Daily snowfall data for eight weather stations in the U.S. were retrieved from the National Climate Data Center (http://www.ncdc.noaa.gov/cdo-web/) for evaluation of snowfall changes throughout the study period (Table S2). Stations were chosen based on proximity of chloride study sites and availability of data during the study period.

Land cover composition and other watershed characteristics were determined from several published GIS datasets and provided in Table 1, and methods are described in Supplemental Information.

2.3. Data analysis

Data analysis included water quality trend modeling, graphical analysis of trends, and exploration of modeling results in comparison to land use, the USEPA water quality criterion, and road salt sales in the U.S.

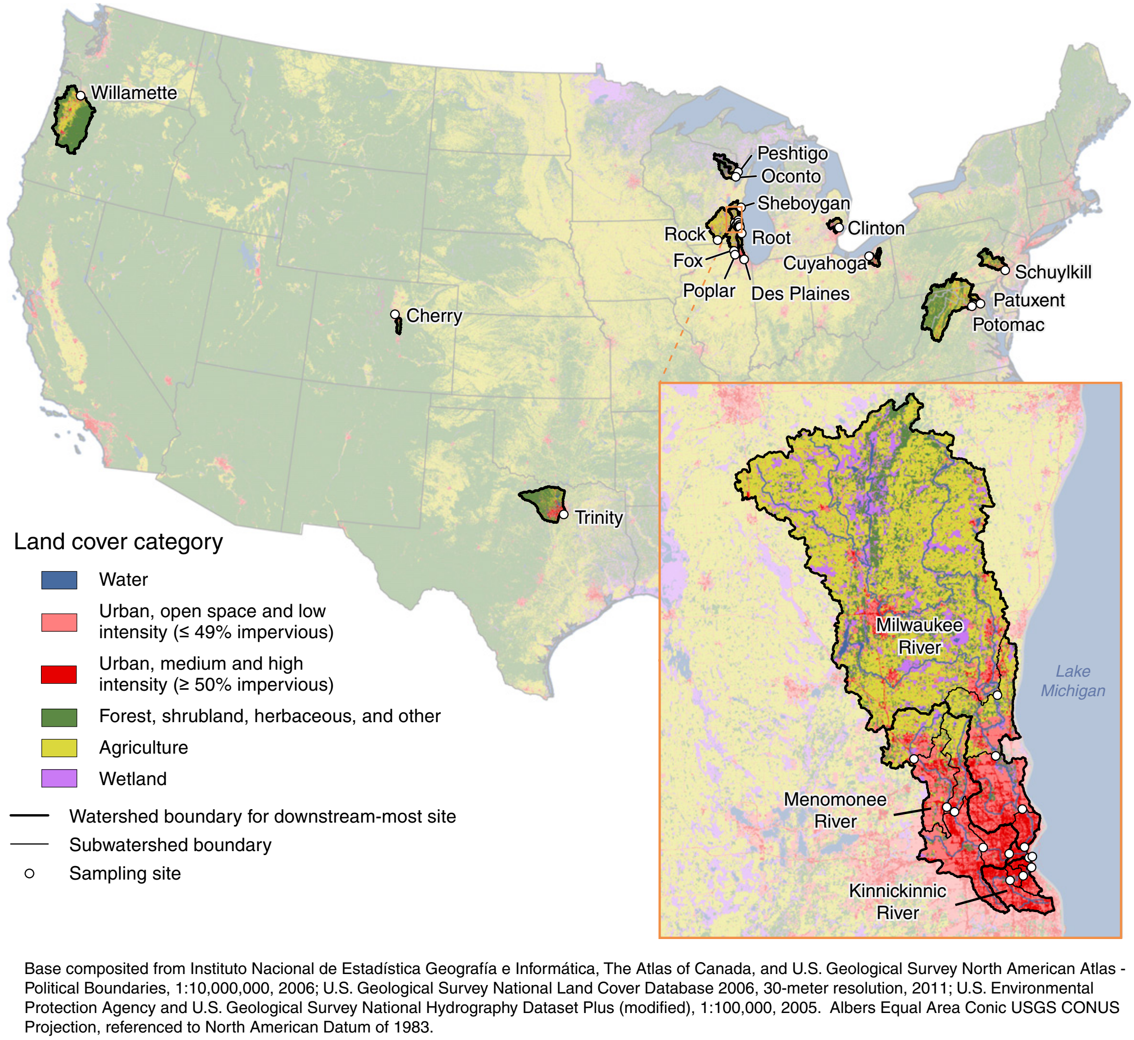

Fig. 1. Study site locations and watershed characteristics.

2.3.1. Rationale for water quality modeling technique

Chloride concentrations in streams have the potential to vary depending on several factors that all arise from the nature of the contamination sources, transport characteristics, and hydrologic characteristics of a given watershed. Considerations when attempting to understand these influential factors are very similar to those outlined previously describing potentially influential factors in stream nutrient concentrations and fluxes (Hirsch et al., 2010). The primary considerations are as follows: As urban development continues, sources of nonpoint pollution such as road salt application tend to increase as well, so it is logical to expect chloride concentrations in streams to change with time. Given that road salt is applied only during cold-weather periods, seasonal differences in chloride concentrations are also expected. The nature of road salt transport to surface waters causes chloride concentrations to change with streamflow. For example, when road salt melts ice and snow during periods of low streamflow, stream chloride concentrations can become very high, but when road salt runoff periods are coincident with high-streamflow periods resulting from snowmelt or rainfall events, chloride concentrations are likely to be lower due to the larger amounts of water available to dilute the road salt.

Long-term changes in chloride concentrations from road salt can follow a variety of temporal patterns responding to factors such as: the rate of urban development, changes in road salt application practices, long-term storage and release processes from large water bodies and groundwater, and changing climate conditions. Other major sources include treated wastewater as well as fertilizer and livestock, with other minor sources also contributing (Kelly et al., 2012b). These influences led to the use of WRTDS, a data analysis technique that can describe long-term change in a flexible manner (not simply as linear or quadratic time trends) and account for the seasonal- and streamflow-related dependencies which may, themselves, be changing over a period of many years or decades (Hirsch et al., 2010). The WRTDS analysis used here is implemented within the EGRET package (Hirsch and De Cicco, 2014) in the R statistical language (R Development Core Team, 2008).

2.3.2. Modeling water quality changes

The WRTDS method is based on weighted linear regression to estimate daily concentration throughout time, discharge (streamflow), and seasonal dimensions of the data used to calibrate the model. For any given estimation point in the data domain (where the point is defined by year, season and streamflow) the model gives increased weight to values similar in time, streamflow, and season to the estimation point. For example, concentrations of samples collected in year two of a sample period will have little influence on model estimates for year 10, concentrations of samples collected during low flow periods will have little influence on model estimates for high flow, and concentrations of samples collected during summer will have little influence on model estimates for winter periods. Weighting for proximity of the estimation point to the observed data by time (the time distance),

Table 1
Watershed characteristics of study sites.

Site name	Metropolitan			Drainage	Percent land cover in 2006				Percent land cover in 1992[c]		
	State	Area	Short Name	area (km^2)	Urban[a]	Agricultural[a]	Forest/other[a]	% Impervious[b]	Urban	Agricultural	Forest/other
Milwaukee River at Pioneer Rd near Cedarburg	WI	Milwaukee	Milw Cedarburg	1555	11.0	56.2	32.8	2.9	9.6	58.5	31.9
Milwaukee River at Brown Deer Rd	WI	Milwaukee	Milw Brown Deer	1674	12.7	54.9	32.4	3.4	11.1	57.4	31.5
Milwaukee River at Estabrook Park	WI	Milwaukee	Milw	1785	17.5	51.4	31.0	5.6	16.0	53.9	30.1
Milwaukee River at Wells St	WI	Milwaukee	Milw Wells	1808	18.5	50.8	30.7	6.3	17.0	53.3	29.8
Milwaukee River at Jones Island at Mouth at Milwaukee	WI	Milwaukee	Milw Jones	2240	29.2	43.8	27.0	11.3	27.1	46.7	26.2
Menomonee River at County Line Road	WI	Milwaukee	Meno County	79	30.1	46.2	23.7	10.0	24.5	53.0	22.4
Menomonee River at 127th St	WI	Milwaukee	Meno 127th	153	52.0	28.5	19.4	17.8	43.0	37.7	19.3
Menomonee River at Hampton Ave	WI	Milwaukee	Meno Hampton	211	51.0	29.6	19.4	18.6	43.3	37.7	19.0
Menomonee River at 70th St Bridge at Wauwatosa	WI	Milwaukee	Meno 70th	318	65.1	20.0	14.9	24.7	59.4	26.1	14.5
Menomonee River at 25th St	WI	Milwaukee	Meno 25th	355	68.6	17.9	13.5	27.9	63.5	23.4	13.1
Kinnickinnic River at S 27th St	WI	Milwaukee	KK 27th	45	99.0	0.0	1.0	49.8	98.8	0.4	0.8
Kinnickinnic River at S 7th St	WI	Milwaukee	KK 7th	53	98.2	0.0	1.8	50.3	98.1	0.4	1.5
Kinnickinnic River at 1st St	WI	Milwaukee	KK 1st	63	98.5	0.0	1.5	50.5	98.4	0.3	1.3
Kinnickinnic River at Jones Island Ferry	WI	Milwaukee	KK Jones	69	98.0	0.0	2.0	51.6	97.8	0.3	1.9
Root River at Racine, WI	WI	Racine	Root	480	29.8	52.7	17.4	10.0	26.0	52.8	21.2
Peshtigo River at Peshtigo, WI	WI	Rural	Peshtigo	2872	4.3	15.5	80.3	0.4	4.6	14.3	81.1
Oconto River near Oconto, WI	WI	Rural	Oconto	2473	4.9	21.8	73.4	0.5	5.2	21.2	73.6
Sheboygan River at Sheboygan, WI	WI	Rural	Sheboygan	1103	8.1	64.7	27.2	2.2	7.7	66.6	25.7
Rock River at Afton, WI	WI	Janesville	Rock	8661	11.3	65.6	23.1	3.2	10.0	66.7	23.3
Willamette River at Portland, OR	OR	Rural	Willamette	28,967	7.3	20.4	72.2	2.6	6.9	20.6	72.4
Des Plaines River at Riverside, IL	IL	Chicago	Des Plaines	1643	63.8	18.8	17.4	27.5	60.0	22.0	18.0
Fox River at Algonquin, IL	IL	Chicago	Fox	3601	24.8	45.2	30.0	7.0	21.8	47.3	31.0
Poplar Creek at Elgin, IL	IL	Chicago	Poplar	92	67.9	7.5	24.6	26.5	62.0	15.0	22.9
Cherry Creek at Denver, CO	CO	Denver	Cherry	1063	21.7	0.6	77.7	6.9	15.9	0.7	83.4
Clinton River at Moravian Drive at Mt. Clemens, MI	MI	Detroit	Clinton	1937	52.3	19.9	27.8	20.0	49.7	23.0	27.3
Cuyahoga River at Independence, OH	OH	Cleveland	Cuyahoga	1836	39.8	17.4	42.8	10.9	34.1	20.7	45.3
Schuylkill River at Philadelphia, PA	PA	Philadelphia	Schuylkill	4888	24.2	29.7	46.1	6.4	18.6	39.1	42.3
Patuxent River near Bowie, MD	MD	Columbia	Patuxent	906	31.9	26.4	41.8	8.7	20.0	44.1	35.9
Potomac River at Chain Bridge, at Washington, DC	DC	Washington, DC	Potomac	29,967	10.1	29.6	60.3	2.1	8.3	32.1	59.6
Trinity River below Dallas, TX	TX	Dallas	Trinity	16,224	22.3	14.4	63.3	7.9	19.3	15.8	64.9

[a] Watershed urban, agriculture, and forest/other percentages for 2006 were determined from the National Land Cover Database 2006 Land Cover dataset (Fry et al., 2011).
[b] Watershed impervious percentages for 2006 were determined from the National Land Cover Database 2006 Percent Developed Imperviousness dataset (Fry et al., 2011).
[c] Watershed urban, agriculture, and forest/other percentages for 1992 were determined from the National Land Cover Database 1992/2001 Retrofit Land Cover Change dataset (Fry et al., 2009).

streamflow (the discharge distance), and season (the seasonal distance) are assigned using a tricube weight function with half-window widths of 10 years, 2 natural log units, and 0.5 years in the time, streamflow, and seasonal dimensions respectively. These values were chosen after experimentation of the smallest values that did not cause unrealistic oscillations. The overall weight on any given observation is the product of the three weights. Estimation by the WRTDS model was performed using measured chloride and corresponding daily streamflow values. This tool has not previously been used to examine chloride trends, but applications using WRTDS have primarily been used for examination of nutrients (Hirsch et al., 2010; Medalie et al., 2012; Green et al., 2014).

2.3.3. Examination of water quality changes

One type of output produced using WRTDS for each of the study locations was graphics showing estimated concentrations for three levels of streamflow (the 10, 50, and 90 percentile points on the daily streamflow frequency distribution), four seasons of the year (centered on February 15 [winter], May 15 [spring], August 15 [summer], and November 15 [fall]), and each year of the period of record. Another type of output is a contour plot of the differences in estimated chloride concentration between the years 1981 and 2010 as a function of time-of-year and streamflow. WRTDS was also used to compute flow-normalized annual chloride concentrations over the period of record. Flow-normalization is a technique that removes the effect of year-to-year variations in streamflow (but not seasonal variations) on average chloride concentrations (Hirsch et al., 2010).

Linear regression was used to explore the response of flow-normalized annual chloride concentrations as well as the number of individual days that these concentrations exceeded the USEPA water quality (exceedance days) to the percent of urban land cover in the watershed. Linear temporal regression was also used to compare the change in national road salt sales in the U.S. to the change in urban land cover in the northern U.S. to coincide with the location of most road salt sales in the U.S. The calculation of expected number of exceedance days was determined using logistic regression based on the output of the WRTDS model for the two periods 1990–1994 and 2006–2010. These dates were chosen based on the inclusion of at least 20 years, while minimizing the number of sites that had to be excluded due to missing data. The non-deicing reference site (Trinity River) and seiche-affected sites (Milw Jones, KK 1st, KK Jones) were not used in these analyses. The period of record did not have sufficient data between 1990 and 2011 for the Clinton, Cuyahoga, and Fox River, so these sites were not included in these analyses. Dates for the Schuylkill and Des Plaines Rivers did not match perfectly, but were near enough to provide an estimate for the later time period. The WRTDS method has been extended here to estimate the daily probability of exceedance of a threshold. Because the WRTDS model provides a conditional mean and conditional variance of concentration for each day as a function of streamflow, time of year, and year (trend) it is possible to compute a conditional probability of exceedance of the threshold under the assumption that the conditional distribution of concentration is log-normal. Using these results from all of the sites, logistic regressions were fit for each of the two 5-year time periods. These logistic regression models estimate the daily probability of exceedance at a site as a function the square root of the percent of the watershed that was urbanized during that time period. The number of predicted exceedances per year was then determined by summing these probabilities for the year. These calculations were implemented in R using the betareg function. Pseudo R-squared values for both models were approximately 0.83.

3. Results

Three major watersheds cover the bulk of the Milwaukee metropolitan area: the Milwaukee River, the Menomonee River, and the Kinnickinnic River. These three watersheds have all experienced increased chloride concentrations from 1980 to 2010 during winter, spring, summer, and fall (Fig. 2). The greatest increases in chloride concentrations were in watersheds with the greatest urban land cover percentage. Concentrations for the Milwaukee study sites were greatest in the Kinnickinnic River followed by the Menomonee River and then the Milwaukee River (drainage areas of 45, 355, and 1808 km^2, with 99, 68.6, and 18.5% urban land cover respectively).

In addition, chloride concentrations increased with decreasing streamflow for all three of these watersheds in each of the four seasons. The mean chloride concentration in the Milwaukee River exceeded 140 mg/L during winter low flow periods and was approaching 100 mg/L during summer low-flow periods toward the end of the study period. Mean chloride concentrations in the Menomonee and Kinnickinnic Rivers exceeded the USEPA chronic water quality criteria of 230 mg/L during the winter and spring at all three flow rates in the latter years of the study, and exceeded 100 mg/L during summer and fall periods at all three streamflow rates toward the end of the study duration.

Similar four-season graphs illustrating streamflow dependency for all remaining study sites except those impacted by backwater influences from Lake Michigan (hereafter referred to as seiche) are provided in the supporting information (Figs. S1–S25). Chloride concentrations also increased over all four seasons and decreased with streamflow at all of these additional sites except three with a few notable exceptions: Chloride concentrations at the Peshtigo River had increasing trends over the course of the study period, but concentrations did not increase with decreasing flow; concentrations were relatively constant in the Willamette River. Both of these sites have primarily forested land cover and little urban influence. With these watershed conditions, there is likely to be low road salt application and this is confirmed by very low chloride concentrations (less than 10 mg/L). Chloride concentrations in the Kinnickinnic River at 7th St. did not vary substantially with flow, but did have a slightly increasing relation with increasing streamflow during winter due to samples with high concentrations during high flow periods in the winter. Changes in concentrations with respect to streamflow at the southern urban reference site (Trinity River) were not consistent through the study period.

The change in concentration over time at three different locations within the Milwaukee River watershed is another illustration of increasing road salt effect with urban land cover. These three monitoring sites increased in downstream order from 11% to 17.5% to 18.5% urban land cover (Fig. 3, top to bottom panels, respectively; NLCD 2006 (Fry et al., 2011)). Even with these relatively minor differences in urban land cover, the effect on chloride concentration changes from 1981 to 2010 is apparent in the Milwaukee River with the Wells St. results indicating higher concentrations during winter than the two upstream sites. The greatest increase in chloride concentrations occurred during winter low-flow periods at all three sites, with greater changes as urban influence in the watershed increased. Although the greatest concentration increase was seen during these low flow winter events, substantial increases in chloride concentration also occurred during higher flow periods and extended throughout the year.

Flow-normalized concentrations estimated from 1980 to 2010 for 30 selected sites on 19 streams indicated that concentrations increased for the majority of the sites (Fig. 4). For the more urban watersheds, increases in concentration were greatest in winter periods, but summer periods also experienced increasing chloride concentrations. For the less urban watersheds, there were increasing trends over time (winter and summer slopes were similar) and the concentrations during winter were greater than or similar to concentrations during the summer. The magnitude of chloride concentrations as well as the slope of concentration change increased as the impervious land cover in the watershed increased. For example, the highest chloride concentrations and the greatest change (increase) in chloride concentration over this time period were sites with the highest degree of impervious area including those in Milwaukee, Chicago, Detroit, Cleveland, and Racine metropolitan areas (Fig. 4, top three rows, Table 1). Chloride concentrations generally decreased with decreasing impervious area in the bottom four rows of Fig. 4. The two exceptions are the sites in Portland (Willamette River) and Dallas (Trinity River) which show little or no trend in chloride concentration over the study period. Land cover in the Willamette River had 72% forest and natural area in the watershed, road salt was not commonly used in Oregon during the study period, and the climate

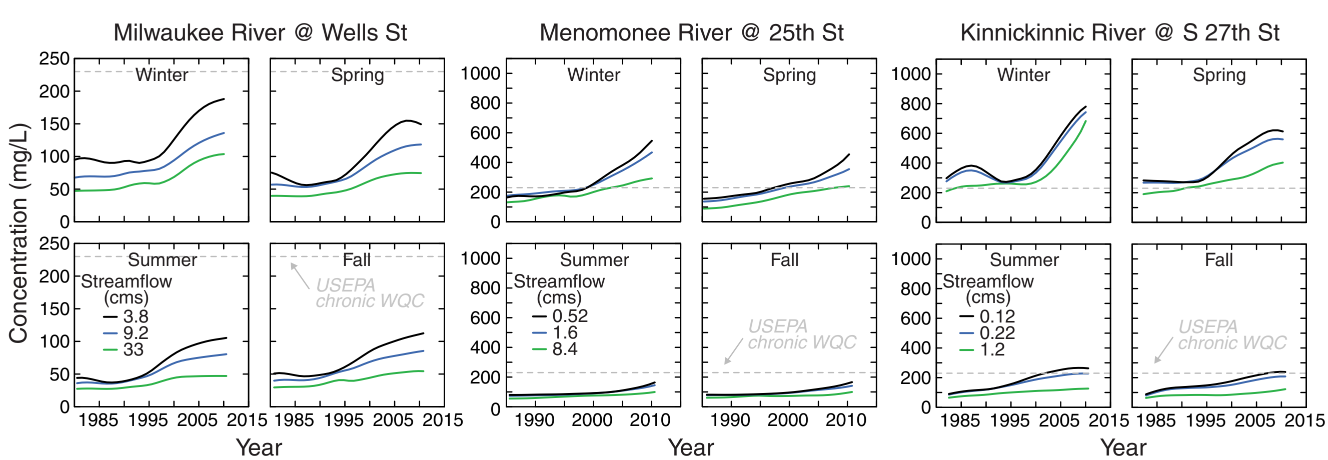

Fig. 2. Chloride concentration estimates at 10, 50, and 90 percentile flow rates from the WRTDS model over time and grouped by season for three Milwaukee streams. Graphs are presented in order of decreasing watershed size and increasing urban land cover from left to right. Streamflow is expressed in cubic meters per second (cms). Dashed line for USEPA chronic water quality criteria represents 230 mg/L.

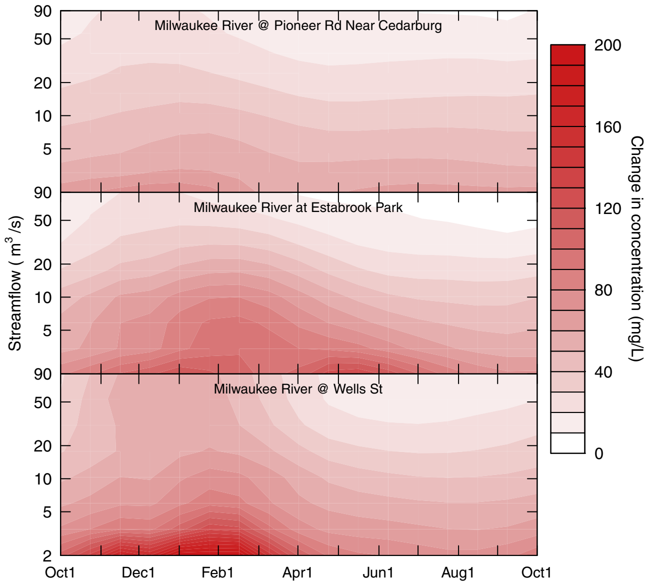

Fig. 3. Contour map of the change in chloride concentration by streamflow and time of year between 1981 and 2010 on the Milwaukee River. Sites are ordered from top to bottom with increasing urban land cover in the watershed. The color legend indicates change in concentration in mg/L.

in the Trinity River is warm enough that road salt application is not common.

Notable differences were observed among sites with low watershed imperviousness in the Midwest U.S. (Rock River; Milwaukee River at Cedarburg, which is upstream from the Milwaukee metropolitan area; and the Sheboygan River) versus those outside of the Midwest (Potomac and Willamette Rivers).

Sites with low imperviousness in the Midwest have higher chloride concentrations, when compared with sites in other areas of the country. Sites with low imperviousness in these different regions also show notable differences in non-urban land cover types; whereas the Midwest sites have large proportions of agricultural land, sites in other regions were dominated by forest and natural areas (Table 1). Concentrations at seiche-affected sites on the Milwaukee and Kinnickinnic Rivers also increased, but the magnitude of these trends was typically muted in comparison with upstream, non-seiche affected sites. Chloride concentrations were lower at study sites with the lowest percent impervious watersheds (less than 0.5%), but increasing trends were still apparent in winter and summer seasons.

Flow-normalized chloride concentration estimates from the WRTDS model were compared with urban land cover in the contributing watershed as 5-yr means for 1990–1994 and 2006–2010 (Fig. 5-A). There was a linear relation between mean concentration and percent urban land cover for both time periods, but regression slopes indicated a change in this relation over time with slopes for these regression equations indicating an increase in chloride concentration of 2.9 and 5.8 mg/L/% urban land cover for the 1990–94 and 2006–10 time periods respectively. Concentrations from 2006 to 2010 were approximately double the concentrations for 1990–1994 for the same percentage of urban land cover.

The logistic models for the probability of water quality criteria exceedance as a function of the square root of the percent of urban land cover in the watershed were significantly different ($p < 0.001$) between the two periods (1990–1994 and 2006–2010; Fig. 5-B). For a watershed with 25% urban area, the expected number of days exceeding 230 mg/L per year increased from 5 to 14, and for a watershed with 90% urban area, it increased from 95 to 231 days per year. An expected value of 17 days exceeding 230 mg/L per year decreased from 50% to 29% urban land cover, and an expected value of 95 exceedance days per year decreased from 95% to 63% urban land cover. About 29% of sites studied exceeded the concentration for the USEPA chronic water quality criteria of 230 mg/L by an average of more than 100 individual days per year during 2006–2011. All regression slopes in Fig. 5 were significant with $p < 0.001$, and R^2 values for all regressions ranged between 0.83 and 0.99. Slopes were significantly different in each of the analyses represented in Fig. 5 ($p < 0.001$ for panels A and B and $p < 0.05$ for panel C).

Beginning in 1987 and ending in 2010, road salt sales in the U.S. increased at an average rate of 3.9%/yr, and urban land cover in the northern part of the U.S. increased at a rate of 2.8%/yr (Fig. 5-C). These trends indicate that road salt usage increased at a rate 40% greater than the increase in urban land cover in the northern U.S. during this period.

4. Discussion

4.1. Temporal trends and relation with land use

Results of the present research indicate that chloride concentrations increased with time in most streams studied in the northern U.S. throughout the study period. While there were trends present in streams with watersheds dominated by urban, agriculture, and forest/natural areas alike, there was a clear increase in concentration as urban land cover (and impervious surfaces) in the watershed increased.

The concentration increase in watersheds with relatively small amounts of urban land use may be influenced by road salt, but may also be a result of other sources such as agricultural runoff which is another potentially important source of chlorides in rural watersheds (Mullaney et al., 2009). Still, the greater winter concentrations suggest that road salt was an important factor in observed trends in the rural watersheds. In contrast with the Midwest sites, which are more highly developed for agriculture, requiring a more extensive road network, the Potomac and Willamette River watersheds have larger percent forest and natural areas (60% and 72% respectively). A detailed watershed-specific investigation would be needed to better understand relative contributions in these rural sites.

The rate of chloride concentration increase outpaced that of urbanization for this study, so urban land cover information alone cannot account for these chloride trends. This changing relation of chloride with urban land cover over time (Fig. 5-A) may be attributed to several potential factors. First, it is possible that more salt was applied per unit urban area during the latter portion of the study period than during the early portion. This appears likely given that road salt sales in the northern U.S. outpaced the rate of increase in urban land cover by 40% during the study period (Fig. 5-C). More salt could be applied per unit area due to three primary reasons: 1) the application rate could have increased as an attempt to maintain more ice-free conditions; 2) the density of impervious area per unit urban area could have increased, thereby increasing the need for road salt, or 3) the difference in weather conditions between the early and latter portions of the study could have warranted different application rates.

Second, the baseline concentrations have been increasing over time due to continued road salt input to the shallow groundwater system and inability of the system to recover to true background concentrations before the next deicing season begins. The result is an increase in baseline concentrations from shallow groundwater discharge to the stream during low flow, as indicated by increasing summer concentrations. Since baseline concentrations increased with time over the course of the study, less additional road salt runoff was needed to reach concentrations of concern in the later years of the study than in the early years, effectively changing the slope of the chloride to urban land cover relation. With baseline concentrations governed by groundwater discharges in many instances, this finding is consistent with other research that has observed elevated chloride concentrations in groundwater which has caused elevated stream concentrations (Kelly, 2008; Eyles et al., 2013).

To explore the possibility of changing weather patterns as potential explanation of increased salt application, snowfall data were examined

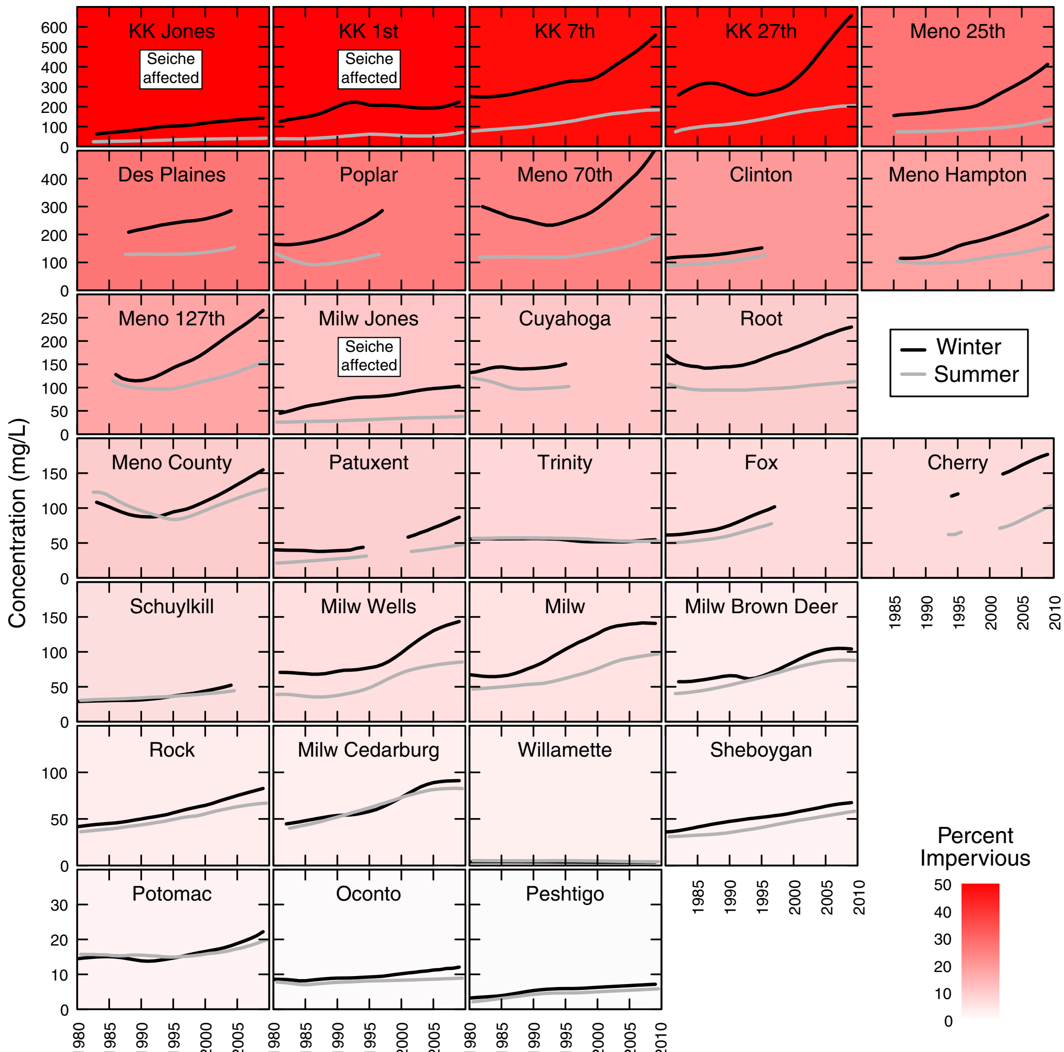

Fig. 4. Winter (black line) and summer (gray line) flow-normalized chloride concentration trends for 30 sites in 19 streams across the United States. The background color represents watershed percent imperviousness as determined using the National Land Cover Database from 2006 (Fry et al., 2011). Sites are ordered by percent imperviousness. Seiche affected is defined by backwater influence from Lake Michigan.

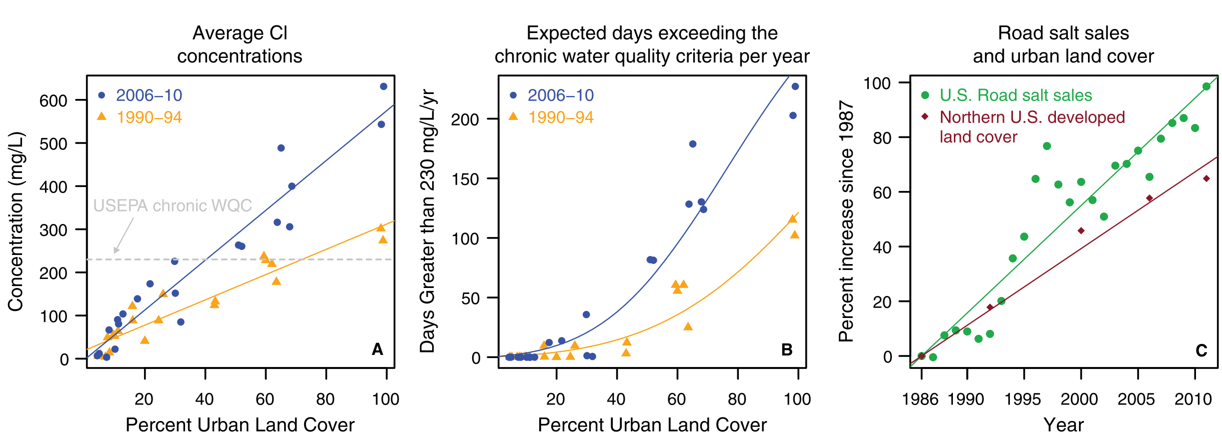

Fig. 5. Average chloride concentration (A) and expected number of individual days per year with concentration exceeding the USEPA chronic water quality criteria of 230 mg/L (B) from modeling results compared to urban land cover percentage in the contributing watershed, and the percent increase in U.S. annual road salt sales compared to the percent increase in urban land cover in the northern U.S. since 1987 (C). Lines (A and C) represent ordinary least squares regression models and curves (B) are based on results of logistic regressions of the probability of daily exceedance as a function of urban land cover. In panel C, U.S. road salt sales are presented as a 5-yr moving average. Dashed line for USEPA chronic water quality criteria represents 230 mg/L (A).

for nine National Weather Service monitoring stations ranging geographically from Washington, D.C., to Denver, Colorado (Table S2, supporting information). For each station, the average total annual snowfall and the average annual number of individual days with snow exceeding 20 mm were computed as a measure of potential for road salt application. An increase in the annual number of days with snow exceeding 20 mm was observed at five stations, and a decrease was observed at four stations. An increase in annual snowfall was observed at six stations, and a decrease was observed at three stations. These data indicated a potentially mixed influence of weather on road salt applications among chloride monitoring sites. Given that 23 of the 30 stream sites were located in the Midwest, the result that data from all four weather stations in the Midwest had increased annual snowfall (average increase of 16%) and days with greater than 20 mm of snow (average increase of 13%) indicated a potential for road salt application increase due to snowfall conditions. In contrast, two of four weather stations in the eastern part of the country had decreased annual snowfall (average overall decrease of 11%) and three of four weather stations had decreased days with greater than 20 mm of snow (average overall decrease of 23%) indicating a potential for road salt application decrease due to snowfall conditions. Snowfall (annual depth and days with greater than 20 mm) in Denver, Colorado decreased by more than 40%. Despite the mixed trends in snow records, stream chloride concentrations increased in each of these three areas of the country, suggesting that increasing baseline concentrations and possible increasing application rates due to factors other than snow cover contribute to the changing relation of chloride with urban land cover over time. Since weather patterns and road salt application methods are locally variable, it would be valuable to extend this study in future research by examining the overall concentrations and the baseline concentrations with respect to precipitation and total salt application on an individual watershed basis.

Given the increasing road salt sales per unit area of urban land cover in the U.S., the increasing baseline chloride concentrations during summer periods, and the difference in snow conditions, it appears multiple factors could plausibly be contributors to the changing relation between average chloride concentrations and urban land cover within the watershed.

4.2. Seasonality

Increasing chloride trends were present all year, including seasons that do not require deicer application; however, the highest concentrations occurred during winter periods. A similar year-round influence has been noted multiple times in previous research (Williams et al., 2000; Kelly, 2008; Perera et al., 2013). This non-deicing season effect has been attributed to salt infiltrating into the shallow groundwater system thereby serving as a “reservoir” of salt that is slowly discharged into streams as baseflow. Relatively slow travel times in the shallow groundwater system could account for the time lag between deicer applications and eventual discharge into the stream.

4.3. Streamflow dependency

Chloride concentrations commonly increased with decreasing streamflow throughout all seasons of the year in most streams studied. The same relation has previously been observed in streams of Illinois (Kelly et al., 2010) and Toronto (Meriano et al., 2009). This behavior can be explained primarily by the factors that govern hydrology throughout the year. During cold-weather months, road salt applications occur during many types of precipitation events. These include a gradient of precipitation forms ranging from purely snowfall events to mixed rainfall and snowfall events to purely rainfall events when freezing temperatures are expected. Precipitation with very little or no liquid precipitation provide little dilution of road salt as it melts snow and ice and eventually drains to nearby streams. These are also low-flow periods, so the stream itself provides little dilution. The combination of these two factors results in high chloride concentrations in the streams. Conversely, during deicing events with greater quantities of liquid precipitation, more dilution of the road salt is provided directly from the precipitation. In addition, when snow is present on the ground, melting is enhanced by contact with rainfall, streamflow is elevated, and dilution potential in the stream is greater. These high-dilution events still have elevated chloride concentrations, but not as high as the low-dilution events.

During non-deicing months, chloride concentrations also decreased with increasing streamflow. Precipitation events again serve to dilute chloride concentrations more than those during low-flow periods that are dominated by groundwater discharge, which is a substantial source of chloride during the non-deicing months.

4.4. Comparison to aquatic toxicity benchmarks

Elevated chloride concentrations resulting from road salt application and runoff in watersheds have potential impacts on aquatic organisms (U.S. Environmental Protection Agency, 1988; Environment Canada, 2001). Increasing trends over time have resulted in increasing exceedances of concentrations that are likely to be harmful to aquatic life. The current research indicates that the relation between urban land cover and the number of daily exceedances of the USEPA chronic water quality criteria concentration of 230 mg/L has changed during the study period (Fig. 5). The number of exceedances for a particular percent of urban land cover was greater during the latter portion of the study as compared to the early portion of the study. As described above for increasing concentrations, an increase in road salt application rates over time, an increase in the baseline concentrations as indicated by summer chloride trends, and changes in snowfall are likely causes of the increased water quality criterion exceedance rate.

Previous research has indicated that degradation of biological integrity is evident beginning below 1% impervious area (Stepenuck et al., 2002; Cuffney et al., 2010; King et al., 2010). Results from the present research are consistent with these findings as chloride concentrations began to increase as soon as urban land cover was present, and concentrations exceeded the chronic water quality criterion beginning at approximately 10% impervious area (approximately 25% urban land cover; Table 1, Fig. 5). A review of road salt effects conducted by Environment Canada concluded that high concentrations of chloride may have immediate or long-term effects on ecosystem populations and that lower concentrations may have adverse effects on community structure, diversity, and productivity (Environment Canada, 2001). Studies reviewed for this Environment Canada effort found that some of the biological components affected included densities of bacteria and algae, drift of stream benthic invertebrates, as well as diversity and community structure of aquatic invertebrates (Evans and Frick, 2001). Other work has determined that elevated chloride concentrations can also influence reproduction of aquatic organisms (Beggel and Geist, 2015). All of this information is primarily based on direct influence from chloride exposures, but indirect exposures caused by mobilization of heavy metals may also have impacts on aquatic organisms (Amrhein et al., 1992; Bäckström et al., 2004; Nelson et al., 2009). These chloride influences are yet another stressor in addition to those commonly thought to impact biological integrity of urban streams such as hydraulic and hydrologic factors, degraded water quality from point and non-point source runoff, and altered habitat and stream channels (Walsh et al., 2005; Steuer et al., 2010).

The multi-season impacts presented in this research suggest the possibility of extended-duration, high-concentration exposure to chloride in urban streams of the northern U.S. This possibility appears credible given that extended-duration (multiple months), high-concentration exposures to chlorides have previously been documented in urban streams receiving road salt runoff (Corsi et al., 2010; Baldwin et al., 2012; Kelly et al., 2012b). Further work to define concentration–duration relations is warranted given that the current USEPA chronic water quality criterion is designed for a 4-day exposure period, and it appears that exposures have potential to be much longer than 4 days. Longer-duration exposures may result in additional impacts on the full life-cycle of aquatic organisms that may not be evident with common evaluation methods.

4.5. Salt management and alternatives

The nature of salt presence in environmental waters makes this issue very difficult to address with common stormwater management practices that rely most commonly on settling or filtration of particulate matter (Waschbusch, 1999; Greb et al., 2000; Horwatich et al., 2011). Since salt dissolves readily in water, these types of management practices will not remove salt from runoff. The only reliable way to reduce the impact of road salt on receiving streams is to reduce applications. There are a host of techniques that have been identified and documented for reduction of road salt application. For example, many municipalities have salt management plans that include a strategy for minimizing road salt usage. Some of these practices include training programs for most effective use, pre-wetting of granular salt to maximize salt retention on paved surfaces, applicators that are calibrated and vary by ground-speed, anti-icing that reduces bonding between snow and pavement and makes plowing more effective, and more efficient predictions of icing conditions to inform deicing activities (Kramberger and Zerovnik, 2008; Fay et al., 2013). In addition, there are a number of alternative chemicals that have been used. These alternative chemicals commonly include other chloride-containing salts such as magnesium chloride or calcium chloride, organic salts such as calcium magnesium acetate, potassium acetate, or sodium acetate, different variations of salt brines, and organic deicers such as glycols. Unfortunately, none of these options are without potential environmental impact as well. All of these alternative deicers have varying degrees of associated aquatic toxicity (Environment Canada, 2001). In addition, organic chemicals used as deicers have an additional impact from increased biochemical oxygen demand (Corsi et al., 2012) and excessive biofilm growth (Mericas et al., 2014). Still, road salt is more common than the alternatives due to the performance effectiveness and relatively low cost compared to alternatives.

5. Conclusions

The U.S. is an urbanizing nation, and with increasing development, previous data and results from this research indicate that road salt applications, chloride concentrations, and resulting adverse impacts on aquatic organisms in streams are likely to increase along with urban development. This research indicates that chloride concentrations in urban streams of the northern U.S. and resulting water quality criteria exceedances have increased at a greater rate than the rate of urban development. In addition, elevated chloride concentrations in these streams through all seasons have implications on long-term exposures to chloride for aquatic organisms. Results of this research provide verification that chloride concentrations in urban streams continue to increase, influencing the potential for aquatic life in affected streams.

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Appendix A. Supplementary data

Methods for the determination of land cover and other watershed characteristics, characteristics of water quality and associated streamflow sites (Table S1), snowfall information at nine National Weather Service Stations (Table S2), WRTDS modeling results during the periods from 1990 to 1994 and 2006 to 2010 for winter and summer periods (Table S3). This material is available free of charge via the Internet at STOTEN TO http://dx.doi.org/10.1016/j.scitotenv.2014.12.012.

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