



Spatial distribution and extent of urban land cover control watershed-scale chloride retention



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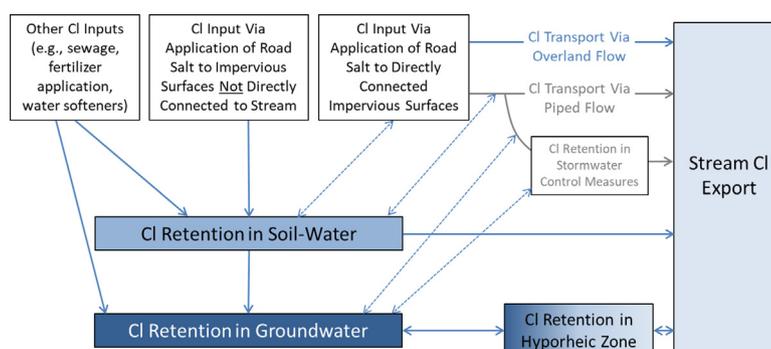
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HIGHLIGHTS

- Application of road salt in cold regions leads to watershed chloride retention.
- Drivers of spatial variability in chloride retention are poorly understood.
- Chloride retention was estimated for 11 watersheds using a mass balance approach.
- Urbanizing watersheds retained ~25% more chloride than heavily urban watersheds.
- A detailed conceptual model outlines processes likely to drive chloride retention.

GRAPHICAL ABSTRACT



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ABSTRACT

In some cold regions up to 97% of the chloride (Cl^-) entering rivers and lakes is derived from road salts that are applied to impervious surfaces to maintain safe winter travel conditions. While a portion of the Cl^- applied as road salt is quickly flushed into streams during melt events via overland flow and flow through storm sewer pipes, the remainder enters the subsurface. Previous studies of individual watersheds have shown that between 28 and 77% of the applied Cl^- is retained on an annual basis, however a systematic evaluation of the spatial variability in Cl^- retention and potential driving factors has not been carried out. Here we used a mass balance approach to estimate annual Cl^- retention in 11 watersheds located in southern Ontario, Canada, which span a gradient of urbanization. We evaluated the influence of multiple landscape variables on the magnitude of Cl^- retention as well as the long-term rate of change in stream Cl^- concentration for the same systems. We found that mean annual Cl^- retention ranged from 40 to 90% and was higher for less urbanized watersheds and for watersheds with urban areas located farther from the stream outlet. This result suggests that less urbanized watersheds and ones with longer flow pathways have more Cl^- partitioned into storage and hence the potential for legacy Cl^- effects on aquatic organisms. While we did measure statistically significant increasing trends in stream Cl^- concentration in some watersheds, there was no consistent relationship between the long-term rate of change in stream Cl^- concentrations and patterns of urbanization and the magnitude of Cl^- retention. Based on our results we present a detailed conceptual model of watershed Cl^- dynamics that can be used to guide future research into the mechanisms of Cl^- retention and release within a watershed.

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1. Introduction

In seasonally frozen environments such as Southern Canada, the Northern United States, and Central and Northern Europe, chloride salts are widely used as de-icers to maintain safe driving conditions. While the beneficial role of road salts for public safety is unequivocal, their movement from paved surfaces to surface waters can result in negative impacts to aquatic organisms (CCME, 2011; Marsalek, 2003; Wallace and Biastoch, 2016). Along with negative toxicological effects on aquatic biota (e.g., reproductive and/or developmental impairment) (Elphick et al., 2011; Gillis, 2011; Kaushal et al., 2005), elevated chloride (Cl^-) concentrations can result in the spread of halophilic organisms and a change in the density gradient of lakes resulting in oxygen depletion (Evans and Frick, 2001). In the terrestrial environment, road salt has been shown to increase the leaching of soil cation nutrients (Schweiger et al., 2015). The inorganic salts commonly used in road salt (NaCl , CaCl_2 , MgCl_2 , KCl) are all highly soluble in water and hence are present in runoff in the dissociated form as monovalent or divalent cations with Cl^- being the principal contributing anion to elevated salinity in freshwater systems (Mayer et al., 1999). Natural sources of these salts include weathering materials, atmospheric precipitation and groundwater; however, in developed areas it is estimated that the majority of the Cl^- entering rivers and lakes is derived from anthropogenic sources including road salts, sewage, industrial effluent, and agricultural fertilizers (Chapra et al., 2009; Mayer et al., 1999; Sonzogni et al., 1983). In the Great Lakes basin, industrial load reductions in the mid-1970s resulted in an approximately 40% reduction of Cl^- loading in Lakes Erie and Ontario (Chapra et al., 2009). However, since the mid-1980s increasing Cl^- trends in the lower Great Lakes (Chapra et al., 2009) and other cold region lakes (Dugan et al., 2017; Mueller and Gaechter, 2012; Novotny et al., 2008; Sibert et al., 2015; Winter et al., 2011, 2012) and streams (Daley et al., 2009; Gardner and Royer, 2010; Jackson and Jobbágy, 2005; Kaushal et al., 2005; Kelly et al., 2008; Löfgren, 2001; Mayer et al., 1999; Meriano et al., 2009; Perera et al., 2009; Price and Szymanski, 2013; Thunqvist, 2004; Winter et al., 2011) have been linked to the growth in urban development and the associated use of road salts for de-icing.

In watersheds with a relatively high proportion of urban land cover (i.e., both pervious and impervious built-up areas), stream Cl^- concentrations often exceed environmental protection guidelines set out by the Canadian Council of Ministers of the Environment (chronic: 120 mgL^{-1} ; acute: 640 mgL^{-1}) (CCME, 2011) during winter high flows and the spring freshet (Wallace and Biastoch, 2016; Winter et al., 2011). These winter and spring Cl^- concentration peaks result when meltwater containing road salt runs off impervious surfaces and travels through stormwater pipes directly to streams (Meriano et al., 2009; Ramakrishna and Viraraghavan, 2005). In some watersheds, elevated Cl^- concentrations persist into the summer and autumn months (Perera et al., 2013; Robinson and Hasenmueller, 2017), which suggest that some portion of the Cl^- containing meltwater is not taking a direct (i.e., piped) route to the stream, but rather is transported along slower subsurface flow pathways (Howard and Haynes, 1993; Robinson and Hasenmueller, 2017). The persistence of elevated Cl^- concentrations into the growing season presents a serious problem for aquatic biota that are sensitive to the toxic effects of Cl^- (CCME, 2011). Previous studies have suggested that these pathways might include infiltration of surface runoff from roads into roadside ditches, interflow through the unsaturated zone, groundwater flow through shallow unconfined aquifers and/or through deeper confined aquifers, flow through the stream hyporheic zone, and flow within the urban karst (Bester et al., 2006; Betts et al., 2015; Daley et al., 2009; Gabor et al., 2017; Howard and Haynes, 1993; Kincaid and Findlay, 2009; Ledford et al., 2016; Meriano et al., 2009; Mullaney et al., 2009; Perera et al., 2013; Pilon and Howard, 1987; Thunqvist, 2004). Untangling the role of different hydrological processes on stream Cl^- dynamics is a complex endeavour; however, a first step in that direction is quantifying the spatio-

temporal variability in annual watershed-scale Cl^- retention and exploring the relationship between watershed characteristics and the magnitude of retention.

The annual rate of Cl^- retention can be reliably estimated using a mass balance approach, where the amount of Cl^- stored or retained in the watershed over one year is calculated as the difference between the mass of Cl^- leaving the watershed in stream water and the mass of Cl^- applied to the watershed (mainly onto impervious surfaces, such as roads and parking lots). Previous studies have reported net retention of Cl^- for individual watersheds on an annual basis ranging from 28 to 77% using this type of approach (Howard and Haynes, 1993; Kelly et al., 2008; Meriano et al., 2009; Novotny et al., 2009; Perera et al., 2010). The large range in Cl^- retention reported in the literature suggests that the rate of, and processes controlling, Cl^- transport from surface to stream vary both temporally and spatially. To more systematically evaluate the factors controlling variability in watershed-scale Cl^- retention, the present study focuses on answering three questions: (1) How spatially and temporally variable is annual, watershed-scale Cl^- retention among watersheds spanning a gradient of urbanization? (2) Do watershed structural and/or land cover characteristics explain the spatial variability in annual, watershed-scale Cl^- retention? (3) Is there a relationship between the magnitude of watershed-scale Cl^- retention and the persistence of chronic stream Cl^- concentrations into the growing season? To address these questions, we estimated annual, watershed-scale Cl^- retention for multiple watersheds located in the rapidly urbanizing region of Southern Ontario. We specifically chose watersheds that span a gradient of urbanization (3.6 to 86.5% urban land cover) so that we could test our hypothesis that the magnitude of annual, watershed-scale Cl^- retention increases as the proportion of urban land cover in the watershed increases. To relate our findings back to potential impacts on stream ecosystems, we evaluated long-term trends in seasonal stream Cl^- concentrations to identify which, if any, of the high Cl^- retention watersheds showed increasing Cl^- concentrations into the summer and autumn months.

2. Methodology

2.1. Study watersheds

Eleven watersheds located within the Greater Golden Horseshoe region of southern Ontario were selected for this study (Fig. 1a). Selection of watersheds was based on the availability of road salt application data and co-located continuous conductivity and streamflow data. Special attention was paid to selecting watersheds that spanned a gradient of urbanization from dominantly agricultural (e.g., Grindstone Creek), to urbanizing (e.g., East Holland River), to heavily urbanized (e.g., Don River) (Fig. 1b; Table 1). The study watersheds are grouped into three different regions: (i) sub-watersheds of Lake Simcoe, (ii) sub-watersheds of Lake Ontario located within the Greater Toronto Area (GTA), and (iii) sub-watersheds of Hamilton Harbour. All 11 watersheds are on glacial till, have very deep bedrock and long hydrologic flowpaths, while some (Pefferlaw Bk., Black R., East Holland R., and Don R.) are linked to the Oak Ridges Moraine. Except for three watersheds (Black R., Pefferlaw Bk., and Grindstone Ck.) permeability of the surficial geology across the study watersheds is low or low-medium (see Table S1 for more information). Mean annual temperature varies across these sub-regions from a low of 6.5°C in the most northern watershed, Hawkestone Ck., to 8.6°C in Black Ck. (Table 2). Average annual precipitation varies between 812 and 985 mm across the watersheds, but there is no systematic gradient across the three regions (Table 2). Snowfall typically occurs from November to April and average annual snowfall varies between 108 and 265 cm across the study watersheds. Mean annual flow increases with watershed area and the mean annual runoff ratio (a dimensionless value relating the amount of runoff to the amount of precipitation received) varies between 31 and 39% (Table 2).

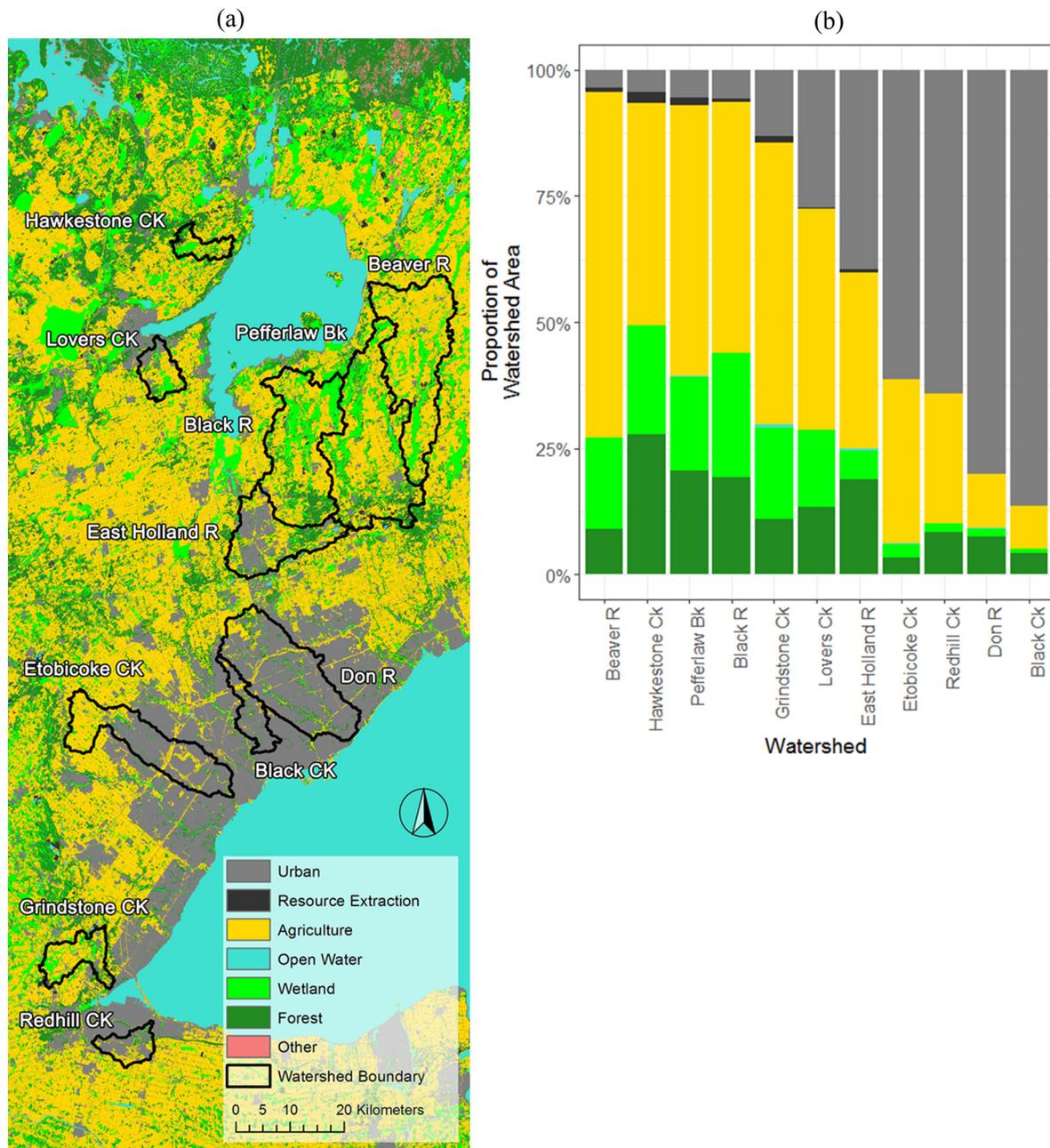


Fig. 1. (a) Location and boundaries of study watersheds (note that watershed boundaries are delineated based on surface topography with the location of water quality measurements representing the pour point) and (b) proportion of watershed area made up of different land cover types (note that watersheds are ordered left to right from the lowest to highest proportion of urban land cover). The legend in panel (a) also applies to panel (b).

2.2. Watershed chloride mass balance analysis

2.2.1. Chloride inputs

Long-term trends in Cl^- inputs are influenced by both industrial activity and population dynamics. In the study region, industrial Cl^- pollution declined in the 1970s; however, population growth and concomitant growth in urban land cover has resulted in increasing Cl^- .

usage for winter road maintenance. Between 2006 and 2011 alone, there was an average change in population of 4.6% across our 11 study watersheds (Table S2). In this study, road salt (sodium chloride; NaCl) is assumed to be the dominant source of Cl^- entering all 11 study watersheds (CCME, 2011; Chapra et al., 2012; Winter et al., 2011). Most of the 11 study watersheds are crossed by 400 series highways (8–12 lanes wide) and/or arterial roads (2–4 lanes wide). These major

roadways, as well as smaller roads, are regularly salted throughout the winter season by companies contracted by the Ontario Ministry of Transportation (MTO), and upper- and lower-tier municipalities. The MTO and most municipalities that apply >500 t of road salts per year have implemented Canada's *Code of Practice for the Environmental Management of Road Salts*, which among other things includes best management practices for the application of salt and guidelines for reporting the total quantity of road salts used per year (Environment Canada, 2004). Although the MTO and municipalities across the study region adhere to approved salt management plans, road salt application rates vary among the study watersheds depending on climatic conditions, operator decisions, and the proportion of total impervious areas that are privately managed.

Chloride concentrations in precipitation have not changed significantly since the late 1980s and are very low (e.g., 2008–2012

Table 1
Structural and land cover characteristics of the 11 study watersheds. Urban SI = urban land use skewness index.

Watershed	Region	Structural		Land cover							
		Area (km ²)	Mean Slope (%)	Urban (%)	Resource extraction (%)	Agriculture (%)	Open water (%)	Wetland (%)	Forest (%)	Lane-length density (km km ⁻²)	Urban SI
Beaver R.	L. Simcoe	329.5	2.773	3.6	0.9	68.2	0.2	18.1	9.0	1.63	0.89
Black R.		319.0	2.804	5.5	0.6	49.8	0.2	24.7	19.3	2.18	1.08
East Holland R.		174.7	4.309	39.5	0.6	35.0	0.4	5.6	18.8	8.96	0.84
Hawkestone Ck.		40.5	3.532	4.1	2.2	44.3	0.1	21.6	27.7	1.28	0.62
Lovers Ck.		59.4	3.268	27.3	0.2	43.8	0.0	15.4	13.3	4.94	0.75
Pefferlaw Bk.	Hamilton Harbour,	406.0	3.656	5.4	1.5	53.8	0.2	18.5	20.6	2.62	1.12
Grindstone Ck.		44.3	4.670	13.2	1.3	55.9	0.5	18.3	10.8	3.18	0.81
Redhill Ck.		81.2	2.397	63.9	0.1	25.9	0.1	1.7	8.3	17.3	1.00
	L. Ontario										
Black Ck. (Humber R.)	L. Ontario	50.6	3.011	86.5	0.0	8.5	0.0	0.8	4.2	20.16	0.95
Don R.		63.9	3.155	80.1	0.0	10.6	0.1	1.6	7.5	20.36	0.96
Etobicoke Ck.		314.6	3.505	61.4	0.0	32.6	0.2	2.5	3.4	14.35	0.72

average \pm standard error Cl⁻ concentration of 0.26 ± 0.02 mg L⁻¹ at Environment and Climate Change Canada's Egbert, ON monitoring station) relative to stream concentrations. Other sources of Cl⁻ to our study watersheds could include water softeners that Cl⁻ are transported to streams via leaky septic systems and sanitary sewers and/or through engineered connections (e.g., combined sewer overflows), and chloride-containing fertilizers (e.g., KCl) applied to agricultural land in some of the watersheds. Water softener usage occurs in some of the smaller communities in the L. Simcoe region where municipal water is supplied dominantly from groundwater; however, the strong seasonality (highest stream Cl⁻ concentrations in winter and early spring) in stream Cl⁻ dynamics in these areas suggests that the application of road salt is the primary source of Cl⁻ in surface waters (Winter et al., 2011). Likewise, the rate and frequency with which KCl is added to agricultural fields is deemed insignificant relative to road salt and hence is not quantified in this study.

A geospatial protocol was developed to distil a large quantity of provincial and municipal road salt application data to the watershed scale. Topographic watershed boundaries were derived using the 30-m digital elevation model in the Ontario Flow Assessment Tool (available online at <https://www.ontario.ca/page/watershed-flow-assessment-tool>). Geospatial road elements in the Ontario Road Network Element layer were then clipped to each watershed and the road length and number of lanes fields were multiplied to get the total lane-length (basic unit of road salt distribution) and the lane-length density (km of lane-length per km² watershed area) for each watershed. The Ontario Road Network Element layer specifies which road segments are under the jurisdiction of the province, upper-level municipalities (i.e., regions),

lower-level municipalities (i.e., cities, towns and townships), and unitary municipalities (e.g., City of Toronto, City of Hamilton). This information was used along with provincial and municipal road salt application data to designate specific road salt application rates to specific road or lane-length segments. For segments where jurisdiction information was missing or unclear, we overlaid municipal boundaries to determine which salt application rates to apply.

At the provincial level, the MTO supplied daily data on road salt (including solid, liquid and sand applications) for each road salt patrol yard (location where road salt is stored and where road salting trucks are deployed from) that fell within our study watersheds. They also provided geospatial data on the patrol area corresponding to each yard that we were able to overlay with the road network to determine which provincial roads corresponded to which yard. At the municipal level, we relied on Environment and Climate Change Canada's voluntary annual (September to May is considered one road salting season) road salt application database (L. Trudell, Environment and Climate Change Canada, pers. comm., November 7, 2014). The Environment and Climate Change Canada database contains information on the type of salt (NaCl, MgCl₂ or CaCl₂), state (solid or liquid), and type of application (straight, mixed with abrasives, or non-chloride). Across the municipalities we considered in this study, the usage of other salts besides NaCl was negligible and hence they were not considered. Liquid salt applications were also excluded from all calculations due to inconsistencies in how the data were coded; however, we estimate that liquids contribute <0.1% of the Cl⁻ applied to roadways. At all jurisdictional levels, a total annual mass of chloride-containing road salts was calculated and was then converted to a total annual mass of Cl⁻ based on proportion of

Table 2
Meteorological and hydrological characteristics of the 11 study watersheds.^a

Watershed	Receiving water body	Mean annual temperature (°C)	Mean annual precipitation (mm)	Average annual snowfall (cm)	Mean annual runoff (mm)	Runoff ratio
Beaver R.	L. Simcoe	6.7	892	157.6	326	0.37
Black R.		7.0	850	157.6	285	0.33
East Holland R.		7.2	833	122.2	254	0.31
Hawkestone Ck.		6.5	985	264.7	319	0.32
Lovers Ck.		6.8	844	264.7	303	0.36
Pefferlaw Bk.	Hamilton Harbour,	6.9	872	157.6	324	0.37
Grindstone Ck.		7.2	818	118.1	342	0.38
Redhill Ck.		7.8	905	118.1	336	0.37
Black Ck. (Humber R.)	L. Ontario	8.6	914	121.5	301	0.37
Don R.		8.0	814	131.2	317	0.39
Etobicoke Ck.		8.3	812	108.5	290	0.36

^a Mean annual temperature, average annual precipitation and mean annual runoff were computed using the Ontario Flow Assessment Tool (available online at <https://www.ontario.ca/page/watershed-flow-assessment-tool>). The tool estimates mean annual temperature and average annual precipitation for a particular watershed by interpolating between nearby Environment and Climate Change Canada (ECCC) weather stations that are part of the historic normal data from 1981 to 2010. Mean annual flow is estimated using historic Water Survey of Canada streamflow data for each watershed from January 1970 onwards and converted to runoff. Average annual snowfall (1981–2010) was obtained from the closest ECCC weather station to the respective watershed outlet (in some cases, the same ECCC station is used for multiple watersheds).

the salt's atomic weight that is made up of Cl^- . This mass was then divided by the total lane-length for the respective municipality to determine a Cl^- application rate (mass per unit lane-length). In some cases where data for a municipality were missing, a rate from an adjacent municipality was used. For each watershed, jurisdiction-based Cl^- application rates were multiplied by the proportion of the total lane-length made up by each jurisdiction and the resulting Cl^- masses were summed.

Road salt application rates by private sector contractors onto commercial, industrial, institutional and residential parking lots are not well documented despite being identified as an important source of Cl^- to watersheds (Perera et al., 2009). For this study, we used the relationship between lane-length density and mean % parking area derived for 7 of the Lake Simcoe sub-watersheds (Thompson, 2015) to estimate the total parking area in each of the study watersheds that would receive road salt applications. We then applied a 'light' per event road salt application rate of 58.1 g m^{-2} , which is likely a conservative estimate (Lembcke et al., 2017), to the annual number of events for each study watershed to arrive at an estimate of private sector Cl^- inputs.

2.2.2. Watershed chloride outputs

In-stream Cl^- loads were calculated using empirical relationships between stream Cl^- concentration and discharge. Samples of water were taken monthly or bi-weekly by the Ontario Ministry of the Environment, Conservation, and Parks, and analyzed for Cl^- concentrations. Samples were taken from years 2002–2010 for all stations, resulting in an average of 118 samples per watershed. Sample numbers per watershed ranged from 42 to 228. Discharge data were supplied for these locations from the Water Survey of Canada. The annual cycle was divided into winter (December through April) and non-winter (May through November) seasons (Long et al., 2015). Separate Cl^- concentration - discharge relationships were specified for each season according to the equations below (Cohn et al., 1992):

$$\ln([\text{Cl}]) = a \ln(Q) + b + \varepsilon \text{ during December–April} \quad (1)$$

$$\ln([\text{Cl}]) = c \ln(Q) + d + \delta \text{ during May–November} \quad (2)$$

where $[\text{Cl}]$ refers to the daily (sampled) stream Cl^- concentration, Q refers to the daily discharge, \ln refers to the natural logarithm, a , b , c , and d are parameters to be calibrated, and ε and δ refer to normally distributed, independent errors with a mean of zero. Note that the variance of the error distribution in the winter and non-winter terms was not assumed to be the same. Once calibrated, the parameters (Table S3) allow us to estimate the log-transformed concentrations for the entire period of record. The retransformation bias was addressed through an accepted Monte-Carlo method (Stow et al., 2006). Eqs. (1) and (2) were fit to all the data available between 2002 and 2010, generating daily estimates of Cl^- concentration. A draw from the residual distributions was added to the daily log transformed predictions of concentration, which was multiplied by the daily flow. Daily loads were then summed to the salting seasons described in Section 2.2.3. This Monte-Carlo approach to calculating annual Cl^- loads was iterated 1000 times. The best estimate of the actual loads was taken as the mean of the 1000 Monte-Carlo iterations (Table S4).

We validated the estimates of Cl^- load generated using Eqs. (1) and (2) with data taken from a continuous, in-situ sensor. The East Holland River site is outfitted with a probe (YSI EXO multiparameter sonde with wiped conductivity/temperature sensor) that measures conductivity continuously. A regression relationship between measured Cl^- concentrations and conductivity (Cl^- concentration = $0.28 \times$ conductivity $- 93$; $r^2 = 0.91$; $p < 0.05$) was used to transform the continuous conductivity measurements into continuous Cl^- concentration measurements (Fig. S1). Multiplying by flow gave estimates of loading,

which were aggregated to salting years. The probe-estimated annual Cl^- loads compared reasonably well with those estimated from the concentration-discharge relationships (r^2 of 0.5, slope of 1.05, $n = 4$) (Fig. S2).

2.2.3. Watershed-scale chloride retention

A Cl^- mass balance analysis was carried out for all 11 watersheds for four years (2007, 2008, 2009, 2010). Given the focus of this study, a year in our mass balance analysis begins in October and ends the following September (e.g., study year 2007 begins in October 2007 and ends in September 2008). To compute the mass of Cl^- retained in a watershed for these years, the annual mass of Cl^- outputs was subtracted from the annual mass of Cl^- inputs. To calculate an average retention for each watershed, the average mass of retained Cl^- for the 4-year period was divided by the corresponding average mass of Cl^- input and expressed as a percentage.

2.3. Watershed characterization

The potential of both watershed structural and land cover variables to explain inter-watershed differences in mean annual Cl^- retention was explored. Watershed structural variables of interest included watershed area, shape factor, mean slope, length of main channel, mean channel slope which were computed using the Ontario Flow Assessment Tool. The proportion of different land cover types (e.g., urban, agricultural, forest, wetland) in each watershed were also summarized using the Ontario Flow Assessment Tool which makes use of the 15-m Southern Ontario Land Resource Information System land cover database. Road, or lane-length, density for each watershed was computed as described in Section 2.2.1.

We also quantified the distribution of urban land cover within each watershed in terms of skewness toward or away from the watershed outlet along surface water flow paths by calculating an urban skewness index (Mineau et al., 2015). Calculation of the index was carried out using ArcHydro tools in ArcGIS (ESRI ArcGIS Desktop release 10.3.1). Urban skewness index values >1 represent urban areas that are located relatively far from the watershed's pour point (e.g., in headwater regions) and values <1 represent urban areas located relatively close to the watershed outlet.

2.4. Statistical analysis

All statistical analyses were completed using the R language and environment for statistical computing (R Core Team, 2017). The effects of watershed structural variables, land cover (including road density) and Cl^- inputs on Cl^- retention were determined individually using a regression analysis. To assess long-term Cl^- concentration trends, Mann Kendall trend (MKT) tests were performed on Ontario Provincial Water Quality Monitoring Network (PWQMN) data from 1993 to 2013 for nine of the eleven study watersheds. Two watersheds (Grindstone Ck. and Redhill Ck.) had limited long term data sets and hence were excluded from the trend analyses. Mann Kendall trend tests use non-parametric statistics to evaluate whether there are monotonic increasing or decreasing trends in a data time series (Libiseller and Grimvall, 2002) and have been widely used in water quality studies around the world (Oni et al., 2013; Worrall et al., 2004; Yenilmez et al., 2011). The MKT test is a particularly useful tool in this study due to its non-sensitivity to missing values and outliers, which are frequently found in the Ontario PWQMN datasets, and its non-sensitivity to autocorrelation in water quality data series. The MKT test was initially conducted on an annual scale and was then applied on a seasonal (salt: Oct-Apr; no-salt: May-Sep) scale using mean values of Cl^- concentration. Statistical significance was evaluated at $p < 0.05$ for all analyses.

3. Results and discussion

3.1. Inter-annual variability in watershed-scale chloride inputs, outputs and retention

Inputs and outputs of Cl^- varied inter-annually for all 11 study watersheds. Annual inputs of Cl^- were consistently lowest in 2007 and highest in 2008 (Fig. 2a). Annual outputs of Cl^- were not consistently ranked in the same order as Cl^- inputs, for example, only 6 of the 11 watersheds displayed the highest Cl^- output in 2008 and 7 showed the lowest Cl^- output in 2007 (Fig. 2b). However, on an annual basis there were clear correlations between Cl^- inputs and outputs for all years with Spearman's rho values ranging 0.855–0.927 ($p < 0.05$). Across all watersheds and all years, annual Cl^- retention (Cl^- input – Cl^- output; expressed as a % of inputs) ranged from 33% to 94% (Fig. 2c). The variance in annual Cl^- retention values between years within each watershed was between 9 and 27%; however, like the Cl^- outputs, the year with the highest Cl^- retention was not consistent across all watersheds (Fig. 2c). With only a maximum of 4 data points per watershed, the relative range (range divided by mean) was used to compare the inter-annual variability in Cl^- inputs, outputs and retention (Fig. 2c). The mean relative range decreased from 1.02 for Cl^- inputs to 0.56 for Cl^- outputs to 0.23 for Cl^- retention, suggesting a dampening effect as Cl^- moves through all the watersheds.

3.2. Drivers of watershed-scale chloride inputs

As expected given the approach for estimating watershed-scale Cl^- inputs, the mean annual mass of Cl^- applied to each watershed (Fig. 2a) is highly dependent on the density of roadways in the watershed (Fig. 3a). Once differences in application rates are accounted for, inter-watershed differences in mean annual Cl^- input reflect regional differences in meteorological conditions. In general, Cl^- inputs are higher for colder areas that receive more snowfall (Fig. 3b, c); however, it should be noted that these relationships are only applicable to watersheds in southern and south-central Ontario where straight rock salt and/or brine is used for road de-icing. The relationships cannot be extrapolated to watersheds farther north where temperatures are too cold for road salt to be effective (and hence not applied).

It should also be noted that while we are very confident in our estimates of Cl^- inputs onto major highways managed by the MTO, we are less confident with our estimates of Cl^- inputs onto regional and municipal roads because we did not have access to application rates for individual salting events like we did from the MTO. In addition, our estimates of Cl^- inputs to private areas (e.g., parking lots) are based on an empirical relationship between road density and parking lot areas for only a subset of the watersheds we studied. Related research has shown that this relationship is not consistent across regions with different land uses (Lichtblau and Oswald, *in review*). Out of concern

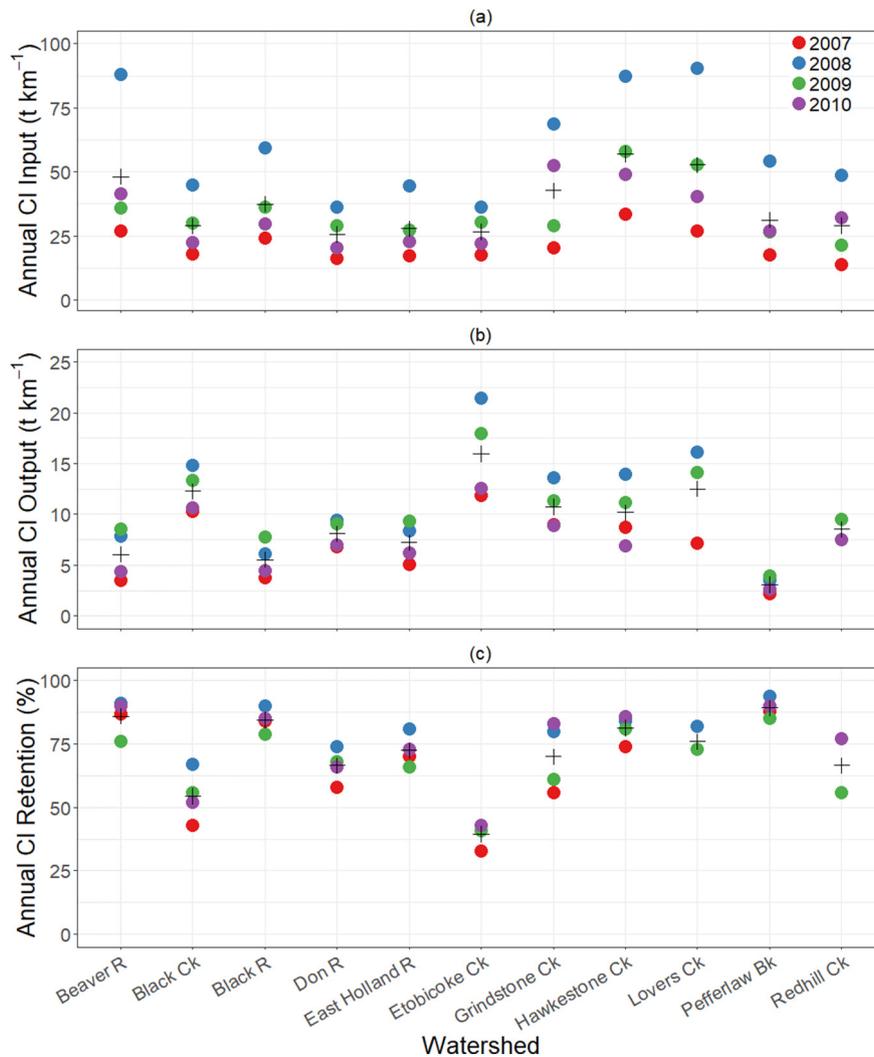


Fig. 2. Annual (2007–2010) values of watershed-scale (a) Cl^- inputs, (b) Cl^- outputs and (c) Cl^- retention. Note that Cl^- inputs and outputs are normalized to the total lane-length (in km) for each watershed. '+' denote mean annual values.

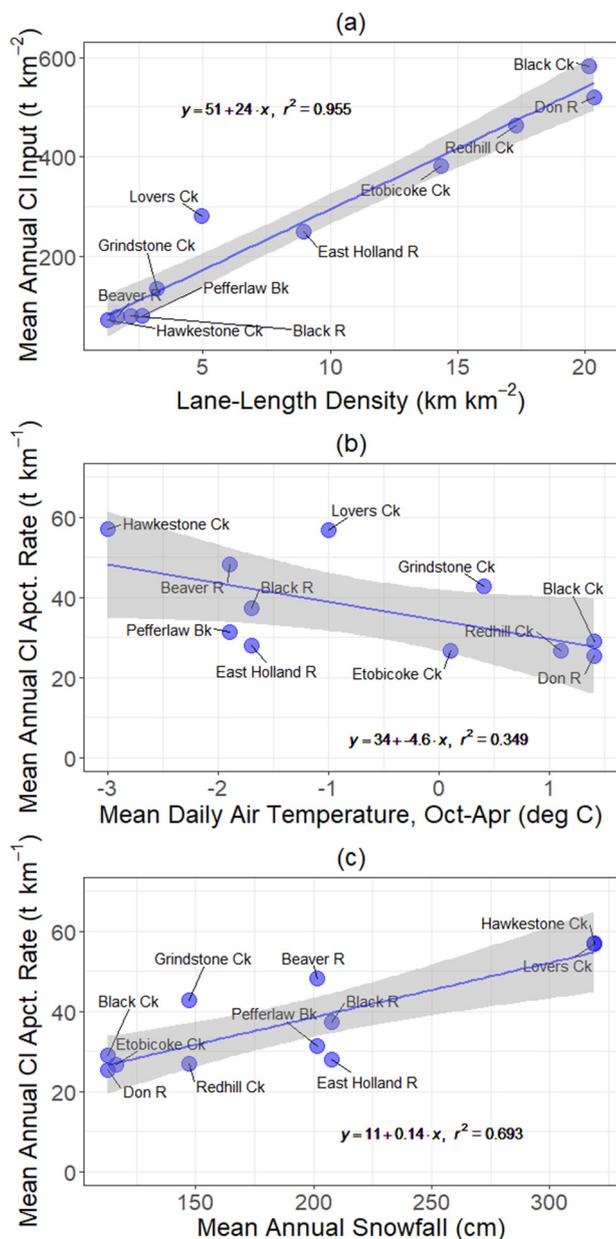


Fig. 3. Relationship across the eleven study watersheds between (a) mean annual Cl⁻ input (normalized to watershed area) and lane-length density; (b) mean annual Cl⁻ application rate and mean daily air temperature for the salting season, and (c) mean annual Cl⁻ application rate and mean annual snowfall. Mean air temperatures and snowfall are calculated for the 4 year study period. Grey shading indicates the standard error around the best fit regression line.

that we would overestimate private salt inputs to our study watersheds because of this variability, we applied a relatively ‘light’ salting rate; however, based on what we know anecdotally about private salting behaviour in our study region, it is highly likely that our private Cl⁻ inputs are underestimated. It is critical that future research quantify the variability in private salting rates and frequency to obtain more accurate estimates of watershed-scale road salt inputs.

3.3. Drivers of watershed-scale chloride retention

Previous studies focused on individual watersheds have shown that between 28 and 77% of the Cl⁻ applied as road salt is retained on an annual basis (Howard and Haynes, 1993; Kelly et al., 2008; Meriano et al., 2009; Novotny et al., 2009; Perera et al., 2010). The large range

in Cl⁻ retention across watersheds could be due to several reasons: (i) differences in how Cl⁻ inputs are estimated in different studies (e.g., inclusion, or not, of private road salt inputs), (ii) inter-annual variability in meteorological and hydrological conditions that drive Cl⁻ inputs and outputs, respectively, and (iii) differences in watershed structure, land cover characteristics, and aquifer capacity and permeability that influence the transit time of water and the timing and magnitude of Cl⁻ transport to the stream. In this study, we systematically estimated annual watershed-scale Cl⁻ inputs, outputs and retention for a 4-year period for 11 watersheds spanning a gradient of urban land cover and land use in a region where road salt is regularly applied in wintertime to maintain safe driving conditions. Our approach is unique in that we can examine the relationships between watershed characteristics and Cl⁻ retention without the confounding effects of different Cl⁻ input approaches and inter-annual variability in meteorological and hydrological conditions.

Across the 11 watersheds, we estimated mean annual Cl⁻ retention for the study period ranging from 40 to 90% (median value of 75%). Differences in Cl⁻ inputs (normalized for total lane-length in each watershed), due to varying meteorological conditions and management decisions, only explain approximately 27% of the spatial variability in watershed-scale Cl⁻ retention with a 0.6% increase in Cl⁻ retention for every 1 t increase in Cl⁻ input (Fig. 4a). This result suggests that differences in Cl⁻ retention across watersheds are not highly dependent on the rate of road salt application in a watershed, but rather on underlying hydrological, geological, and/or biogeochemical processes that control its movement from surface to stream. One limitation of this study is that we are using overly simplistic representations of the flow processes that move Cl⁻ through watersheds, for example we do not currently have information on the mean transit times of our watersheds that we could use as a predictor variable in our analysis. So, in the absence of explicit information on the transport processes occurring across our study watersheds we examined the relationships between various watershed structural variables (e.g., mean slope of watershed, mean channel slope) and mean annual Cl⁻ retention, but found that none of the relationships were statistically significant. Interestingly, the three watersheds with dominantly high permeability surficial geology (see Table S1) were all at the high end of our mean annual Cl⁻ retention estimates. The low and low-medium permeability watersheds were spread across our Cl⁻ retention gradient. If surficial geology were the sole driver of watershed Cl⁻ retention, then it stands to reason that permeability and watershed Cl⁻ retention would be positively related, however, this is not what our data suggest. We then focused on land cover characteristics as potential controls on Cl⁻ retention and found that lane-length density ($r^2 = 0.55$; Fig. 4b) was a strong predictor of the variation in Cl⁻ retention across watersheds. Unexpectedly though, road density and Cl⁻ retention were negatively correlated. We suggest two possible explanations for this relationship: (1) more urbanized watersheds (i.e., ones with higher lane-length density) are more likely to have their impervious surfaces directly connected to the stream via storm sewers, thereby minimizing opportunities for saline surface water to infiltrate into the ground and percolate to groundwater and (2) more urbanized watersheds are more likely to be approaching a steady-state in terms of Cl⁻ movement through the subsurface. Currently we do not have access to spatially explicit storm sewer data for all 11 study watersheds to test the first hypothesis listed above; however, we believe this line of inquiry is critical for understanding the dominant transport processes that move Cl⁻ from impervious surfaces to the stream. With respect to the second hypothesis, we strongly advocate for consistent monitoring of groundwater Cl⁻ concentrations, especially in urbanizing watersheds, that could be used to explore long-term trends.

Although mean annual Cl⁻ retention was strongly related to the proportion of urban land cover in each watershed and overall lane-length density, there was still considerable unexplained variability in Cl⁻ retention especially in the less urbanized watersheds. In the absence of

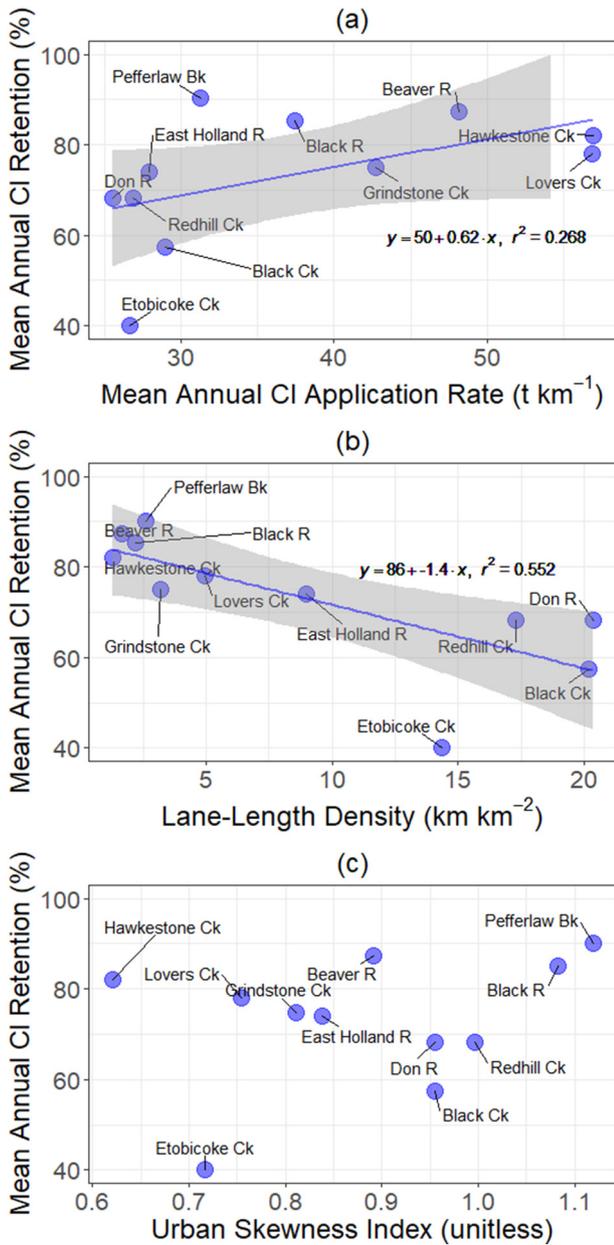


Fig. 4. Relationship across the eleven study watersheds between mean annual Cl^- retention and (a) mean annual Cl^- input (normalized to total lane-length per watershed); (b) watershed lane-length density, and (c) the urban land cover skewness index. Grey shading indicates the standard error around the best fit regression line (when significant).

mean transit time and storm sewer network data for each watershed we decided to examine the effect of urban land cover position on mean annual Cl^- retention. We expected that watersheds with urban land cover distributed farther away from the stream outlet would result in chloride-laden urban runoff travelling over a longer distance with more potential for losses to groundwater via exchange in the stream hyporheic zone. On its own we found that the relationship between the skewness index of urban land cover and mean annual Cl^- retention was not statistically significant (Fig. 4c). However, when the urban land cover skewness index was included in a multiple linear regression with lane-length density, we were able to explain approximately 72% of the variability in mean annual Cl^- retention (Mean Annual Cl^- Retention (in %) = -1.51 Lane-Length Density (in km km^{-2}) + 39.6 Urban Skewness Index (unitless) + 51.5 ; $r^2 = 0.72$; $p < 0.05$). The importance of the urban skewness index in this relationship suggests that the transit time

of water from points of surface road salt application to the stream is an important determinant of overall watershed-scale Cl^- retention.

It is important to note that the Etobicoke Creek watershed is a consistent outlier in all the above relationships. This may be a result of not including the application of de-icing agents at the Pearson International Airport (we estimate that approximately 16 km^2 of the airport property overlaps with the Etobicoke Creek watershed, which represents 7.4% of the total watershed area) in our Cl^- input estimates for this watershed.

3.4. Long-term chloride concentration trends

Only 9 of the 11 study watersheds had sufficiently long stream Cl^- concentration datasets that could be used for mean annual and seasonal Cl^- concentration trend analysis. Mann-Kendall trend tests indicated significant increasing trends in mean annual stream Cl^- concentrations in 5 of the 9 streams (Pefferlaw Bk., Black R., Lovers Ck., East Holland R., and Don R.; Table 3). Two seasons (May – Sep: no road salt; Oct – Apr: road salt) were used for a seasonal Mann Kendall test. During the road salting season, 4 of the 9 streams had significant increasing trends in Cl^- concentrations (Pefferlaw Bk., Black R., Lovers Ck., and East Holland R.; Table 3). During the non- road salt season 5 of the 9 watersheds had increasing Cl^- concentration trends (Pefferlaw Bk., Black R., Lovers Ck., East Holland R., and Don R.; Table 3). It is important to note that the lack of an increasing trend in Cl^- concentration should not be interpreted as evidence that Cl^- loading has not been elevated due to de-icing activities. No trend in stream Cl^- concentrations could indicate that Cl^- inputs have remained stable over time due to no new urban growth (e.g., in the highly urbanized Etobicoke Creek and Black Creek watersheds) or a reduction in Cl^- inputs in response to urban growth and growing awareness of the environmental impacts of road salt.

A recent study reported that long-term changes in stream Cl^- concentration were significantly higher for more urbanized watersheds (Stets et al., 2018); however, in this study correlations between current lane-length density and the long-term rate of change in stream Cl^- concentration were negative, but not statistically significant, for salting season (Spearman's $\rho = -0.200$, $p = 0.606$) and there was no relationship for the non-salting season. Exploration of the relationship between the long-term rate of change in stream Cl^- concentrations and the rate of change in lane-length density (or urban land cover) over the same period was beyond the scope of this study; however, we believe it is a critical line of inquiry for future research. Our trend analysis may have been limited by the relatively short PWQMN Cl^- datasets available for Hawkstone Ck. and Etobicoke Ck., which were the only two watersheds that showed decreasing trends across seasons. We also examined the relationship between mean annual Cl^- retention and the rate of

Table 3

Summary statistics for the seasonal Mann-Kendall trend analysis of stream Cl^- concentrations including rate of change in Cl^- concentrations ($\text{mg L}^{-1} \text{y}^{-1}$) and p-value.^a

Watershed	Period	Seasonal Trends		Annual Trend
		Road Salt (Oct–Apr)	No Road Salt (May–Sept)	
Beaver R.	1994–2013	1.4, $p=0.34$	1.0, $p=0.14$	1.4, $p=0.17$
Black R.	1993–2013	3.9, $p<0.05$	5.0, $p<0.05$	4.6, $p<0.05$
East Holland R.	1993–2013	2.8, $p<0.05$	3.3, $p<0.05$	3.5, $p<0.05$
Hawkstone Ck.	2005–2013	-0.62, $p=0.53$	-1.5, $p=0.14$	-1.7, $p=0.09$
Lovers Ck.	1993–2013	4.9, $p<0.05$	4.4, $p<0.05$	4.9, $p<0.05$
Pefferlaw Bk.	1993–2013	4.3, $p<0.05$	4.9, $p<0.05$	4.6, $p<0.05$
Grindstone Ck.	Limited long-term data.			
Redhill Ck.	Limited long-term data.			
Black Ck.	1993–2013	1.1, 0.25	1.0, $p=0.30$	1.3, $p=0.20$
Don R.	1993–2013	1.0, $p=0.31$	3.0, $p<0.05$	2.3, $p<0.05$
Etobicoke Ck.	2002–2013	-1.4, $p=0.17$	-0.69, $p=0.49$	-1.2, $p=0.23$

^a Note that trend analysis was only performed on 9 of the 11 watersheds due to a lack of long-term data for Grindstone Ck. and Redhill Ck. Shaded cells indicate that no significant trend was found.

change in stream Cl^- concentrations. Given the negative relationship noted above, we expected a positive relationship between Cl^- retention and changes in stream Cl^- ; however, in both seasons, the relationship was positive, but not statistically significant (salting season: Spearman's $\rho = 0.583$, $p = 0.099$; non-salting season: Spearman's $\rho = 0.452$, $p = 0.222$). Based on these results, the influence of land cover and the current magnitude of watershed Cl^- retention on stream Cl^- trends is still not clear.

3.5. Conceptual model of watershed chloride transport

Previous studies have shown a positive relationship between the extent of urban land cover in a watershed and average stream Cl^- concentrations (e.g., Betts et al., 2014; Corsi et al., 2015; Winter et al., 2011); however, the results of our study show that this relationship does not extend to the magnitude of Cl^- retention in the watershed. Rather, annual Cl^- retention is higher for less urbanized watersheds. In many of the rural and urbanizing watersheds we studied, extensive storm sewer networks are not present and hence the directly connected impervious area in the watershed is a relatively small proportion of the total impervious area. Assuming that the movement of Cl^- along subsurface pathways is a dominant factor contributing to long-term Cl^- retention, the extent to which meltwater and precipitation running off impervious surfaces is able to infiltrate adjacent pervious surfaces (as opposed to being piped directly to the stream) may be important to consider in future studies.

Our study utilized a simple annual mass balance approach (Fig. 5a) similar to previous studies (Godwin et al., 2003; Kelly et al., 2008) to explore the spatial variability in watershed-scale Cl^- .

retention; however, the fractions of annual Cl^- inputs that follow slow subsurface pathways versus faster surface, or piped, pathways to

the stream are not specified. Hence, our approach to estimating Cl^- inputs does not reflect empirical data on the proportion of total impervious area in a catchment that is directly connected to the stream. Also, our study only considers Cl^- inputs from road salt, but we realize that this approach may not be appropriate for other regions where, for example, road salt is not as ubiquitous and/or water softener usage is more extensive. The expanded conceptual model in Fig. 5b still reflects the need to consider all Cl^- sources, but also includes representation of the 'flowpath division' (i.e., slow subsurface pathways versus faster surface pathways) that occurs at the surface depending on the extent of storm sewer infrastructure. Previous studies focused on assessing the vulnerability of municipal supply wells have explicitly considered these pathways (Betts et al., 2015; Salek et al., 2018), however, mass balance studies focused on untangling legacy Cl^- effects from stream Cl^- dynamics have not. Our expanded conceptual model also goes beyond only considering subsurface storage of Cl^- in groundwater to also consider Cl^- retention in soil water (Kincaid and Findlay, 2009), the hyporheic zone and stormwater control features (Casey et al., 2013; Snodgrass et al., 2017). New research that quantifies the magnitude and timing of Cl^- retention and release from all these hydrologic compartments is needed to develop a process-based understanding of the spatial variability in watershed-scale Cl^- retention and to predict legacy Cl^- effects on future stream Cl^- export. This research should include analyses of the transit time of water through individual hydrologic compartments and entire watersheds to better understand the range in legacy Cl^- effects across regions that receive road salt inputs.

4. Conclusions

The application of road salt to maintain safe winter travel conditions leads to the accumulation of Cl^- in aquifers and elevated Cl^-

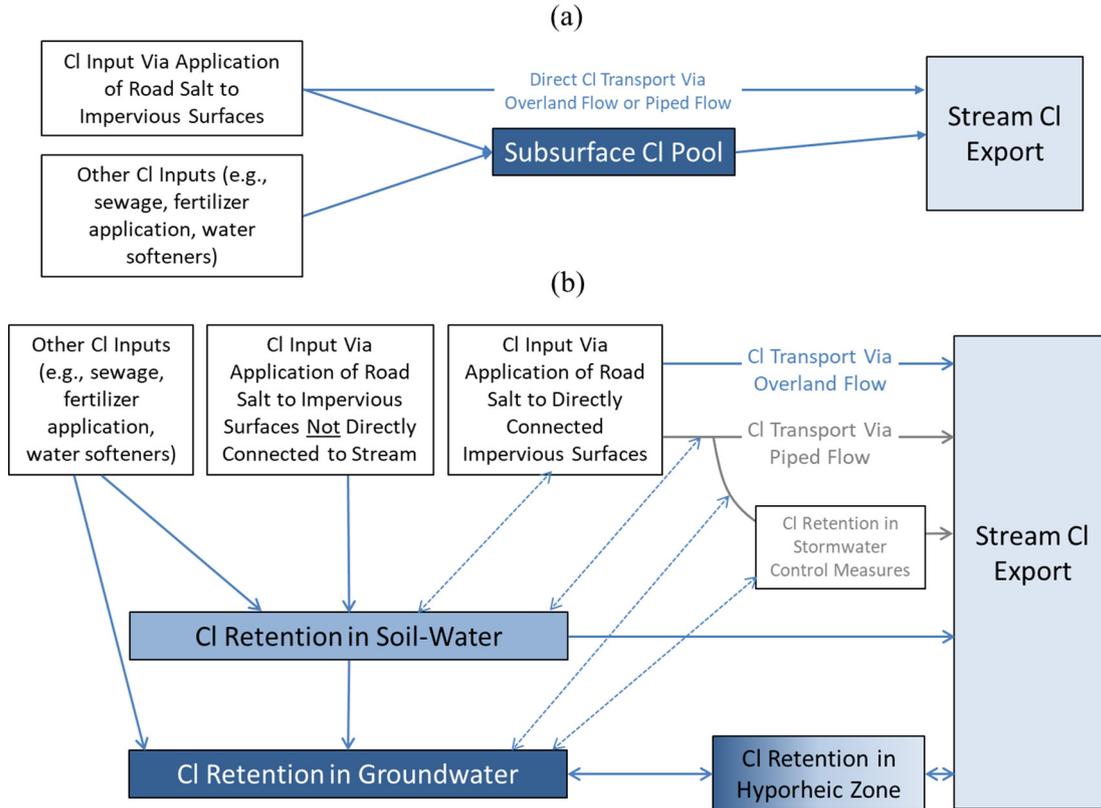


Fig. 5. (a) Example of simple conceptual model of watershed Cl^- sources, stores and pathways; (b) Expanded conceptual model of watershed Cl^- sources, stores and pathways, which differentiates road salt inputs to impervious areas that are not directly connected to the stream and hence move to the stream along subsurface flow pathways. The expanded model also includes multiple potential compartments for Cl^- retention. Dashed lines represent Cl^- transport into and out of the subsurface through cracked pavement, leaky storm sewer pipes and stormwater control measures (e.g., stormwater management ponds).

concentrations in stream, rivers and lakes. Stream Cl^- concentrations typically correlate positively with indices of urbanization (e.g., road density); however, it was previously unclear how landscape characteristics influenced watershed Cl^- retention. Accordingly, this study sought to answer three inter-related research questions: (1) How spatially and temporally variable is annual, watershed-scale Cl^- retention among watersheds spanning a gradient of urbanization? (2) Do watershed structural and/or land cover characteristics explain the spatial variability in annual, watershed-scale Cl^- retention? (3) Is there a relationship between the magnitude of watershed-scale Cl^- retention and the persistence of chronic stream Cl^- concentrations into the growing season? This research shows that spatial variability in annual watershed Cl^- retention among watersheds is larger than inter-annual variability for any individual watershed. While the watershed structural characteristics that we examined did not significantly affect mean annual Cl^- retention, we found that the spatial distribution and extent of urban land cover did. Interestingly, mean annual Cl^- retention is largest for rural watersheds and decreases steadily with an increase in urban land cover and more Cl^- is retained in watersheds with urban land cover located more distant from the watershed outlet. While some of the watersheds we studied showed long-term increasing Cl^- trends in both the salting and non-salting seasons, there was no clear relationship to urban land cover or Cl^- retention. The results of this research suggest that the hydrologic processes that transport Cl^- from paved surfaces to streams vary depending of the level and spatial distribution of urbanization, and we hypothesize, the extent of impervious areas that are directly connected to streams via storm sewer infrastructure. While there is no doubt that the transit time of water through a watershed will influence the timing and magnitude of Cl^- retention and release, the locations where Cl^- is applied, the manner in which these locations are hydrologically connected to waterways and water bodies (e.g., directly connected via storm sewer pipes, connected via groundwater flow), and the timing of Cl^- retention in different hydrologic compartments (e.g., stormwater management ponds) are critical pieces of information to ascertain. Our conceptual model detailing these processes and flow pathways, along with other potential stores of legacy Cl^- , provides a foundation for improving our understanding of, and ability to model, watershed Cl^- dynamics.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.10.242>.

References

- Bester, M.L., Frind, E.O., Molson, J.W., Rudolph, D.L., 2006. Numerical investigation of road salt impact on an urban wellfield. *Ground Water* 44, 165–175. <https://doi.org/10.1111/j.1745-6584.2005.00126.x>.
- Betts, A.R., Gharabaghi, B., McBean, E.A., 2014. Salt vulnerability assessment methodology for urban streams. *J. Hydrol.* 517, 877–888. <https://doi.org/10.1016/j.jhydrol.2014.06.005>.
- Betts, A., Gharabaghi, B., McBean, E., Levison, J., Parker, B., 2015. Salt vulnerability assessment methodology for municipal supply wells. *J. Hydrol.* 531, 523–533. <https://doi.org/10.1016/j.jhydrol.2015.11.004>.
- Casey, R.E., Lev, S.M., Snodgrass, J.W., 2013. Stormwater ponds as a source of long-term surface and ground water salinisation. *Urban Water J.* 10, 145–153. <https://doi.org/10.1080/1573062X.2012.716070>.
- CCME, 2011. *Canadian Water Quality Guidelines for the Protection of Aquatic Life: Chloride*. Winnipeg.
- Chapra, S.C., Dove, A., Rockwell, D.C., 2009. Great Lakes chloride trends: long-term mass balance and loading analysis. *J. Great Lakes Res.* 35, 272–284. <https://doi.org/10.1016/j.jglr.2008.11.013>.
- Chapra, S.C., Dove, A., Warren, G.J., 2012. Long-term trends of Great Lakes major ion chemistry. *J. Great Lakes Res.* 38, 550–560. <https://doi.org/10.1016/j.jglr.2012.06.010>.
- Cohn, T.A., Caulder, D.L., Gilroy, E.J., Zynjuk, L.D., Summers, R.M., 1992. The validity of a simple statistical-model for estimating fluvial constituent loads—an empirical study involving nutrient loads entering Chesapeake Bay. *Water Resour. Res.* 28, 2353–2363.
- Corsi, S.R., De Cicco, L.A., Lutz, M.A., Hirsch, R.M., 2015. River chloride trends in snow-affected urban watersheds: increasing concentrations outpace urban growth rate and are common among all seasons. *Sci. Total Environ.* 508, 488–497. <https://doi.org/10.1016/j.scitotenv.2014.12.012>.
- Daley, M.L., Potter, J.D., McDowell, W.H., 2009. Salinization of urbanizing New Hampshire streams and groundwater: effects of road salt and hydrologic variability. *J. North Am. Benthol. Soc.* 28, 929–940. <https://doi.org/10.1899/09-052.1>.
- Dugan, H.A., Bartlett, S.L., Burke, S.M., Doubek, J.P., Krivak-Tetley, F.E., Skaff, N.K., Summers, J.C., Farrell, K.J., McCullough, I.M., Morales-Williams, A.M., Roberts, D.C., Ouyang, Z., Scordo, F., Hanson, P.C., Weathers, K.C., 2017. Salting our freshwater lakes. *Proc. Natl. Acad. Sci. U. S. A.* 114, 4453–4458. <https://doi.org/10.1073/pnas.1620211114>.
- Elphick, J.R., Bergh, K.D., Bailey, H.C., 2011. Chronic toxicity of chloride to freshwater species: effects of hardness and implications for water quality guidelines. *Environ. Toxicol. Chem.* 30, 239–246. <https://doi.org/10.1002/etc.365>.
- Environment Canada, E.P.S., 2004. *Code of Practice for the Environmental Management of Road Salts*. Ottawa, ON.
- Evans, M., Frick, C., 2001. *The Effects of Road Salts on Aquatic Ecosystems*. Environ. Canada – Natl. Water Res. Inst.
- Gabor, R.S., Hall, S.J., Eiriksson, D.P., Jameel, Y., Millington, M., Stout, T., Barnes, M.L., Gelderloos, A., Tennant, H., Bowen, G.J., Neilson, B.T., Brooks, P.D., 2017. Persistent urban influence on surface water quality via impacted groundwater. *Environ. Sci. Technol.* <https://doi.org/10.1021/acs.est.7b00271> (acs.est.7b00271).
- Gardner, K.M., Royer, T.V., 2010. Effect of road salt application on seasonal chloride concentrations and toxicity in south-central Indiana streams. *J. Environ. Qual.* 39, 1036–1042. <https://doi.org/10.2134/jeq2009.0402>.
- Gillis, P.L., 2011. Assessing the toxicity of sodium chloride to the glochidia of freshwater mussels: implications for salinization of surface waters. *Environ. Pollut.* 159, 1702–1708. <https://doi.org/10.1016/j.envpol.2011.02.032>.
- Godwin, K.S., Hafner, S.D., Buff, M.F., 2003. Long-term trends in sodium and chloride in the Mohawk River, New York: the effect of fifty years of road-salt application. *Environ. Pollut.* 124, 273–281. [https://doi.org/10.1016/S0269-7491\(02\)00481-5](https://doi.org/10.1016/S0269-7491(02)00481-5).
- Howard, K.W.F.F., Haynes, J., 1993. Groundwater contamination due to road de-icing chemicals – salt balance implications. *Geosci. Can.* 20, 1–8.
- Jackson, R.B., Jobbágy, E.G., 2005. From icy roads to salty streams. *Proc. Natl. Acad. Sci. U. S. A.* 102, 14487–14488. <https://doi.org/10.1073/pnas.0507389102>.
- Kaushal, S.S., Groffman, P.M., Likens, G.E., Belt, K.T., Stack, W.P., Kelly, V.R., Band, L.E., Fisher, G.T., 2005. Increased salinization of fresh water in the northeastern United States. *Proc. Natl. Acad. Sci. U. S. A.* 102, 13517–13520. <https://doi.org/10.1073/pnas.0506414102>.
- Kelly, V.R., Lovett, G.M., Weathers, K.C., Findlay, S.E.G., Strayer, D.L., Burns, D.J., Likens, G.E., 2008. Long-term sodium chloride retention in a rural watershed: legacy effects of road salt on streamwater concentration. *Environ. Sci. Technol.* 42, 410–415. <https://doi.org/10.1021/es071391l>.
- Kincaid, D.W., Findlay, S.E.G., 2009. Sources of elevated chloride in local streams: groundwater and soils as potential reservoirs. *Water Air Soil Pollut.* 203, 335–342. <https://doi.org/10.1007/s11270-009-0016-x>.
- Ledford, S.H., Lautz, L.K., Stella, J.C., 2016. Hydrogeologic processes impacting storage, fate, and transport of chloride from road salt in urban riparian aquifers. *Environ. Sci. Technol.* 50, 4979–4988. <https://doi.org/10.1021/acs.est.6b00402>.
- Lembcke, D., Thompson, B., Read, K., Betts, A., Singaraja, D., 2017. Reducing road salt application by considering winter maintenance needs in parking lot design. *J. Green Build.* 12, 1–12. <https://doi.org/10.3992/1943-4618.12.2.1>.
- Libiseller, C., Grimvall, A., 2002. Performance of partial Mann-Kendall tests for trend detection in the presence of covariates. *Environmetrics* 13, 71–84. <https://doi.org/10.1002/env.507>.
- Löfgren, S., 2001. The chemical effects of deicing salt on soil and stream water of five catchments in southeast Sweden. *Water Air Soil Pollut.* 130, 863–868. <https://doi.org/10.1023/A:1013895215558>.
- Long, T., Wellen, C., Arhonditsis, G., Boyd, D., Mohamed, M., O'Connor, K., 2015. Estimation of tributary total phosphorus loads to Hamilton Harbour, Ontario, Canada, using a series of regression equations. *J. Great Lakes Res.* 41, 780–793. <https://doi.org/10.1016/j.jglr.2015.04.001>.
- Marsalek, J., 2003. Road salts in urban stormwater: an emerging issue in stormwater management in cold climates. *Water Sci. Technol.* 48, 61–70.
- Mayer, T., Snodgrass, W.J., Morin, D., 1999. Spatial characterization of the occurrence of road salts and their environmental concentrations as chlorides in Canadian surface waters and benthic sediments. *Water Qual. Res. J. Can.* 34, 545–574.
- Meriano, M., Eyles, N., Howard, K.W.F., 2009. Hydrogeological impacts of road salt from Canada's busiest highway on a Lake Ontario watershed (Frenchman's Bay) and lagoons, City of Pickering. *J. Contam. Hydrol.* 107, 66–81. <https://doi.org/10.1016/j.jconhyd.2009.04.002>.

- Mineau, M.M., Wollheim, W.M., Stewart, R.J., 2015. An index to characterize the spatial distribution of land use within watersheds and implications for river network nutrient removal and export. *Geophys. Res. Lett.* 42, 6688–6695. <https://doi.org/10.1002/2015GL064965>. Received.
- Mueller, B., Gaechter, R., 2012. Increasing chloride concentrations in Lake Constance: characterization of sources and estimation of loads. *Aquat. Sci.* 74, 101–112. <https://doi.org/10.1007/s00027-011-0200-0>.
- Mullaney, J.R., Lorenz, D.L., Arntson, A.D., 2009. Chloride in groundwater and surface water in areas underlain by the glacial aquifer system, northern United States. *US Geol. Surv.* 41.
- Novotny, E.V., Murphy, D., Stefan, H.G., 2008. Increase of urban lake salinity by road deicing salt. *Sci. Total Environ.* 406, 131–144. <https://doi.org/10.1016/j.scitotenv.2008.07.037>.
- Novotny, E.V., Sander, A.R., Mohseni, O., Stefan, H.G., 2009. Chloride ion transport and mass balance in a metropolitan area using road salt. *Water Resour. Res.* 45, W12410. <https://doi.org/10.1029/2009WR008141>.
- Oni, S.K., Futter, M.N., Bishop, K., Köhler, S.J., Ottosson-Löfvenius, M., Laudon, H., 2013. Long-term patterns in dissolved organic carbon, major elements and trace metals in boreal headwater catchments: trends, mechanisms and heterogeneity. *Biogeosciences* 10, 2315–2330. <https://doi.org/10.5194/bg-10-2315-2013>.
- Perera, N., Gharabaghi, B., Noehammer, P., 2009. Stream chloride monitoring program of city of Toronto: implications of road salt application. *Water Qual. Res. J. Can.* 44, 132–140.
- Perera, N., Gharabaghi, B., Noehammer, P., Kilgour, B., 2010. Road salt application in Highland Creek watershed, Toronto, Ontario – chloride mass balance. *Water Qual. Res. J. Can.* 45, 451–461.
- Perera, N., Gharabaghi, B., Howard, K., 2013. Groundwater chloride response in the Highland Creek watershed due to road salt application: a re-assessment after 20 years. *J. Hydrol.* 479, 159–168. <https://doi.org/10.1016/j.jhydrol.2012.11.057>.
- Pilon, P., Howard, K.W.F., 1987. Contamination of sub-surface waters by road de-icing chemicals. *Water Pollut. Res. J. Can.* 22, 157–171.
- Price, J.R., Szymanski, D.W., 2013. The effects of road salt on stream water chemistry in two small forested watersheds, Catoctin Mountain, Maryland, USA. *Aquat. Geochem.* 20, 243–265. <https://doi.org/10.1007/s10498-013-9193-8>.
- R Core Team, 2017. R: A Language and Environment for Statistical Computing.
- Ramakrishna, D.M., Viraraghavan, T., 2005. Environmental impact of chemical deicers - a review. *Water Air Soil Pollut.* 166, 49–63. <https://doi.org/10.1007/s11270-005-8265-9>.
- Robinson, H.K., Hasenmueller, E.A., 2017. Transport of road salt contamination in karst aquifers and soils over multiple timescales. *Sci. Total Environ.* 603, 94–108. <https://doi.org/10.1016/j.scitotenv.2017.05.244>.
- Salek, M., Levison, J., Parker, B., Gharabaghi, B., 2018. CAD-DRASTIC: chloride application density combined with DRASTIC for assessing groundwater vulnerability to road salt application. *Hydrogeol. J.*, 1–15. <https://doi.org/10.1007/s10040-018-1801-7>.
- Schweiger, A.H., Audorff, V., Beierkuhnlein, C., 2015. Salt in the wound: the interfering effect of road salt on acidified forest catchments. *Sci. Total Environ.* 532, 595–604. <https://doi.org/10.1016/j.scitotenv.2015.06.034>.
- Sibert, R.J., Koretsky, C.M., Wyman, D.A., 2015. Cultural meromixis: effects of road salt on the chemical stratification of an urban kettle lake. *Chem. Geol.* 395, 126–137. <https://doi.org/10.1016/j.chemgeo.2014.12.010>.
- Snodgrass, J.W., Moore, J., Lev, S.M., Casey, R.E., Ownby, D.R., Flora, R.F., Izzo, G., 2017. Influence of modern stormwater management practices on transport of road salt to surface waters. *Environ. Sci. Technol.* 51, 4165–4172. <https://doi.org/10.1021/acs.est.6b03107>.
- Sonzogni, W.C., Richardson, W., Rodgers, P., Monteith, T.J., 1983. Chloride pollution of the Great Lakes. *Water Pollut. Control Fed.* 55, 513–521.
- Stets, E.G., Lee, C.J., Lytle, D.A., Schock, M.R., 2018. Increasing chloride in rivers of the conterminous U.S. and linkages to potential corrosivity and lead action level exceedances in drinking water. *Sci. Total Environ.* 613–614, 1498–1509. <https://doi.org/10.1016/j.scitotenv.2017.07.119>.
- Stow, C.A., Reckhow, K.H., Qian, S.S., 2006. A Bayesian approach to retransformation bias in transformed regression. *Ecology* 87, 1472–1477. [https://doi.org/10.1890/0012-9658\(2006\)87\[1472:ABATRB\]2.0.CO;2](https://doi.org/10.1890/0012-9658(2006)87[1472:ABATRB]2.0.CO;2).
- Thompson, B., 2015. *The Identification of Salt Vulnerable Areas in the Lake Simcoe Watershed*. Newmarket.
- Thunqvist, E.-L., 2004. Regional increase of mean chloride concentration in water due to the application of deicing salt. *Sci. Total Environ.* 325, 29–37. <https://doi.org/10.1016/j.scitotenv.2003.11.020>.
- Wallace, A.M., Biastoch, R.G., 2016. Detecting changes in the benthic invertebrate community in response to increasing chloride in streams in Toronto, Canada. *Freshw. Sci.* 35, 353–363. <https://doi.org/10.1086/685297>.
- Winter, J.G., Landre, A., Lembcke, D., O'Connor, E.M., Young, J.D., 2011. Increasing chloride concentrations in Lake Simcoe and its tributaries. *Water Qual. Res. J. Can.* 46, 157. <https://doi.org/10.2166/wqjrc.2011.124>.
- Winter, J.G., Howell, E.T., Nakamoto, L.K., 2012. Trends in nutrients, phytoplankton, and chloride in nearshore waters of Lake Ontario: synchrony and relationships with physical conditions. *J. Great Lakes Res.* 38, 124–132. <https://doi.org/10.1016/j.jglr.2011.09.003>.
- Worrall, F., Harriman, R., Evans, C.D., Watts, C.D., Adamson, J., Neal, C., Tipping, E., Burt, T., Grieve, I., Monteith, D., Naden, P.S., Nisbet, T., Reynolds, B., Stevens, P., 2004. Trends in dissolved organic carbon in UK rivers and lakes. *Biogeochemistry* <https://doi.org/10.1007/s10533-004-8131-7>.
- Yenilmez, F., Keskin, F., Aksoy, A., 2011. Water quality trend analysis in Eymir Lake, Ankara. *Phys. Chem. Earth* 36, 135–140. <https://doi.org/10.1016/j.pce.2010.05.005>.