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Road Salt Application in Highland Creek Watershed, Toronto, Ontario – Chloride Mass Balance

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Occurrence of increasing chloride concentrations in urban streams of cold climates, mainly due to road salt application, has raised concerns on its adverse effects on aquatic and terrestrial ecosystems. Therefore, there is a need for a better understanding of processes associated with road salt application and subsequent discharge into the environment in order to develop management practices to minimize detrimental effects of chlorides. The chloride mass analysis for the Highland Creek watershed based on four years of hourly monitoring data indicates that approximately 60% of the chlorides applied on the watershed enter streams prior to subsequent salting period, 85% of which occurs during the period between November and March. Contribution of private de-icing operations on chloride mass input within Highland Creek watershed was estimated to be approximately 38%, indicating its significance in overall chloride mass balance. Salt application rates, as well as chloride output in the streams, vary spatially based on land use, influencing chloride concentrations in surface waters. The estimated groundwater chloride concentration of 275 mg/L indicates that some aquatic organisms in Highland Creek would potentially be at risk even outside the winter period under dry weather flow conditions.

***Key words*: water quality, road salts, chloride mass balance, de-icing, chloride output, stormwater, monitoring**

Introduction

Road salts are used extensively in Canada to de-ice roadways. Approximately 5 million tonnes of road salts is used in Canada annually (Environment Canada 2004). With 5,500 km of a dense road network (a significant area of parking lots, sidewalks, and driveways) approximately 200,000 tonnes of road salts are used in the City of Toronto annually. Road salts contain mostly sodium chloride with smaller quantities of other common chloride salts (calcium chloride, magnesium chloride, and potassium chloride) and trace amounts of other substances. At elevated concentrations, these various salts can adversely impact aquatic and terrestrial ecological receptors (D'Itri 1992; Environment Canada and Health Canada 2001; Marsalek 2003; Bäckström et al. 2004; Ramakrishna and Viraraghavan 2005). The Canadian Council of Ministers of the Environment (CCME) recommends a maximum of 250 mg/L chlorides and 200 mg/L of sodium in drinking water to minimize impacts to the taste of water. Sodium retained in the soils causes soil compaction and increases permeability (Novotny et al. 1999). Environment Canada and Health Canada's risk assessment (Environment Canada and Health Canada 2001) determined that chloride concentrations in surface waters of approximately 230 mg/L potentially pose risks to aquatic organisms over long-term (weeks) periods of exposure, while concentrations of 800-1,000 mg/L potentially pose risks during short-term (days) exposures. US EPA (1988) had previously set similar water quality criteria. New information indicates that water hardness provides a level of protection against the impacts of high chloride concentrations in surface waters, leading the US EPA to a process of modifying its water quality criterion. The CCME is currently developing a water quality guideline. The use of road salts across large regions of Canada, at loadings that have caused harm to the environment led Environment Canada to consider declaring road salt "toxic", to list road salt on Schedule I of the Canadian Environmental Protection Act, and to thus develop the Road Salt Code of Practice in 2004 as a risk management tool. The objective of the code is to encourage municipal, provincial and federal road authorities to implement best-management practices while using and applying road salts.

Road salts that are applied to control snow and ice get transported to surface waters via multiple pathways, and therefore exhibit temporal and spatial variation in concentration in surface waters. Road salt is washed off as snow melt or with rain, and is transported to surface water as overland flow. Meltwater that percolates into the ground transports chlorides to groundwater, which over time will migrate to surface waters. There is a lot of evidence for increased chloride concentrations in surface water and groundwater due to road salt application in Canada, the United States, and Europe (Mayer et al. 1999; Williams et al. 2000; Godwin et al. 2003; Thunqvist 2004; Kaushal et al. 2005; Lundmark and Olofsson 2006). Mayer et al. (1999) presented a spatial

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map of chloride concentrations for Canada based on an annual watershed-wide road salt application amounts and annual runoff. They indicated that watersheds in southern Ontario, southern Quebec, and the Maritimes have the highest chloride loadings from road salts. There are very few published studies in Canada documenting the mass balance of chlorides in urbanized areas resulting from the application of de-icing salts (Howard and Haynes 1993; Howard et al. 1993; Meriano et al. 2009). A chloride mass balance study in the metropolitan area of Minneapolis/St. Paul, Minnesota highlights the concerns of continued accumulation of chlorides in the groundwater and surface water (Novotny et al. 2009).

The City of Toronto presented an important case study in which to document the chloride mass balance. Surface waters in the Toronto area are important aquatic habitats and are host to dozens of fish species, including anadromous salmonids that use systems such as the Humber River, Rouge River, Don River, and Highland Creek as spawning and nursery habitats (Kilgour et al. In press). These sensitive habitats are potentially threatened by chloride concentrations that have been reported as high as 1,500 for some long-term averages, and as high as 6,000 mg/L in short-term concentrations (Perera et al. 2009). According to Perera et al. (2009) monitoring locations at Highland Creek watershed and downstream areas of Humber River and Don River watersheds recorded chloride concentrations during the winter period above 1,500 mg/L approximately 10-15% of the time and above 230 mg/L up to 80% of the time. Drainage areas of these monitoring locations are highly urbanized and other areas with lower urbanization (upper reaches of Humber River and Rouge River watersheds) indicated much lower chloride concentrations. As part of its response to the Code of Practice, the City of Toronto began a process of collecting detailed chloride concentration data in specific, highly-sensitive watercourses to determine a baseline against which to judge the effectiveness of best-management practices, as to provide information that would lead to a better understanding of the chloride mass balance in heavily urbanized systems.

This paper discusses chloride mass balance for the Highland Creek Watershed in Toronto. The calculations are based on the stream chloride monitoring program of the City of Toronto, daily salt application records of the City and the Ontario Ministry of Transportation (MTO), and estimates on private use of road salts within the watershed. As a part of the research an analysis on chloride concentration of the baseflow was also undertaken to quantify the short-term and long-term outputs in watershed chloride mass balance. Analysis conducted under different time horizons are presented to highlight various temporal processes associated with road salts in the environment. Spatial variations in chloride mass balance is also presented using monitoring data from two additional sub-watersheds within Highland Creek. All the mass balance analyses were conducted considering only chlorides associated with road salts mainly due to its conservative nature. Although not discussed in this paper, similar results could be extracted for sodium; however, sodium has a higher retention in soils due to cation exchange.

Methodology

Study Area

Highland Creek watershed located in City of Toronto has been selected for the project. It is approximately 100 km^2 in area and situated almost entirely within the City of Toronto boundary. The area considered for this study is approximately 84.9 km^2. The area is highly urbanized and has a dense road network. The roads within the watershed are maintained by the City of Toronto except for approximately 2% of the watershed within the Town of Markham, Highway 401 which is under the MTO, and a few private roads. What prompted the Highland Creek watershed to be selected for this project was the availability of previous data, location mainly within one jurisdiction, and being a highly urbanized area. This area received approximately 810 mm of precipitation with a snow fall of 155 cm during the study period. Average baseflow was estimated to be 173 mm and evapotranspiration is approximately 350 mm.

The City of Toronto has maintained a chloride-monitoring station at Highland Creek near Morningside Avenue since November 2004, adjacent to the Water Survey of Canada (WSC) flow gauge 02HC013 (Fig. 1). To supplement the existing monitoring station, two additional stations were set up at two different locations of the watershed in February 2007. These two locations were selected to represent the two main tributaries of Highland Creek and are located closer to

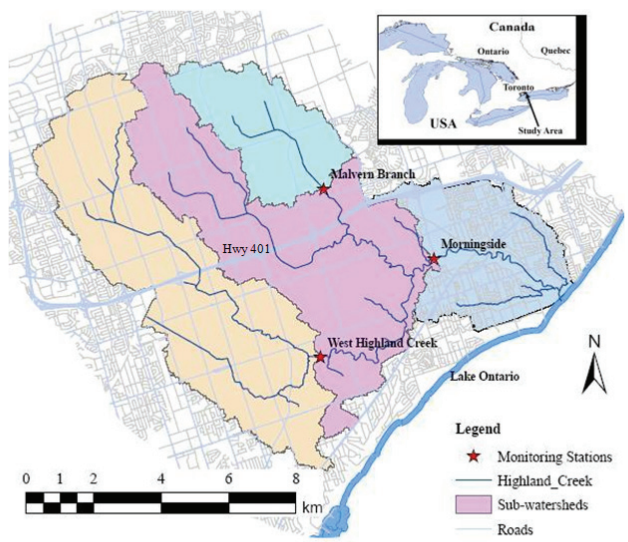

Fig. 1. Locations of the monitoring stations and associated sub-watersheds.

TABLE 1. Characteristics of the sub-watersheds defined by monitoring stations

Sub-watershed:		*Morningside*	*West Highland Creek*	*Malvern*
Drainage Area (km²):		*84.9*	*36.9*	*12.4*
Land use (% Area)	Commercial	5.3	5.5	3.6
	Industrial	13.2	10.4	35.9
	Institutional	6.3	6.6	4.1
	Multi-Family Residential	5.7	7.5	2.5
	Single-Family Residential	29.5	32.8	17.1
	Open	21.5	17.3	21.9
Imperviousness (% Area)	Total Imperviousness	53.2	54.3	59.8
	Road Pavements	14.6	14.9	11.2
	Parking Lots/Driveways	8.1	7.4	11.2

the Toronto Region Conservation Authority (TRCA) and WSC flow gauging stations TRCA 56 and 02HC058, respectively. The data provided by these stations allow the development of separate mass balances, and help to quantify spatial variability in the chloride mass balance in the greater watershed. The monitoring stations and corresponding sub-watersheds are identified by the location (Morningside) or the tributary (Malvern and West Highland Creek). Table 1 presents land use characteristics of the sub-watersheds considered for this paper. Land use categories used were commercial, industrial, institutional, multi-family residential, single-family residential, and open areas based on the City of Toronto land use maps.

Chloride Mass Calculation

The chloride mass balance for watersheds were conducted considering inputs and outputs of chloride mass associated with the watershed. The only significant chloride input into the study area is road salts applied as a de-icer. There is no wastewater treatment plant within the study area, and chloride input from precipitation, water softeners, and other sources are negligible. Chloride output of the watershed is the chloride mass in stream flow that is leaving the watershed. Data from stream chloride monitoring program was used to calculate chloride mass (load) in stream water. The chloride mass in the stream was computed as the product of stream flow and chloride concentration. However, this mass includes the chloride contribution from groundwater through baseflow. The chloride mass due to surface runoff was computed by deducting the chloride mass associated with baseflow. Base flow was estimated using a digital filter proposed by Arnold and Allen (1999) with daily stream flow values. Chloride concentration in baseflow was determined by the monitoring data collected during the fall (prior to any road salt application) when the effect of road salts from surficial soils is negligible. It was assumed that during this period, stream chloride concentration under dry flow conditions would approach the chloride concentration in baseflow. It is noted a water year starting from the beginning of November to the end of October the next year was considered for mass balance calculations to prevent fragmentation of salt application period into two years.

Chloride concentration data. Chloride concentrations in surface waters were measured using Hach 900 Max auto samplers (Mississauga, Ont.) fitted with electrical conductivity probes. Difficulty in finding economical and reliable sensor to monitor continuous chloride concentration in the streams was solved by the use of electrical conductivity sensors as a surrogate to chloride concentration. Use of electrical conductivity for chloride concentration due to their direct correlation has been reported in literature (Howard and Haynes 1993; Granato and Smith 1999). Electrical conductivity readings compensated for 25°C or specific conductance values were used to estimate chloride concentrations using a bilinear equation as presented in Fig. 2 (Perera et al. 2009). Bi-linear relationship improved the accuracy of chloride concentration estimates by accounting for the contribution from other ions in the water on specific conductance.

The monitoring stations were visited often (every 1-3 wks) to check their performance, take samples and

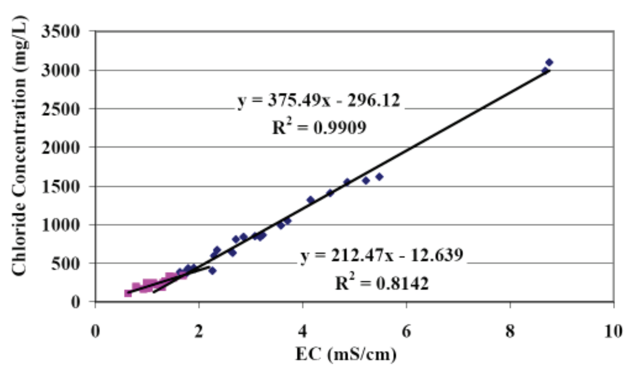

Fig. 2. Correlation between specific conductance and [Cl-].

TABLE 2. Availability of chloride concentration monitoring data

Station	*Period*	*Data Logging Frequency*
Morningside	Nov. 27, 2004 – May 22, 2008 May 22, 2008 – Oct. 30, 2008	1hr 15 min
Malvern	Feb. 28, 2007 – Mar. 6, 2008 Mar. 6, 2008 – Oct. 30, 2008	1hr 15 min
West Highland Creek	Feb. 15, 2007 - Mar. 6, 2008 Mar. 6, 2008 – Oct. 30, 2008	1hr 15 min

to change the batteries. The sensors were cleaned and recalibrated as required. Grab samples taken during the site visits were analyzed at the City of Toronto Water Analysis Laboratory. Table 2 summarizes the chloride concentration data availability for each monitoring station. Considering the size of the sub-catchments, hourly data logging was found to be sufficient for accurate estimates of chloride loading and mass balance.

Monitoring data quality assurance and quality control. Errors in specific conductance measurements generally occurs due to fouling of sensors and drift in calibration. Additionally, errors are introduced if the sensor is buried in sediments or ice is formed around it. Frequent site visits to clean and to recalibrate the sensor enabled the identification and correction of those errors.

Fouling error and error due to drift in calibration were defined as follows (considering the large range of specific conductance values, corrections were made considering a percentage error rather than a constant error):

$$\text{Fouling Error}(\%) = \left(\frac{(FC_a - FC_b) - (PC_e - PC_s)}{FC_b}\right) \times 100$$

where,

FC_a = field specific conductance reading after the sensor is cleaned

FC_b = field specific conductance reading before the sensor is cleaned

PC_e = portable specific conductance reading at the start of servicing, and

PC_s = portable specific conductance reading at the end of servicing.

$$\text{Calibration drift error }(\%) = \left(\frac{V_s - V_c}{V_c}\right) \times 100$$

where,

V_s = specific conductance of the calibration standard solution

V_c = field specific conductance reading in the calibration standard solution

Because fouling and drift in calibration take place gradually, the correction was made by prorating chloride concentrations from start to end date of the correction period. The correction period is the duration between two consecutive site visits with sensor cleaning and/or recalibration. Fouling of sensors was common during the study period, especially in the spring, but drift in calibration was very rare. Figure 3 presents a period between two site visits where correction for sensor fouling was applied to monitored specific conductance.

Additionally specific conductance data were checked with precipitation, stream flow, road salt application rates, and ambient temperature data for anomalies between site visits. There were several occasions when field specific conductance was missing due to low battery, sensor problems, and during sensor cleaning and recalibration. In most of these instances the duration of missing data spanned only a few hours except for disturbance at Morningside station during a storm on August 19, 2005, and on one occasion the sensor was buried with sediments for two weeks at Malvern station. Missing data for small durations were in filled using a linear trend between the values on the both sides of the data gap.

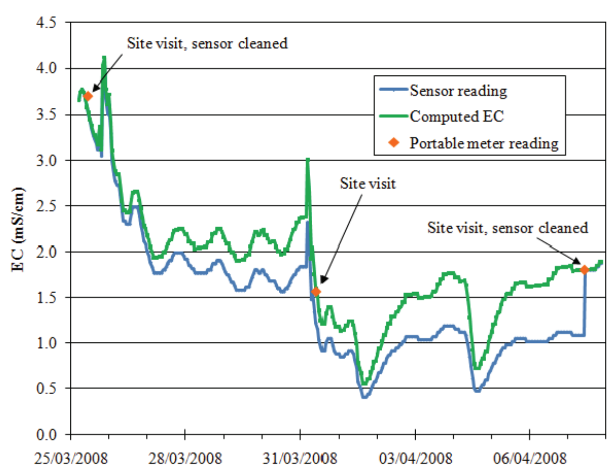

Fig. 3. Correction for fouling between two consecutive sensor cleaning.

Stream flow data. Chloride-monitoring stations were initially set up close to the existing flow gauges operated by WSC and TRCA for the convenience of obtaining high-quality flow data. Morningside and West Highland Creek stations are operated by WSC and Malvern station is operated by TRCA.

Highland Creek flow gauge at Westhill (near the Morningside chloride monitoring station) had not been in operation since 1998, but was commissioned again in January 2006. Therefore, estimated flow rates were used to calculate chloride mass for the period between November 2004 and December 2005. The flow estimation was performed after developing a correlation between Highland Creek flows and Don River flows (WSC flow gauge 02HC024). Don River watershed, with a drainage area of 316 km^2, is located adjacent to Highland Creek watershed and has similar land use. Correlation was tried with different lag times and a 2 hr lag provided a linear correlation with a coefficient of determination (R^2) of 0.87.

Road Salt Application Data

City of Toronto and Ontario Ministry of Transportation. The City of Toronto and the MTO keep daily records of salt application rates. Both agencies have salt application trucks equipped with calibrated spreader controls that can provide accurate estimates of salt application data. Uncertainty in the road salt application data from the City of Toronto and MTO is low because of spreader calibration.

Daily road salt application quantities by the City of Toronto for each sub-catchment were determined from GIS data describing the routes that trucks use when applying salt. For each truck route, percentage of road lane lengths located within each sub-catchment was calculated. Total daily salt application of each truck was multiplied by these percentages to determine the salt quantity applied on each sub-catchment by each truck. Considering the similar road network and road salt application practices, salt applied by the Town of Markham (approximately 2% of the watershed) was estimated using City of Toronto daily application rates. MTO road salt application quantity on a daily basis was also interpolated in a similar manner using total daily salt quantities applied on the segment of Highway 401 between Highway 400 and Morningside Avenue.

Private Road Salt Application. The largest uncertainty in chloride mass balance in Highland Creek watershed is the quantity of road salts used on parking lots and driveways. Howard and Haynes (1993) assumed that application rates for parking lots in shopping complexes were the same as for major roads, while other parking lots received half the rate of a major road. Further, an average annual rate of 4 kg of road salts was assumed to be used per household. Kelly et al. (2008) considered the road salt application rate on commercial and residential parking areas to be equal to the rate used by the State Department of Transportation. Contribution of chloride mass due to private winter maintenance practices reported in literature varies from 14-40% (Howard and Haynes 1993; City of Madison 2006; Sassen and Kahl 2007). However, this percentage depends on density of roads and amount of parking lot and driveway areas.

For this study, commercial properties such as shopping complexes and institutional properties were assigned a rate two times higher compared to salt application rate on road pavements on a unit area basis, considering their increased sensitivity due to higher exposure to general public. Industrial and multi-family residential areas were assumed to use the same amount used on road pavements. These salt application rates are averages and it is important to note in some properties the rates would be more, for example major shopping complexes may apply three or four times the rate compared to salt applied on roads to maintain snow free parking lots.

The extent of paved areas under different land use was determined from ortho-photos taken in 2005 with the use of GIS. The City of Toronto provided detailed land use maps for the study area. It was assumed there have not been significant land use changes in the Highland Creek watershed between 2004 and 2008, and that the 2005 air photos would provide accurate estimates of the paved area. The final value for approximate private use of road salts was estimated to be approximately 38% of the total application. This value is towards the upper limit of the reported values in the literature (Sassen and Kahl 2007), but is justified considering the proportion of parking lots and the observed increase in long-term groundwater chloride concentration within the study area. According to the data from Salt Institute (Novotny et al. 2009), the national average in the USA of the proportion of deicing salts bought by private entities is 24% of the total deicing salts sold by rock salt producers. This proportion should be higher for urban areas considering the length of deiced road pavement area in non-urban areas (where deiced parking areas are non-significant).

Results and Discussion

Chloride output within Highland Creek Watershed

There is no continuous groundwater quality data for the Highland Creek watershed. Therefore, baseflow chloride concentrations were estimated assuming low-flows containing only baseflow, an assumption considered justified on the basis of the very rapid response of overland flow due to the highly developed nature of the Highland Creek watershed.

Stream chloride concentrations in Fig. 4 for dry-weather, non-winter conditions were calculated values based on measured specific conductance. Non-winter period is defined as the period from the last salt application and the first day of road salt application the following winter season. Dry weather flow conditions were assumed when

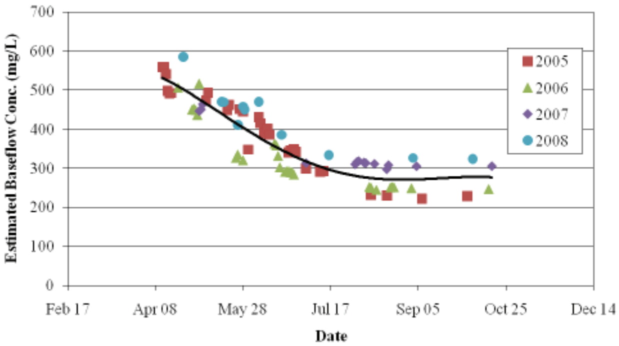

Fig. 4. Chloride concentrations under summer dry weather flow conditions at Morningside Monitoring station.

baseflow separation is within 5% of stream flow and when there are at least three preceding days without a total rainfall of more than 0.5 mm. It was difficult to obtain dry flow chloride concentrations during wet periods in some years.

Chloride concentration under low-flow (dry-weather) conditions in Highland Creek is high immediately following the winter period, reflecting the direct impact of road salt application. Dry weather flow chloride concentration then decreased gradually through summer until late September/October. Chloride concentration at the end of the fall period reaches a stable value until road salt application during the subsequent winter period. This phenomenon indicated that chlorides were in storage in surficial soil layers, as well as potentially in shallow groundwater, with slow release during the subsequent summer and fall. Several researchers reported retention of chlorides within a watershed on an annual basis (Howard and Haynes 1993; Howard and Maier 2007; Kelly et al. 2008; Kincaid and Findlay 2009; Meriano et al. 2009; Novotny et al. 2009).

Because chlorides are stored in surficial soils and groundwater and are released to surface water through the non-winter period, chloride mass in stream water was separated into two components; short- and long-term outputs. Short-term output is defined as the chloride mass contributed by direct runoff and shallow groundwater until the next winter season. Long-term output is a function of chlorides associated with deep groundwater and thus baseflows, and is considered to be a result of road salt application during previous years. From Fig. 4, the long-term baseflow chloride concentration was estimated to be 275 mg/L for the Morningside sub-watershed. It is important to note that the baseflow concentration exceeds the US EPA guideline for chronic (long-term) exposures of 230 mg/L (US EPA 1988) and suggests that at least some aquatic organisms would be always at risk, potentially 5-10% of taxa based on the species sensitivity distribution presented in Environment Canada and Health Canada (2001).

Figure 4 also indicates that there is a year to year increase in baseflow chloride concentration during the study period. This is in agreement with the observations made by Howard and Haynes (1993) for the same watershed. They predicted that average chloride concentration in groundwater would gradually increase even without an increase of salt application rates.

Mass Balance

The daily mass balance for chlorides in Highland Creek watershed (at Morningside monitoring station) is presented in Fig. 5. Based on the rationale described in section 3.1, chloride mass in stream water was divided into two components: short-term and long-term chloride outputs. Chlorides stored in the shallow layers of soils as a result of road salt application during preceding winter and discharged into streams were considered the short-term chloride output. Yearly data is presented considering a water year starting from the beginning of November to the end of October the next year. The sub-sequent sections discuss the mass balance results under different time-scales to identify different temporal variabilities that are difficult to capture with a daily mass balance.

Figure 5 shows variability in total yearly salt application, chloride mass in stream flow, and short-term output. It is important to note that these yearly salt application estimates are higher compared to the values reported in Howard and Haynes (1993) for the same watershed. The main difference is the estimates of chloride input by private de-icing operations (38% as opposed to 14%). In addition to the changes in salt application data tracking/reporting, total lane km maintained by the City of Toronto also increased by approximately 20% from 1995 to 2008 (Perera et al. 2009). Understandably, contribution to chloride mass in stream flow is dominated by short-term chloride output during winter and early spring, and long-term contribution is significant mainly during summer and fall. It is also evident that the cumulative short-term chloride output approaches a constant value towards the end of October (the end of water year) indicating chlorides mass in the stream during that period is mainly

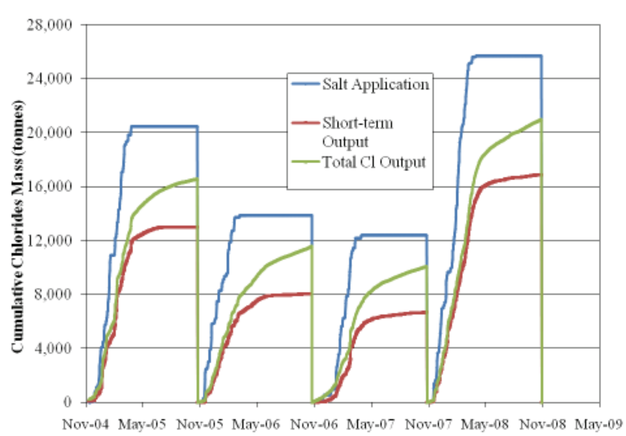

Fig. 5. Daily mass balance for Highland Creek at Morningside Avenue.

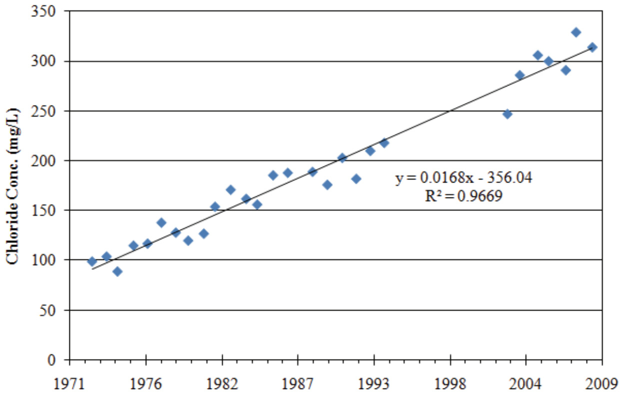

Fig. 6. Chloride concentration in Highland Creek under dry weather flow conditions during September/October months of the year.

due to groundwater contribution. Figure 5 also shows a difference between the cumulative chloride mass that was applied on the watershed and the total output indicating some storage in the groundwater. This fact is supported by the annual increase in long-term chloride concentration in groundwater as presented in Fig. 4. The increase in storage of chlorides in groundwater was compared with the long-term dry weather stream chloride concentration prior to winter salting period. Figure 6 presents laboratory analytical results of chloride concentration at Highland Creek since 1972, from the Ontario Provincial Water Quality Monitoring Network. Only the dry weather concentrations sampled during September/October months are included to determine the trend in long-term groundwater chloride concentrations.

Figure 6 indicates an increasing trend in estimated groundwater chloride concentrations with a slope of 0.017 mg/L per day which corresponds to approximate increase of 6 mg/L per year. This agrees with the conclusion of Howard and Haynes (1993) that under current chloride loadings, groundwater chloride concentration in Highland Creek watershed would continue to increase. Similar trends were reported by other researchers (Bester et al. 2006; Kelly 2008).

Monthly mass balance. Figure 7 presents chloride mass balance on a monthly basis considering errors in estimates due to uncertainties are less when considered in a longer time scale. It summarizes the road salt application and how much of it discharges into the streams on a monthly basis. Depending on the year, months of December, January, and February show higher chloride input. This is in contrast to months of March and April when chloride output is higher. Short-term chloride output continues to decrease until the end of the water year. This clearly shows the storage of chlorides within the watershed during winter period and subsequent slow release into the streams.

Seasonal mass balance. Figure 8 presents the chloride mass balance on a seasonal basis. Considering the observations made on inputs and outputs of watershed chloride mass balance, a water year (November to October) was divided into three seasons: November to March, April to June, and July to October. The November to March period includes winter and early spring to account for salt application and spring snow melt. The July to October season predictably shows the least impact from road salt application, and the April to June period is an intermediate season. Similar trends have been reported by other researchers (Howard and Haynes 1993; Kelley et al. 2008).

The November to March season defines the period in which most of the activities related to road salt application and chloride washoff occur. Almost all the road salts are applied during this season except for occasional salting occurring on April. Majority of the chlorides applied on paved areas also washed off in the same period during snow melt events in the winter and spring thaw. Approximately 85% of the annual short-term chloride output occurs during the period of November to March. April to June season still shows

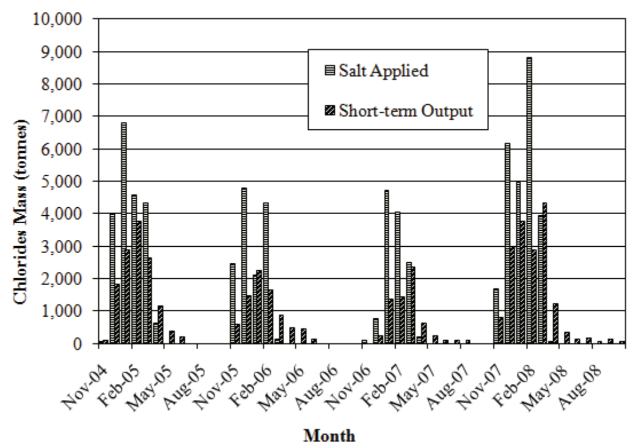

Fig. 7. Monthly mass balance for Highland Creek.

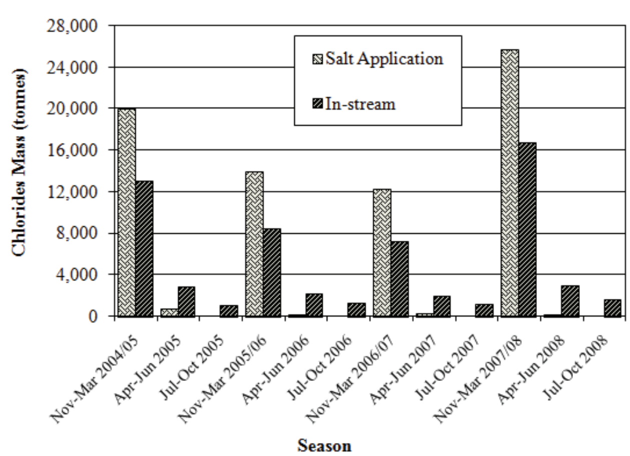

Fig. 8. Seasonal mass balance for Highland Creek.

significant runoff of chlorides (approximately 13%) and July to October season indicates the least significant season related to chloride mass balance in the watershed.

Yearly mass balance. Highland Creek watershed mass balance for chloride was also analyzed on a yearly basis. It is noted that a water year starting from November to October of the following year was considered for this purpose. Figure 9 presents the annual variability in chloride mass balance for Highland Creek watershed (area draining to Morningside monitoring station location).

There was a high year to year variability in the quantity of chlorides from road salts. It was dependent on climatic condition of each winter period as well as road salt management practices employed by the city of Toronto and MTO. Winters of 2004/05 and 2007/08 were relatively harsh and that is reflected in the total amount of salts applied during those periods. Approximately 60% of the chlorides applied on the watershed discharges into the streams as short-term output with an annual variability between 54-66%. Howard and Haynes (1993) reported approximately 45% of the salt applied runs off as with overland flow on an annual basis. However, considering the different approach in evaluating the chloride load in stream flow (short-term and long-term outputs in contrast to runoff and baseflow components), high proportion of imperviousness within the watershed, and the fact that most of the road pavements are directly connected to the streams via catch basins, storm sewers and outfalls, a higher rate of short-term output is justified. It is also noted the sum of chlorides in runoff and baseflow is less than total amount of chlorides contributed by road salt application indicating a net increase in chloride input to groundwater storage. Novotny et al. (2009) reported that as much as 77% of the annual total chloride input is retained within the watershed. They summarize other studies on chloride retention which ranges from 28-65%. Table 3 summarizes important parameters related to annual road salt mass balance in Highland Creek watershed.

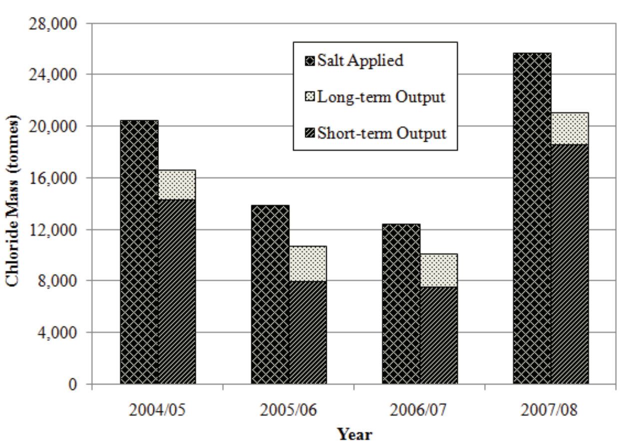

Fig. 9. Annual chloride mass balance for Highland Creek.

Yearly variability of these chloride mass components should be analyzed in the context of weather conditions prevailed during each year and each season. Table 4 summarizes the climatic and flow data for the period 2004-2008 in relation to road salt application and chloride washoff obtained from the Environment Canada weather station at Buttonville Airport (WMO ID 71639), and WSC flow gauge at West Hill (02HC013).

Annual total snowfall and mean winter temperature are good indicators of total amount of road salt application each year. Although the total amount chlorides due to road salts applied on paved surfaces has a high year to year variability (e.g. 12,400 tonnes in 2006/07 and 25,700 tonnes in 2007/08), the normalized salt application rate demonstrated less variability with a range of 1.21-1.66 tonnes/km^2 of catchment area per centimetre of snowfall. Coefficient of variation of total annual road salt use is 34%, while the coefficient of variation of normalized application rate is 15%. If the mean winter temperature is considered, variability in annual salt application rate is further reduced because lower mean winter temperature explains higher normalized rates for years 2004/05 and 2006/07. Total annual road salt application by the City of Toronto has been showing a decreasing trend during last few years when normalized by the annual snowfall and lane kilometres (Perera et al. 2009; Kilgour et al. In press). Annual rainfall and specially rainfall during winter determine relative contribution between the chloride mass as short-term and long-term outputs. Usually slow snowmelt enhances infiltration of chlorides into groundwater and rain on snow flushes chlorides into the stream faster.

Spatial Variations Chloride Mass Balance

Spatial variation of chloride mass balance within the Highland Creek watershed was evaluated to determine the effects of land use. Table 5 summarizes the total annual road salt usage chloride output in comparison to stream flow conditions and groundwater chloride concentrations within the three sub-watersheds considered. The data is from year 2007/08.

Morningside and West Highland Creek sub-watersheds show similarities in road salt application rates, chloride loads, and long-term groundwater chloride concentrations. This is due to their resemblance in land use as indicated in Table 1. There is a larger variability in long-term groundwater chloride concentration among the sub-watersheds indicating the effects of land use on flow and water quality response on each watershed. Malvern sub-watershed received a larger road salt application per unit area mainly due to its high proportion of industrial areas. It has a similar proportion of runoff to other areas but it exhibits a higher proportion of short-term output of chlorides. This fast response in chloride washoff is indicative of larger area of industrial land use (Table 1). Industrial areas usually have direct connections to the storm sewer system resulting in faster drainage of chlorides during snowmelt and rain-on-snow events. This same reason explains lower long-term chloride

TABLE 3. Annual chloride mass statistics

Year	*Annual road salt application (Cl tonnes)*	*Proportion of Cl mass as short-term output (%)*	*Net Cl mass input to groundwater (tonnes)*
2004/05	20,500	63	3,900
2005/06	13,900	58	2,300
2006/07	12,400	54	2,300
2007/08	25,700	66	4,700

TABLE 4. Annual summary of climatic and flow data for Highland Creek watershed

Year:	*2004/05*	*2005/06*	*2006/07*	*2007/08*
Annual snowfall (cm)	154	128	88	251
Annual rainfall (mm)	622	855	490	778
Winter rainfall (mm)	199	277	185	201
Mean winter temperature^0(C)	-3.7	-2.4	-3.2	-3.0
Annual runoff (mm)	218	357	202	380
Annual baseflow (mm)	181	169	152	188
Annual normalized salt application rate (Cl^- tonnes/km^2/cm of snowfall)	1.56	1.28	1.66	1.21

TABLE 5. Spatial variation of road salt application, water quantity, and quality response in Highland Creek watershed

Sub-watershed:	*Morningside*	*West Highland Creek*	*Malvern Branch*
Total road salt application (tonnes/km^2)	303	308	380
Proportion of Runoff in stream flow (%)	68	76	73
Proportion of short term Output in stream chloride load (%)	66	64	81
Chloride accumulation within the watershed (tonnes)	4,700	2,300	360
Estimated chloride conc. in groundwater (mg/L)	275	350	200

concentration in groundwater and also higher chloride peaks during salting events in the Malvern sub-watershed.

Novotny et al. (2009) also reported spatial variability in sub-watershed chloride mass balance in Minneapolis/ St. Paul, Minnesota in terms of salt application amounts and chloride retention within the watershed. Percentage of chlorides retained within the watershed varied between 55-83%. They highlighted the effect of imperviousness on spatial variation of chloride mass balance but did not discuss different land uses in detail. Mayer et al. (1999) indicates the spatial variability in average annual chloride concentrations in a much larger scale.

Conclusions

Compared to the previous literature on chloride mass balance in urban areas, this paper presents results for a longer period (four years) with a higher data collection frequency (at least hourly). Based on the results of this research the following conclusions can be made:

- Total amount of road salts applied on paved areas has a high variability and is dependent on several climatic factors (total snowfall, type and rate of precipitation, mean winter temperature). However, the variability of the road salt application rate decreases significantly when the rate is normalized based on total snowfall and mean winter temperature. Coefficient of variation of salt application rate when normalized by snowfall is half of the coefficient of variation of total annual application rate.

- Amount of road salt applied by private contractors on parking lots and driveways is estimated to be approximately 38% of the total road salts applied within the Highland Creek watershed. Therefore, impact of private deicing operations on watershed chloride mass balance is significant and any attempts to reduce the amount of road salts being applied on urban areas should also target this chloride source. It is important to note that in some private properties, the salt application rate could be several times higher than the rate applied on road pavements.

- Approximately 60% of the chlorides from applied road salt is removed from the watershed as short-term chloride output prior to the next winter season. Effect of short-term chloride output on aquatic ecosystems is more significant during November to March season as 85% of the short-term output occurs during this period.

- A portion of the chlorides infiltrated through pervious areas is retained in the surficial soils and/or shallow groundwater and is continuously discharged into stream water throughout the rest of the year. In the Highland Creek watershed, following each winter, chloride concentration in groundwater decreases until it reaches approximately 275 mg/L towards the end of October. The groundwater chloride concentration exceeds the US EPA guideline for chronic (long-term) exposures of 230 mg/L and at least some aquatic organisms in Highland Creek would always be at risk under dry flow conditions.

- Road salt application and short-term and long-term chloride output in Highland Creek watershed show spatial variability depending on land use. In addition to the road density, a high percentage of commercial, industrial and multi-family residential land use increases amount of road salts used for deicing. Therefore, areas with these land uses should be given priority for implementation of any salt management best practices.

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