



Local factors and sources affecting freshwater chloride concentrations in the Toronto region

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ABSTRACT

Increasing chloride concentrations in freshwater streams throughout many areas of North America have raised concern over freshwater salinization. Road salt has been implicated; however, chloride source identification is lacking in the Toronto region. We assessed trends in chloride concentrations in streams and groundwater between 2000 and 2021 within the Toronto region and identified factors contributing to trends. Chloride concentrations increased in 36 of 47 streams and in 5 of 13 groundwater wells. There were no significant relationships between changes in stream chloride concentrations and changes in winter climatic conditions over the study period; however, changes in stream chloride concentrations were positively related to changes in road density. Chloride:bromide ratios indicated that road salt and/or septic effluent was the dominant source of chloride in streams. Inputs varied throughout the year with road salt and/or septic effluent having a higher proportion of inputs during the salting season compared to the non-salting season where a higher proportion of inputs were from basin brines and/or animal waste, landfill leachate, and pristine aquifer. Commercial, industrial, institutional, and medium density residential land uses were also positively correlated with stream chloride. Parking lot cover increased in several catchments suggesting that these too may contribute to trends. These results highlight the importance of continued and enhanced investment in long-term monitoring of freshwater ecosystems. It also highlights the need for urgent action to better control and monitor road salt usage by public and private applicators since urban growth continues to drive increasing chloride trends.

1. Introduction

Chloride concentrations in freshwater streams (Corsi et al., 2015; Daley et al., 2009; Gardner and Royer, 2010; Mazumder et al., 2021) and lakes (Chapra et al., 2009; Dugan et al., 2017; Dugan and Rock, 2021; Novotny et al., 2009; Winter et al., 2011) continue to rise throughout many areas of North America. Increasing concentrations have led to concerns over freshwater salinization of both surface water and groundwater (Howard and Haynes, 1993; Ledford et al., 2016; Mackie et al., 2021; Meriano et al., 2009; Oswald et al., 2019). Freshwater salinization syndrome refers to the salinization and alkalization of

freshwater caused by atmospheric deposition, geology, and land use resulting in impacts on aquatic life, infrastructure, contaminant mobilization, carbonate transport, and ocean acidification (Kaushal et al., 2018). Concerns over chloride in the Great Lakes have been recognized in the Canada-Ontario Agreement on Great Lakes Water Quality and Ecosystem Health (MECP and ECCO, 2021). This agreement outlines efforts to restore, protect, and conserve the Great Lakes basin based on obligations under the 1972 Great Lakes Water Quality Agreement.

Chloride can be toxic to aquatic organisms with acute effects (e.g., death) above 640 mg/L and chronic effects (e.g., lower growth and reproduction) above 120 mg/L (CCME, 2011). However, recent research

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suggests that these thresholds may not sufficiently protect aquatic life since toxicity studies often do not accurately reflect environmental conditions (Arnott et al., 2023; Dugan and Arnott, 2022). Chloride can have numerous physical, chemical, and biological effects on ecosystems (Dugan and Arnott, 2022). Physical and chemical impacts include altered mixing and thermal stratification of the water column (Dugan and Arnott, 2022; Evans and Frick, 2001), increased transport of particulate-bound metals such as copper, cadmium, lead, and zinc to streams (Reinosdotter and Viklander, 2007; Mayer et al., 2008; Findlay and Kelly, 2011), and increasing eutrophication through phosphorus mobilization (Radosavljevic et al., 2022). Aquatic species affected by chloride include wetland plants, zooplankton, aquatic insects, mussels, amphibians, and fish (Findlay and Kelly, 2011; Todd and Kaltenecker, 2012; Szocs et al., 2014; Wallace and Biastoch, 2016; Hintz et al., 2017; Hintz and Relyea, 2017). Chloride impacts individuals by causing problems with osmoregulation, decreased birth and growth rates, behavioural changes, and death (Denoeil et al., 2010; CCME, 2011). Impacts on individual species also cascade to impact entire populations, communities, and food webs (CCME, 2011; Hintz et al., 2017).

Chloride-based winter salts dissolve in water and their constituent ions (e.g., Na^+ and Cl^-) can undergo ion exchange reactions with soils (e.g., Na^+) or behave more conservatively (e.g., Cl^-) and be transported to surface waters and groundwater (Bastviken et al., 2006; Ramakrishna and Viraraghavan, 2005). Transport of chloride to surface waters can result in exceedances of the Canadian Water Quality Guidelines (CWQGs) for the protection of aquatic life for chloride (CCME, 2011), thereby putting aquatic ecosystems at risk of reduced abundance and diversity. The accumulation of chloride in the subsurface is equally concerning given the importance of groundwater for sustaining stream baseflow in the growing season, the relatively slow velocity of groundwater flow, and hence the potential for significant lags between decreases in winter salt application and decreasing stream chloride concentration trends. These concerns highlight a need to better understand the sources and main drivers of observed increasing chloride concentrations in streams and groundwater to inform approaches to manage chloride and mitigate chloride pollution.

In addition to chloride-based deicers (e.g., road salt), there are other chloride sources including erosion and atmospheric deposition (natural sources), wastewater, water softeners, agricultural fertilizers, animal waste, and industry (anthropogenic sources; Gutchess et al., 2016). The ratios of numerous water quality parameters have been used as a technique to describe and differentiate the origin of source waters (Dror et al., 1999; Alcalá and Custodio, 2008; McArthur et al., 2018; Yolcubal et al., 2019; Oberhelman and Peterson, 2020). The chloride to bromide mass ratio was initially developed for determining the origins of groundwater and has been applied in numerous studies (e.g., Davis et al., 1998; Panno et al., 2006; Freeman, 2007; Frisbee et al., 2022). The conservative nature of both chloride and bromide allows for discrete ratios to be identified and attributed to specific sources (Kelly et al., 2012). Although chloride-based road salts dominate other chloride sources in highly urbanized watersheds, a mixture of chloride sources is possible in less developed areas or within mixed land use watersheds. Hence, the identification of chloride sources is a critical step toward understanding the drivers of long-term stream chloride trends and potential management solutions (Rosenberry et al., 1999; Panno et al., 2006).

The Toronto region spans 42 km of shoreline along the northwest shoreline of Lake Ontario, and its watersheds contain 4 million people in one of the fastest-growing urban areas in North America (Kidd, 2016). Chloride trends in streams and groundwater have been assessed in various studies (e.g., Mazumder et al., 2021; Sorichetti et al., 2022) although have never been assessed in fine detail across the urban-rural gradient within the Toronto region. The application of chloride-based deicers (e.g., sodium chloride, NaCl) has been implicated as the major driving factor of increasing chloride concentrations in areas that experience freezing temperatures throughout the winter Perera et al. (2009).

As such, changes in urban land uses that require winter maintenance (e.g., roads) are a major contributor (Mazumder et al., 2021) although much less is known about the influence of urban land use types other than roads (e.g., commercial, industrial, parking lots).

The overall objective of this study was to fill knowledge gaps related to fine-scale chloride trends, sources, and drivers in the Toronto region during the salting and non-salting seasons. The specific objectives were to: (1) quantify temporal trends in surface water and groundwater chloride concentrations, (2) estimate the dominant sources of chloride, (3) relate chloride trends to weather and road density trends, and (4) relate chloride concentrations to spatial variation in land use. Based on this work we also discuss recommendations for monitoring and management.

2. Methods

2.1. Study area

The study area covers approximately 3500 km², spanning nine watersheds and several major ravine systems (Fig. 1). Urban areas occur in the south near Lake Ontario, including the cities of Mississauga, Toronto, and Ajax; and more rural landscapes dominate the north consisting of a mix of crops (e.g., corn, soybean, wheat, hay), livestock production, and natural areas (forests, meadows, swamps). The area contains five physiographic regions including the Horseshoe Moraine and Guelph Drumlin Field, Oak Ridges Moraine, South Slope, Peel Plain, and Lake Iroquois Plain (Chapman and Putnam, 1984). The Oak Ridges Moraine stands out as one of the most distinctive physiographic units of southern Ontario (Chapman and Putnam, 1984). The Oak Ridges Moraine is a west-east trending ridge of sandy land extending approximately 160 km just north of the city of Toronto and the Lake Ontario shoreline, rising to a maximum elevation of approximately 400 masl which is 325 m above the average water level of Lake Ontario (ORMGP, 2023). Due to its predominantly sandy surface soils and hummocky topography, the Oak Ridges Aquifer Complex serves as the primary recharge area and the Newmarket Till serves as the regional aquitard restricting downward groundwater flow to the underlying Thorncliffe and Scarborough Aquifer complexes (CTC Source Protection Committee, 2022; ORMGP, 2023).

Bedrock within the study area is primarily comprised of shale of the Georgian Bay and Queenston Formations; however, carbonate rock of the Lockport-Amabel and Lindsay Formations can be found along the western boundary and a small “finger” which extends into the north-central portion of the study area (CTC Source Protection Committee, 2022). The underlying shale and limestone are characterized as having low hydraulic conductivity and regionally considered to function as an aquitard although enhanced permeability at the contact zone between the overburden and bedrock can be observed, more so where limestone occurs compared to shale (ORMGP, 2023).

2.2. Stream chloride temporal trend analysis

Since 2002, grab samples have been collected the third week of every month at 47 stations including 13 Provincial Water Quality Monitoring Program (PWQMN) stations and 34 Regional Watershed Monitoring Program stations (Fig. 1). The Ministry of the Environment, Conservation and Parks (MECP) PWQMN sampling protocols were followed in both programs (MECP, 2020). Samples are stored on ice and delivered to either MECP Laboratory Services Branch, the City of Toronto's Dee Avenue Laboratory, or the York-Durham Regional Environmental Laboratory within 24 h of sampling where they were analyzed for chloride and bromide. These are accredited labs providing comparable results.

From 2002 to 2003, water quality samples were collected approximately eight times per year from approximately April to November. In 2004, the Regional Watershed Monitoring Program expanded its water quality sampling to be year-round in addition to augmenting the

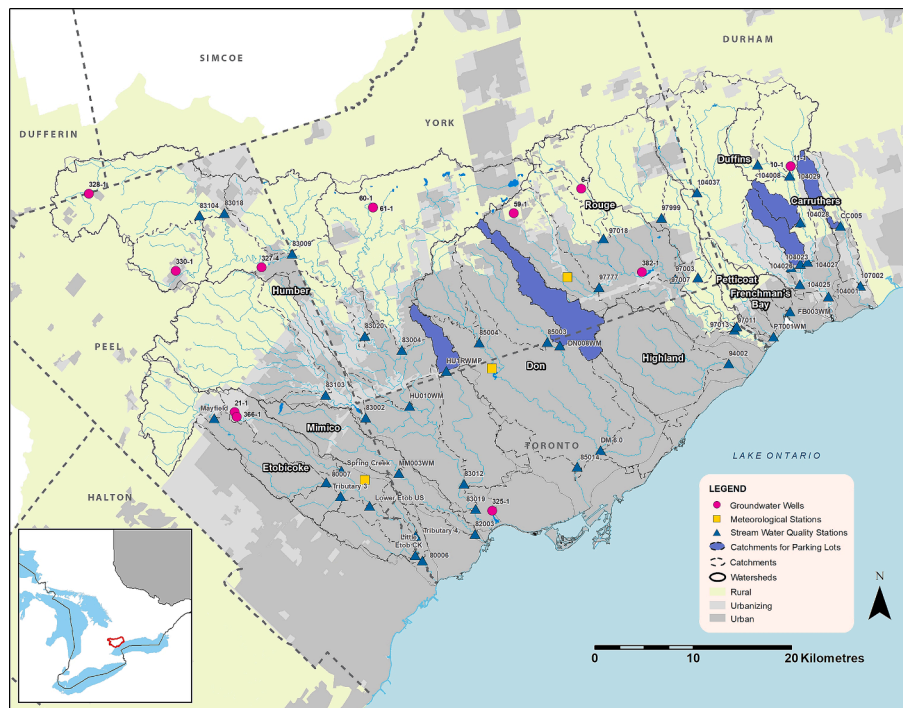


Fig. 1. Map of stream water quality monitoring stations, groundwater wells, meteorological stations, catchments, and catchments for parking lot quantification across the Toronto region. The Oshawa meteorological station is not shown since it is outside the study area (43.86667, -78.833333). Urban – identified as urban in Official Plans but includes natural areas within an urbanized area (development intensity ranges from low to high density development). Urbanizing – identified in Official Plans as committed for development. Rural – all areas outside of urban and urbanizing including agriculture, rural properties, and natural areas.

PWQMN dataset with samples between December and March. Winter samples were not collected if the stream was ice-covered between 2004 and 2005. From 2006 onwards, an auger was used for ice-covered streams ensuring at least one water quality sample was collected per month.

We analyzed temporal trends for chloride at each station using the Seasonal Kendall Test (Helsel et al., 2020). The overall seasonal Kendall statistic is computed by performing a Mann-Kendall calculation for each season and calculating the median of the results of each season. We defined two seasons to compare temporal trends: salting (November to April) and non-salting (May to October). Trends were assessed in R statistical software using the ‘censeaken’ function from the *NADA2* package (R Core Team, 2021).

2.3. Groundwater chloride temporal trend analysis

We retrieved chloride data in groundwater from the Provincial Groundwater Monitoring Network (PGMN) and the Oak Ridges Moraine Groundwater Program (ORMGP). Due to data availability, salting and non-salting seasonal data were pooled for a “Fall” (September–November) trend analysis between 2009 and 2021 at 13 stations. Data were averaged when years contained more than one sample. Fall Mann-Kendall trends in groundwater chloride concentrations were assessed using the ‘mk.test’ function in the *trend* package in R (R Core Team, 2021).

2.4. Chloride source identification (chloride:bromide ratios)

We used chloride:bromide ratios to investigate sources of chloride for all 47 stream monitoring stations. Chloride:bromide ratios were calculated for each paired observation; non-detect data were not used in this analysis. Detection limits for bromide varied with a median detection limit of 0.1 mg/L (range 0.01–31.6 mg/L) with 90% of non-detects at or below a detection limit of 1 mg/L. As with the chloride trend analysis, data were categorized into salting and non-salting season. The

likely source of chloride for individual samples were assessed through chloride:bromide vs. chloride plots using source boundaries delineated by Panno et al. (2006). Source boundaries differentiate between road salt and/or septic effluent, basin brines and/or animal waste, seawater, landfill leachate, field tiles, precipitation, and pristine aquifer. A full list of source definitions is provided in Panno et al. (2005) including the following: septic effluent represents discharge from private septic systems, and chloride from basin brines represent samples from wells at least 100 m in depth and originated as ancient seawater that was trapped during deposition of the sediments. Pristine aquifer groundwater samples were collected from confined sand and gravel aquifers at depths of up to 100 m.

Because the chloride source zones developed by Panno et al. (2006) have not been extensively used for freshwater sources in southern Ontario, we explored the applicability of these delineated sources using water samples from landfill leachate (Propp et al., 2021), rural groundwater sources (Ontario Geological Survey), and a parking lot (Lorna Murison, pers. Comm.). The landfill leachate data was sourced from Propp et al. (2021) with ground and surface water samples collected near landfills that are no longer operational. The parking lot data consisted of six samples from parking lot catch basins collected between September 2021 and January 2022. The rural groundwater aquifer data included 35 remote wells that had been tested for chloride and bromide concentrations. The use of chloride source zones developed by Panno et al. (2006) for stream water may also be affected by sampling (e.g., baseflow or stormflow). The water quality data used in this study were typically from monthly samples that are collected irrespective of flow conditions, therefore samples collected at non-baseflow conditions (i.e., higher discharge) could be diluted by inputs (e.g., precipitation) and appear to represent other sources rather than road salt.

2.5. Catchment delineation

Catchments draining to each stream water quality station were delineated using ArcGIS (ESRI Inc. 2019; Fig. 1). To generate flow

accumulation and flow direction grids, we produced a Digital Elevation Model (DEM) using Toronto and Region Conservation Authority's (TRCA's) 2019 Light Detection and Ranging (LiDAR) data (10 cm) and sampled to 10 m resolution filtered to the ground with a 1-km buffer outside the study area.

Pour points (i.e., drainage points) representing the monitoring station were created and manually aligned with flow lines from the flow accumulation grids. Catchments delineated using the flow accumulation grids were compared to the current watercourse layer and 125-ha drainage line catchments to ensure overlap. Catchment areas that were not overlapping with the current watercourse were mostly due to underground stream segments and thus not captured by the DEM. Underground stream segments were verified using orthophotography data and additional pour points (with the upstream above-ground section) were added to these catchment areas. Surrounding catchments or further downstream water quality monitoring station catchments would be affected by these adjustments and were updated to reflect these new boundaries. The catchment area was refined by subtracting areas that extended beyond the boundaries of 125-ha catchments by creating new pour points at the boundary. Sewersheds were also incorporated into the final catchment area boundaries by adding combined sewer that overlapped with the catchment areas and any further downstream water monitoring catchments associated with it using the methods outlined in [Ariano and Oswald \(2022\)](#).

2.6. Land cover

2.6.1. Road density

We calculated road density (m/ha) within each of the catchment boundaries between 2000 and 2019 using a simplified version of road layers from the Ontario Road Network: Segment with Address recommended for mapping and general spatial analysis ([OMNRF, 2019](#)). Road data from the year most closely associated with earliest (T_1) and latest (T_2) water quality samples was used. For example, road density data from 2000 were used for stations with start dates of 2000 or 2002 since roads data were available from 2000 but not again until 2005. The most recent roads data used were from 2019 and this was used to represent the most recent year of water quality data. Changes in average road density between the earliest sampling year and 2019 were examined using the Wilcoxon Signed Rank test due to non-normal data and unsuccessful data transformations. Linear regression was used to determine the relationship between 1) 2019 road density and 2021 stream chloride concentrations, and 2) change in road density ($T_2 - T_1$) and the slope of the chloride trendline for stations with increasing trends in order to determine if trends are due to changes in road density.

2.6.2. Land use

To relate land use and 2017 stream chloride concentrations we used TRCA's 2017 land use layer (<https://trca-camaps.opendata.arcgis.com/datasets/>). We used 2017 chloride data since 2017 was the most recently available land use data and it is not updated annually, therefore temporal analyses were not possible. Land use was grouped into 25 categories including aggregate extraction, agricultural, airport, beach/bluff, cemetery, commercial, estate residential, forest, golf course, high density residential, industrial, lacustrine, landfill, meadow, medium density residential, mixed commercial entertainment, railway, recreational/open space, riverine, roads, rural residential, successional forest, vacant land, or wetland. The area and proportion of each land use type within each catchment was quantified ([Electronic Supplemental Material \(ESM\) Table S1](#)). Using the 'prcomp' function in the R *factoextra* package, a Principal Components Analysis (PCA) was applied on the proportion of each land use within each catchment and related to chloride concentration (2017) based on the CWQG (<120 mg/L, 120–640 mg/L, or > 640 mg/L; [R Core Team, 2021](#)). A non-parametric Spearman correlation was used to assess the correlation between PC1 and chloride concentration. Non-parametric Spearman correlation uses Greek rho (ρ)

to assess the association between variables.

2.6.3. Parking lots

Changes in parking lot cover were assessed as a possible chloride source at a sub-set of station catchments (HU1RWMP, DN008WM, 104026, 104028, CC005). These catchments were selected since they had changes in chloride that were greater than expected due to changes in road density (anomalies) and due to their smaller size (considering manual digitizing was required). Parking lot cover was compared between two time points corresponding approximately to the time points used for chloride trend analysis. We used 2021 as the second time point (T_2) for all five catchments. The first time point (T_1) was 2006 for catchments 104026, DN008WM, and HU1RWMP, 2009 for 104028, and 2015 for CC005. GoogleEarth Pro was used to manually digitize parking lots considering only lots i) within the catchment boundary even if the lot overlapped boundaries, ii) with a paved surface (i.e., no lots with bare soil), and iii) not associated with private, small, driveways related to single-family residential dwellings. The cumulative area of each digitized parking lot for past and present time points were calculated for each catchment.

2.7. Weather patterns

We downloaded historical weather data from four meteorological stations with sufficient weather data (Toronto Pearson International Airport, Toronto North York, Toronto Buttonville Airport, and Oshawa) using the *weathercan* package in R ([Lazerte and Albers, 2018](#); [Fig. 1](#)). Frequency was specified as daily and the date range was specified as October 1999 to April 2020.

We considered several winter event scenarios that could trigger salting due to the formation of ice or are a trigger for plowing and salting based on the City of Toronto's Salt Management Plan ([City of Toronto, 2016](#)). First, days when snow fell in any quantity were classified as 'snowy day'. Second, days when both snow and rain occurred were classified as 'snowy and rainy day'. Third, when rainfall occurred during the day that was at risk of freezing at night (i.e., a day with rainfall of any quantity followed by a minimum temperature below 0 °C on the following day indicating potential for black ice formation). Lastly, we identified 'thaw-freeze events' that consisted of a thawing of existing snow on ground followed by cold temperatures that could refreeze the previously melted snow into ice (also a potential black ice condition). This scenario occurred when there was existing snow on the ground and a maximum temperature above 0 °C during the day and the minimum temperature of the following day was below 0 °C.

Under the City of Toronto's Salt Management Plan, there is a tiered system to respond to snowfall events to ensure safe road conditions ([City of Toronto, 2016](#)). This response is based on the quantity of snow that has fallen leading to a change in the snow on the ground. By applying these criteria to daily meteorological data, we also identified three different types of winter storm events. A day classified as Storm Type 1 had a total 2-day measured snowfall >5 cm. We used the same method for storm types 2 and 3 however these required 15 and 25 cm of snow, respectively. We assessed mean temperature, total precipitation, total rainfall, total snowfall, number of snowy days, number of snowy and rainy days, number of potential black ice events, and number of days under Storm Type 1 conditions for trends. Over the study period, there were not enough Storm Type 2–3 conditions to warrant trend analyses.

Only trends in the salting season data were considered since this is the period when road salt is used. For each site, we aggregated variables of interest by year and month for the trend analysis. We calculated the mean temperature for the month from daily mean temperature measurements and the monthly total of precipitation, rain, and snow using the sum of all daily values. We did not include snow on the ground in the trend analysis due to the autocorrelation of the data. For each winter event scenario, the total number of days per year under each set of conditions were calculated. We used the seasonal Mann-Kendall and Sen

slope calculation for each parameter at each site using the ‘censeaken’ function from the NADA2 package in R (Julian and Helsel, 2022).

3. Results

3.1. Stream chloride temporal trend analysis

Thirty-six of 47 stream water quality stations had statistically significant ($p < 0.05$) increasing trends in overall chloride concentration (Table 1, Fig. 2). It is important to note that the starting year for the trend analysis varied among stations. Of the 36 stations showing significant increasing trends overall, 26 had data starting in either 2000 or 2002. Of the 10 other stations with significant increasing trends overall, 5 started in 2006, 1 in 2009, 3 in 2010, and 1 in 2015. Of the 11 stations

with no significant trends overall, 5 only started being monitored in 2013 (Etobicoke Creek watershed sites), 4 started in 2002, 1 started in 2006, and 1 started in 2009. For stations with significant increasing trends overall, there was variation in the magnitude of these increases ranging from 0.5 to 15 mg Cl/L/year. Median chloride concentrations exceeded 120 mg/L guidelines for 25 stations (53%) in the earliest sampling year and 34 stations (72%) by 2021. Stations having higher median concentrations in 2021 also had a larger increase in chloride concentration (slope from trend analysis) (non-salting: $\rho = 0.801$, $p < 0.0001$; salting: $\rho = 0.820$, $p < 0.0001$; overall: $\rho = 0.878$, $p < 0.0001$; ESM Fig. S1). The number of stations with statistically significant increasing trends varied by season with 24 stations increasing in the salting season and 30 stations increasing in the non-salting season (Table 1). No stations had statistically significant decreasing trends;

Table 1

Temporal trends in stream chloride concentration at 47 monitoring stations across the Toronto region. Trends can be interpreted as 1 - significant positive trend ($p < 0.05$), 0.5 - approaching significant positive trend ($0.05 < p < 0.10$), 0 - no significant trend. Stations are arranged top to bottom representing west to east across the Toronto region.

Watershed	Station name	Non-salting season chloride trend (May-Oct)	Salting season chloride trend (Nov-Apr)	Overall chloride trend	Chloride trend slope (non-salting)	Chloride trend slope (salting)	Chloride trend slope (overall)	2021 Median chloride concentration (mg/L)	Min year of trend analysis	Max year of trend analysis
Etobicoke	80006	0	0	0	3.2	10.7	6.8	493	2002	2021
Etobicoke	80007	1	0	1	5.1	6.9	6.7	412	2002	2021
Etobicoke	Little Etob CK	0	0	0	-14.7	-20.8	-12.2	817	2013	2021
Etobicoke	Lower Etob US	0	0	0	-1.4	-32.8	-3.4	380	2013	2021
Etobicoke	Mayfield	1	1	1	2.8	3.4	2.9	156	2002	2021
Etobicoke	Spring Creek	0	0	0	1.2	-22.1	-0.3	487	2013	2021
Etobicoke	Tributary 3	0	0	0	-10.3	-58.4	-13.8	900	2013	2021
Etobicoke	Tributary 4	0.5	0	0	-13.3	8.9	-7.8	405	2013	2021
Mimico	82003	0	0	1	6.2	24.3	12.1	892	2002	2021
Mimico	MM003WM	0	0	0	7.7	22.9	10.4	885	2006	2021
Humber	83002	1	1	1	6.1	7.1	6.3	385	2002	2021
Humber	83004	1	1	1	3.2	4.8	3.5	173	2002	2021
Humber	83009	0	1	1	0.2	0.8	0.5	37	2002	2021
Humber	83012	0.5	0.5	1	4.8	22.2	7.9	603	2002	2021
Humber	83018	1	1	1	0.6	0.9	0.7	61	2002	2021
Humber	83019	1	1	1	2.4	6.9	3.7	239	2000	2021
Humber	83020	1	0.5	1	0.9	0.8	0.8	74	2002	2021
Humber	83103	1	1	1	4.1	8.3	6.1	279	2002	2021
Humber	83104	1	1	1	1.3	1.4	1.4	68	2002	2021
Humber	HU010WM	1	1	1	1.1	3.7	1.4	150	2006	2021
Humber	HU1RWMP	1	0	1	15.9	22.8	14.7	1080	2006	2021
Don	85003	1	0	1	6.3	5.9	5.6	284	2002	2021
Don	85004	1	0	1	11.1	14.4	10.1	584	2002	2021
Don	85014	1	1	1	5.8	13.6	8.2	359	2000	2021
Don	DM 6.0	0	0	0	2.7	-2.2	1.5	458	2002	2021
Don	DN008WM	1	0	1	8.0	15.1	8.0	373	2006	2021
Highland	94002	0	0	0	2.3	-5.0	-0.02	412	2002	2021
Rouge	97003	1	0	1	6.0	4.2	5.7	274	2006	2021
Rouge	97007	1	1	1	3.3	5.1	3.8	160	2006	2021
Rouge	97011	1	0.5	1	5.5	6.6	6.5	258	2002	2021
Rouge	97013	1	1	1	3.6	4.9	3.9	169	2002	2021
Rouge	97018	1	1	1	1.2	1.9	1.6	77	2002	2021
Rouge	97777	1	0	1	8.9	1.1	7.6	393	2002	2021
Rouge	97999	1	1	1	3.6	3.8	3.7	150	2002	2021
Duffins	104001	1	1	1	1.3	3.3	2.0	87	2002	2021
Duffins	104008	0	1	1	0.2	1.7	1.0	64	2002	2021
Duffins	104023	1	1	1	3.4	4.9	3.9	100	2010	2021
Duffins	104025	0	1	1	0.2	1.4	0.6	67	2002	2021
Duffins	104026	1	1	1	7.8	12.8	9.0	211	2010	2021
Duffins	104027	1	1	1	1.0	1.9	1.4	49	2002	2021
Duffins	104028	1	1	1	10.7	10.2	10.4	175	2010	2021
Duffins	104029	1	1	1	0.4	1.5	0.9	36	2002	2021
Duffins	104037	0	0	0	0.5	1.9	0.9	113	2002	2021
Petticoat	PT001WM	0	1	1	7.8	9.7	9.2	433	2009	2021
Frenchman's	FB003WM	0	0.5	0	-3.8	8.7	3.3	409	2009	2021
Carruthers	107002	1	1	1	7.2	9.3	8.1	217	2002	2021
Carruthers	CC005	1	0.5	1	8.8	4.3	6.1	99	2015	2021

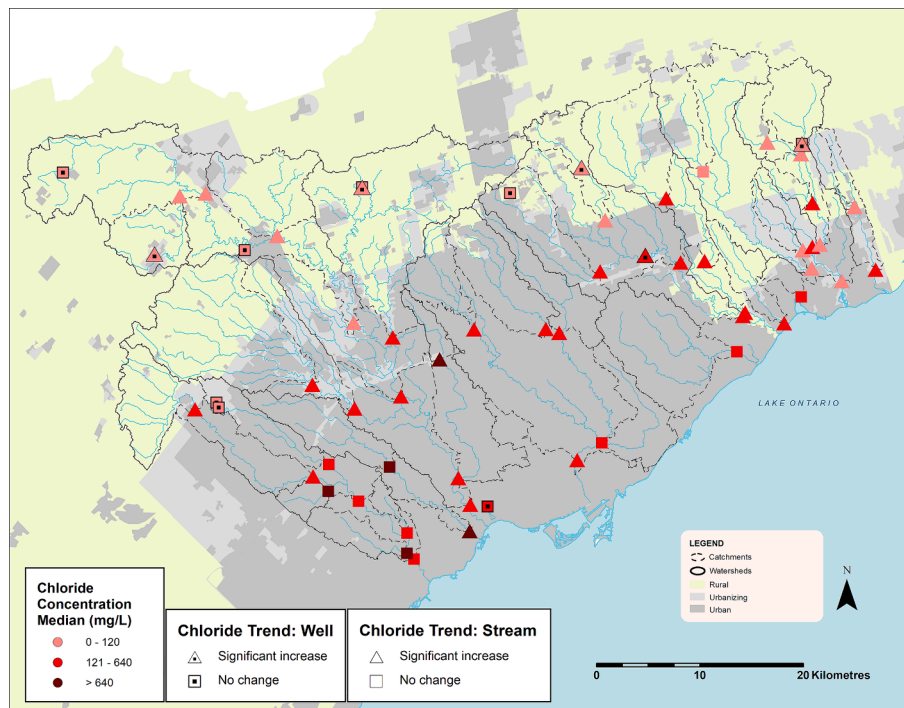


Fig. 2. Spatial representation of overall temporal trends in stream chloride concentration at 47 stream monitoring stations and 13 groundwater wells across the Toronto region between 2000 and 2021 (significant at $p < 0.05$).

however, stations DM 6.0 and 94002 had negative slopes over the past 20 years.

3.2. Groundwater chloride temporal trend analysis

Chloride concentrations increased significantly at 5 of 13 wells (all $p < 0.05$) with 1 well approaching a significant increase ($0.05 < p < 0.10$; Table 2, Fig. 2). These wells had a range of current chloride concentrations (2–527 mg/L) and were found in both rural and urban areas (rural – 3 wells, urban – 2 wells). Five wells had no change in chloride concentration (rural – 3 wells, urban – 2 wells) and two wells, both in urban areas, approached a significant decrease in chloride. The station with the highest chloride concentration in 2021 (386 mg/L) was well ID 325-1 located in the lower Humber River watershed (an urbanized area).

Table 2

Temporal trends in chloride concentration at 13 groundwater wells across the Toronto region. Trends can be interpreted as 1 - significant positive trend ($p < 0.05$), 0.5 - approaching significant positive trend ($0.05 < p < 0.10$), 0 - no significant trend. Stations are arranged top to bottom representing west to east across the Toronto region.

Watershed	Formation	Groundwater well name	Abbrev.	Overall chloride trend	Chloride concentration (current; mg/L)	Min year of trend analysis	Max year of trend analysis
Etobicoke	Mackinaw/Oak Ridges	W0000021-1	21-1	0	102	2009	2021
Etobicoke	Mackinaw/Oak Ridges	W0000366-1	366-1	0.5	45.9	2009	2021
Humber	Thorncliffe	W0000060-1	60-1	1	11.5	2009	2021
Humber	Scarborough	W0000061-1	61-1	0	1.8	2009	2020
Humber	Sunnybrook	W0000325-1	325-1	0	386	2009	2021
Humber	Thorncliffe	W0000327-4	327-4	-0.5	15.2	2009	2021
Humber	Bedrock	W0000328-1	328-1	-0.5	117	2009	2021
Humber	Mackinaw/Oak Ridges	W0000330-1	330-1	1	80.8	2009	2021
Rouge	Mackinaw/Oak Ridges	W0000006-1	6-1	1	52.5	2009	2021
Rouge	Mackinaw/Oak Ridges	W0000059-1	59-1	0	4.8	2009	2021
Rouge	Lower Newmarket	W0000382-1	382-1	1	527	2009	2021
Duffins	Scarborough	W0000010-1	10-1	0	5.4	2009	2021
Duffins	Thorncliffe	W0000011-1	11-1	1	2	2009	2021

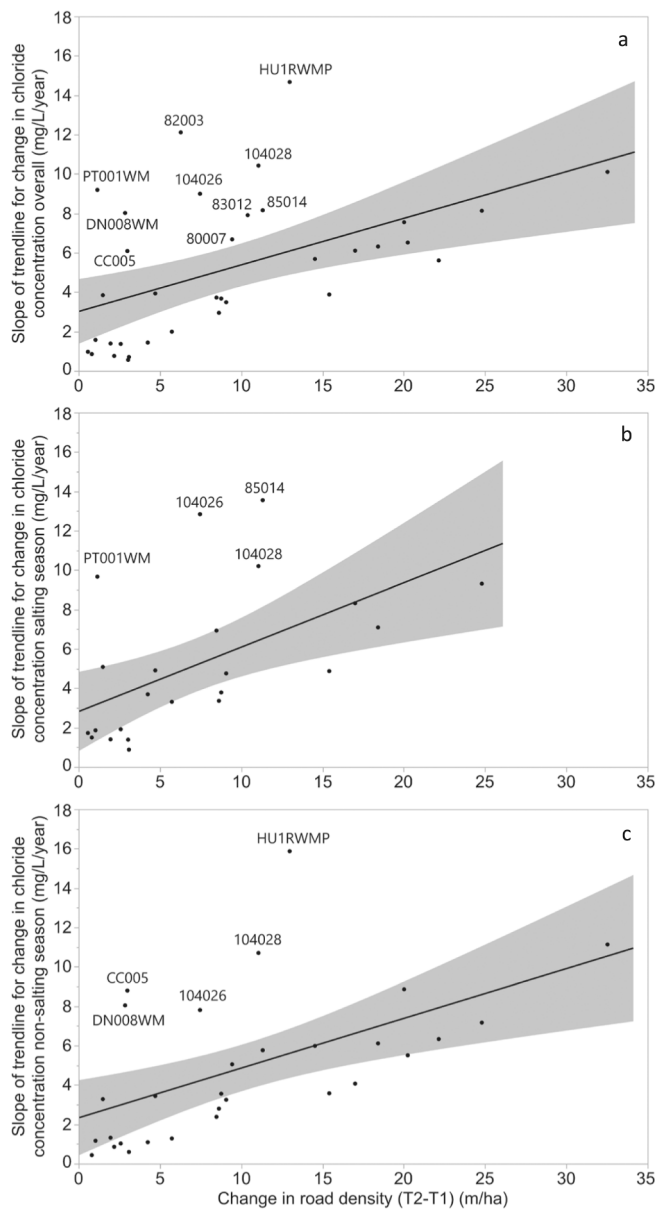


Fig. 4. Relationship between changes in road density and changes in chloride concentration (slope) for overall (top), salting season (middle), and non-salting season (bottom). Grey shaded area represents 95% confidence intervals.

indicated more urban-associated features such as commercial, medium density residential, high density residential, roads, mixed commercial/entertainment, industrial, recreational/open space, cemetery, and railway. No variables showed substantial contributions (e.g., loading $> |0.40|$) to PC1 but loadings were >0.25 for institutional (0.30), commercial (0.29), recreational open space (0.28), roads (0.27), medium density residential (0.27), and high density residential (0.25). Variables with substantial contributions to PC2 included golf course (-0.49) and lacustrine (-0.44). PC1 was significantly negatively correlated with 2017 stream chloride concentrations ($\rho = -0.911$, $p < 0.0001$, Fig. 7). There was more variation in chloride concentration among stations with more urban-related land uses compared to those with more natural cover (as seen in Fig. 7).

3.4.3. Parking lots

Parking lot cover varied among catchments with two catchments having comparably high cover (HU1RWMP, DN008WM) and three having lower cover (104026, 104028, CC005; Table 3). Parking lot

cover increased between T_1 and T_2 for all catchments although the magnitude of the increase varied. Cover increases were greater in catchments with a high initial cover compared to catchments with a low initial cover.

3.4.4. Weather patterns

We found no significant trends for mean temperature, total precipitation, total rainfall, and total snowfall between 1999 and 2020 (all $p > 0.05$). In addition, there were no significant trends for winter event scenarios that could trigger road salting, the number of thaw-freeze events, snowy days, snowy-rainy days, or storm type 1 conditions.

4. Discussion

4.1. Stream chloride

The increase in chloride found in this study is consistent with the findings of other studies examining data from Ontario and elsewhere (Kaushal et al., 2005; Kelly et al., 2008; Todd and Kaltenecker, 2012; Raney and Eimers, 2014; Mazumder et al., 2021). Increases in stream chloride concentrations during the warm season (Table 1) are of particular concern since this is the time when many aquatic species reproduce causing a greater impact on population persistence (Lawson and Jackson 2021). While chloride can be flushed into streams quickly with precipitation or snow melt events, retention of chloride in soil, groundwater, and stormwater presents a concern (Marsalek, 2003; Kelly et al., 2008; Perera et al., 2010; Casey et al., 2013; Robinson et al., 2017; Oswald et al., 2019; Lam et al., 2020). The retention of chloride within these areas are likely leading to a time lag effect on stream concentrations (Kelly et al., 2008). Additionally, broader use of modern stormwater control measures that focus on capturing runoff from roads and parking lots with the goal of increasing infiltration are likely to play a role in elevated stream concentrations (McQuiggan et al., 2022).

Chloride retention is higher in less urbanized watersheds suggesting that chloride concentrations will continue to rise in rural areas long after any mitigation, such as road salt management, has occurred (Kelly et al., 2008; Oswald et al., 2019). Faster increases in stream chloride within more heavily urbanized catchments are also occurring in the eastern United States (Rossi et al., 2022) along with faster increases in streams with already high chloride (Moore et al., 2020). Stream chloride concentrations are increasing faster in catchments with more impervious cover, and chloride increases moderately correlate with the percentage of groundwater retention (Rossi et al., 2022).

While the Toronto region has 13 PWQMN stations which were included in this study, this is the first time that temporal trends have been assessed at 34 additional water quality stations that are part of Toronto and Region Conservation Authority's Regional Watershed Monitoring Program. This analysis provides further evidence of the magnitude of the issue along with the opportunity to examine finer scale variation in chloride across a range of catchment land uses (heavily urbanized to more rural areas). Associating catchment-scale chloride trends to land use data and source information provides localized information to target specific management for chloride such as remediation or salt management. For example, these data could be used to inform restoration planning such as specific species to plant that are salt-tolerant or are able to remove salt from riparian soils (McSorley et al., 2016; Mann et al., 2020). Data could also be used to identify salt vulnerable areas which can then inform mitigation such as limiting salting near specific watercourses, in areas with sensitive aquatic species, or areas for improved stormwater controls or green infrastructure. Overall, these data provide fine scale information on water quality impairment and detailed information that can be used to inform mitigation measures and determine the effectiveness of chloride control and other watershed management programs through long-term monitoring.

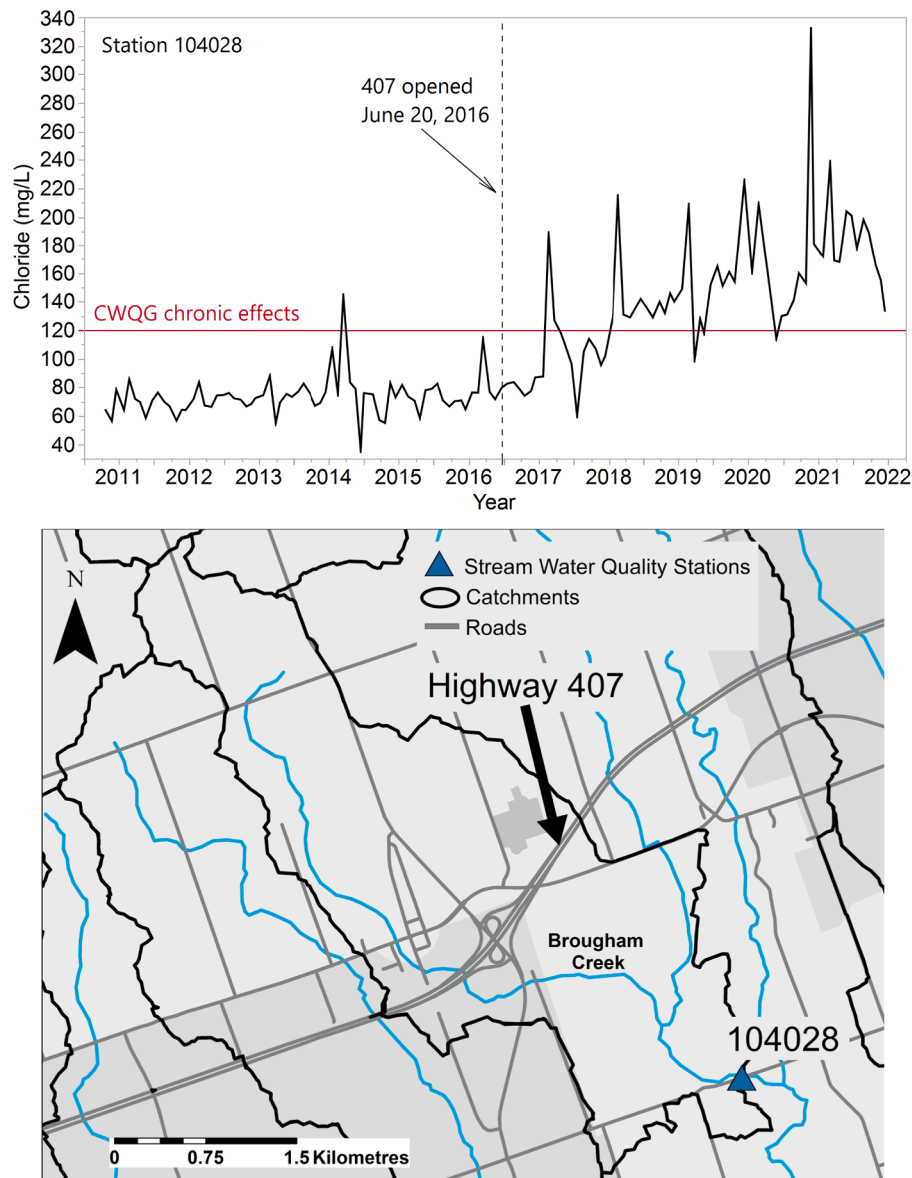


Fig. 5. Chloride concentration at stream water quality station 104028 between 2011 and 2021 showing the date Highway 407 was opened between Brock Road and Harmony Road. Canadian Water Quality Guideline (CWQG) of 120 mg/L for chronic effects is shown.

4.2. Groundwater chloride

Even though only limited groundwater data were available, approximately half of the groundwater wells indicated increasing concentrations of chloride between 2009 and 2021 (Fig. 2, Table 2). These results are consistent with previous studies that also found elevated chloride in urban areas or increasing trends in chloride (Kincaid and Findlay, 2009; Perera et al., 2010; Sorichetti et al., 2022). Rising chloride (and sodium) in groundwater, and higher concentrations in urban areas, are a concern from a human health and aesthetics perspective (drinking water guidelines; Health Canada, 2022), risks to the ecosystem functions and services groundwater provides (Griebler and Avramov, 2015), and groundwater as a pathway for transporting chloride to stream water and lakes (Meriano et al., 2009; Mackie et al., 2021; Szklarek et al., 2022). Annex 8 of the Great Lakes Water Quality Agreement recognizes these concerns by seeking to advance research on the linkage between road salt in groundwater and its influence on stream and lake chloride and this study provides a starting point for further

investigation into groundwater/stream water interactions (EPA and ECCO, 2022).

4.3. Chloride sources

The continued investigation into chloride sources across northern regions is an integral part of improving water quality and addressing excess chloride. We found that road salt and/or septic effluent were the predominant chloride sources in the Toronto region although inputs from basin brines and/or animal wastes, landfill leachate, pristine aquifers, and field tiles also contributed chloride but to a lesser extent (Fig. 3).

In the more urban areas, road salt and/or septic effluent dominated chloride sources. In these areas, salt could come from roads or other areas where it has been applied, while septic effluent could be from municipal wastewater or sewer cross connections. Several stations had a road salt and/or septic effluent source although were not overly influenced by built-up areas (more rural areas). This potentially indicates the

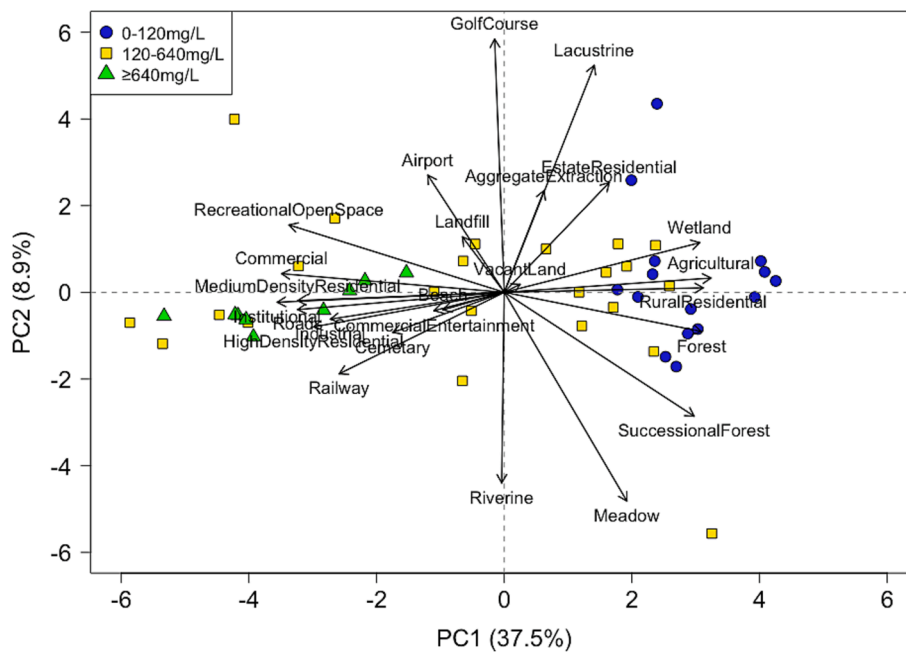


Fig. 6. Ordination of 2017 land use and 2017 stream chloride concentrations at 47 stations across the Toronto region grouped based on Canadian Water Quality Guideline thresholds.

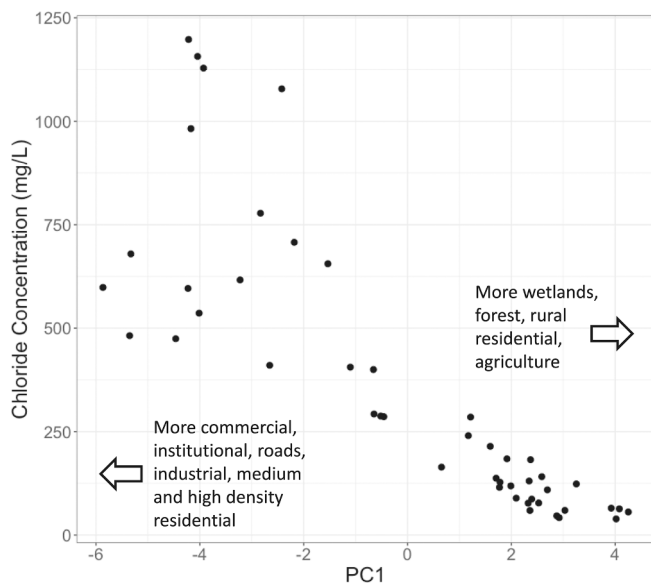


Fig. 7. Correlation between PC1 and 2017 stream chloride concentrations at 47 stations across the Toronto region.

Table 3
Temporal changes in parking lot cover for five catchments with greater increases in chloride over time than predicted by changes in road density (anomalies).

Stream station catchment	Year		Parking lot cover (ha)		Change in parking lot cover (ha)	Catchment size (ha)
	T ₁	T ₂	T ₁	T ₂		
HU1RWMP	2006	2021	204	246	42	1203
DN008WM	2006	2021	311	339	28	4087
104026	2006	2021	0.64	0.77	0.13	1434
104028	2009	2021	0.39	1.34	0.95	969
CC005	2015	2021	0.09	0.64	0.55	985

impact of highways and regional road systems or leaky septic systems; however, more detailed spatial analysis is required to understand the hydrologic connectivity of different chloride sources to the monitoring stations (ESM Fig. S5).

While the Toronto region is more heavily urbanized in southern areas near the lake, agriculture is more prevalent in the northern areas with scattered patches of natural cover. Field tiles were a chloride source for a very small percentage of samples (only in 5 catchments: 104037, 104025, 97013, 97999, Mayfield) and these catchments had high agricultural cover (>45%). There was no clear correlation between basin brine/animal waste chloride sources during the non-salting season and agricultural cover. It is possible that these sources better reflect basin brines since they occurred primarily in the far west or east portions of the study area; areas known to have marine shale deposits; however, more research is needed to further separate chloride sources and their relationship to catchment land use. These results suggest that continued focus should be given to road salt management and remediation but also that other sources should continue to be investigated, monitored, and mitigated.

4.4. Land use

Road density increased significantly in stream water quality station catchments. Catchments with larger changes in road density also tended to have larger changes in stream chloride concentration (Fig. 4). Several stations had higher changes in chloride than expected based on road density changes, and these could have been due to various factors including changes in practice resulting in high salt use per unit of road area. For example, Corsi et al. (2015) found that salt sales increased 40% faster than road density in the northern US from the late 1980s to 2010. The construction of high traffic, multi-lane roads can also result in marked increases (Fig. 5). The extension of Highway 407 from Brock Road in Pickering to Harmony Road in Oshawa opened on June 20, 2016. Anomalous stations were south of Highway 407 across the study area with stream stations in the east section (near the newly opened section of Highway 407) including 104028 and CC005.

These results are consistent with the findings of other studies making the link between road density and chloride either spatially or temporally (Winter et al., 2011; Kelting et al., 2012; Todd and Kaltenecker, 2012;

Mazumder et al., 2021). In addition to roads, this study highlights that several other land use types were positively correlated with chloride concentrations including institutional, commercial, industrial, and medium density residential (Fig. 6). This suggests that while correlated with roads, higher proportions of these land use types could also lead to higher downstream chloride concentrations. This is a concern since salt application in areas such as parking lots related to these land use types could include 40% of all salt application (Environment Canada, 2012).

Overall, these results suggest strong links between land and stream. While we could not examine changes over time in fine-detailed land use types, there have been considerable changes in land use across the study area over the past 20 years. In metropolitan Toronto, the human population has increased by 1.3 million and the urban area has expanded by 340 km² between 2001 and 2021 (Bouchard and Shiab, 2022). Eighty-two percent of neighbourhoods built during this period are low density zones (2467 people/km²) which rely strongly on cars due to few nearby services and amenities (Bouchard and Shiab, 2022). This increase in urban area was reflected in our dataset where road density increased (by on average 5%; Fig. 4) and parking lot cover increased (by up to 42 ha; Table 3). The urban area did not change uniformly across the study area and this may be reflected in stream chloride concentrations. For example, two stream water quality stations (DM 6.0 and 94002) had what appeared to be negative slopes (although not statistically significant) for chloride concentration over the past 20 years. Even though these stations had negative slopes, the median chloride concentrations in 2021 were very high (458 and 412 mg/L; Table 1). These catchments have been highly urbanized since the mid-1900s and had two of the lowest changes in road density of all stations (both <2%), again highlighting the strong influence of land use change in driving stream chloride trends.

4.5. Weather patterns

No significant trends existed for climatic variables or winter event scenarios during the study period (1999–2020). Our results differ from previous climatic trend studies using data from the Province of Ontario, which overall suggest that Ontario is getting warmer and wetter with decreasing snowfall and fewer freeze–thaw days (Mekis and Vincent, 2011; Vincent et al., 2018; Ouyang et al., 2021; Ahmed et al., 2022). The lack of any significant trends in the climatic variables of interest suggests that either changes in climate are not driving changes in chloride concentrations over the period of interest or that climatic conditions in environmental datasets are not a good surrogate for road salt application rates. It should be noted, however, that longer datasets (i.e., >20 years) may be necessary to detect significant changes in climate. The Oshawa and Toronto Buttonville climate stations showed nearly significant decreasing trends in total snowfall ($p = 0.17$), number of snowy days ($p = 0.11$), and total precipitation ($p = 0.08$), respectively. For the Oshawa station, this could signal a shift toward more rainfall, which could increase the risk of black ice conditions (although not corroborated by the winter event scenario analysis).

5. Conclusions

This study provides additional evidence to support concerns over freshwater salinization despite a growing understanding among scientists and practitioners of the negative impacts on freshwater ecosystems and anecdotal evidence that road salt usage is decreasing. It also provides novel information on the contributions of chloride from various sources, and the potential influence of more fine scale urban land uses (commercial infrastructure, parking lots, high traffic/multi-lane roads) on stream chloride. While chloride source identification points to road salt as a driving factor in the salting season, other sources make up a larger proportion of inputs during the non-salting season than they do in the salting season suggesting that while road salt mitigation should be a priority, other sources must also be further investigated and mitigated.

Nonetheless, limiting road construction/urban development and limiting salt application should both be prioritized to reduce salt contributions to legacy pools and direct contributions to freshwater ecosystems.

There remain many gaps in chloride research in freshwater systems. Cunillera-Montcusi et al. (2022) summarize priorities including expanding temporal and spatial scales of study, establishing a better understanding of salinity thresholds for species (e.g., community-level, trait-based, adaptation), integration of basin characteristics (e.g., geology), biological impacts of chemical cocktails caused by salinization, along with higher-frequency chloride data. Mazumder et al. (2021) also provide a summary of future research related to salt legacy in streams including recording salt application rates (both public and private), examining spatial and temporal patterns of other chloride sources, groundwater-surface water interactions, and improved water quality modelling. This study provides new information on chloride trends at a smaller spatial scale and chloride sources but leaves room for future studies and these are highlighted here.

Monitoring and management - This study highlighted the importance of long-term datasets and the need for continued long-term monitoring and additional sampling of groundwater due to low sample sizes. It has also highlighted the need for centralized reporting of salting quantities by road management agencies and certification/tracking of salt application by private contractors to relate environmental chloride concentrations to salt application. This would allow scientists and road management organizations to track the effectiveness of salt management programs. This study also provides a starting point for identifying salt vulnerable areas across the Toronto region which could also inform prioritization of stormwater management chloride controls and green infrastructure (both of which also require further research related to chloride removal/management).

Chloride sources and land use - The dataset produced in this study could be used to answer additional questions including temporal changes in chloride sources, chloride:bromide ratios in groundwater, and using total nitrogen vs chloride:bromide to further separate N-enriched sources (e.g., septic effluent, animal wastes) from road salt (Panno et al., 2006). Further research into specific land use types (commercial, industrial, parking lots) is needed to determine their relative influence on chloride concentrations, their relationship to chloride sources, and factors affecting the variation in chloride concentration in urbanized areas (e.g., observed in Fig. 7). Additional research is also needed on base cations (e.g., sodium, calcium, magnesium, potassium) associated with alkalization along with other contaminants that are mobilized through chloride (e.g., metals).

Weather patterns - Future research on climatic trends that potentially drive road salt usage could also focus on identifying more specific winter event scenarios. This study aggregated the number of winter weather scenarios as a count per month by salting season to determine if a trend existed over the study period. Examining the relationship between the chloride concentration of a specific water quality sample (i.e., at a specific site and time) and the type of winter weather events leading up to that sampling date could offer insight into the types of winter conditions that lead to elevated chloride concentrations in waterways, and by extension which types of winter events could drive changing chloride concentration trends.

CRediT authorship contribution statement

Lyndsay A. Cartwright: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Supervision, Project administration, Visualization, Writing – original draft. **Luke Moslenko:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft, Writing – review & edit. **Andrew Chin:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – review & edit. **Garrett Des Vignes:** Data curation, Formal analysis, Investigation,

Methodology, Visualization, Writing – original draft, Writing – review & edit. **Krista M. Chomicki**: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – review & edit. **Kristina Anderson**: Data curation, Writing – original draft, Writing – review & edit. **Tim Van Seters**: Conceptualization, Methodology, Writing – review & edit. **Jonathan Ruppert**: Conceptualization, Funding acquisition, Project administration, Writing – review & edit. **Daniela Macleod**: Methodology, Supervision, Project administration, Writing – review & edit. **Nikola Erich**: Data curation, Formal analysis, Investigation, Methodology, Writing – review & edit. **Suad Sidow**: Data curation, Formal analysis, Investigation, Methodology, Writing – review & edit. **Russell Bastow**: Data curation, Formal analysis, Investigation, Methodology, Writing – review & edit. **Sophie Antonyshyn**: Data curation, Formal analysis, Investigation, Methodology, Writing – review & edit. **Alexander Ivanov**: Data curation, Formal analysis, Investigation, Methodology, Writing – review & edit. **Joao Pedro Campos**: Data curation, Formal analysis, Investigation, Methodology, Writing – review & edit. **Chad T. Harvey**: Conceptualization, Investigation, Methodology, Supervision, Project administration, Writing – review & edit. **Claire Oswald**: Conceptualization, Funding acquisition, Investigation, Methodology, Supervision, Project administration, Visualization, Writing – review & edit.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jglr.2023.09.006>.

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