Journal of Hydrology 531 (2015) 523-533

Contents lists available at ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol

Salt vulnerability assessment methodology for municipal supply wells



HYDROLOGY

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ARTICLE INFO

Article history: Received 18 June 2015 Received in revised form 3 November 2015 Accepted 4 November 2015 Available online 10 November 2015 This manuscript was handled by Geoff Syme, Editor-in-Chief, with the assistance of Abhijit Mukherjee, Associate Editor

Keywords: Road salt Water quality Vulnerability GIS Groundwater Chloride

SUMMARY

De-icing agents containing chloride ions used for winter road maintenance have the potential to negatively impact groundwater resources for drinking water supplies. A novel methodology using commonly-available geospatial data (land use, well head protection areas) and public accessible data (salt application rates, hydrometric data) to identify salt vulnerable areas (SVAs) for groundwater wells is developed to prioritize implementation of better management practices for road salt applications. The approach uses simple mass-balance terms to collect chloride input from 3 pathways: surface runoff, shallow interflow and baseflow. A risk score is calculated, which depends on the land use within the respective municipal supply well protection area. Therefore, it is plausible to avoid costly and extensive numerical modeling (which also would bear many assumptions, simplifications and uncertainties). The method is applied to perform a vulnerability assessment on twenty municipal water supply wells in the Grand River watershed, Ontario, Canada. The calculated steady-state groundwater recharge chloride concentrations in the case study evaluation, with an $R^2 = 0.84$. The new method provides a simple, robust, and practical method for municipalities to assess the long-term risk of chloride contamination of municipal supply wells due to road salt application.

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1. Introduction

Use of de-icing agents containing chloride and sodium ions (road salt) is one of the most commonly employed management strategies used by winter road maintenance agencies to prevent the buildup of snow and ice on road surfaces. Chloride-based road salt lowers the freezing point of water, inhibiting the formation of ice. Approximately 5 million tonnes of road salt is applied annually on roadways across Canada (Environment Canada, 2004) and approximately 18 million tonnes is used annually in the US (Jackson and Jobbagy, 2005). Road salt is primarily applied in major urban centers due to the high density of road networks and parking lots.

Chloride ions do not biodegrade, readily precipitate, volatilize, or bio-accumulate (CCME, 2011). Therefore, most of the effort in minimizing the impact of road salt is focused on optimizing salt application rates and implementing various beneficial management practices (TAC, 2003). Numerous studies have developed thresholds and guidelines for road salt (US EPA, 1988;

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Environment Canada and Health Canada, 2001; TAC, 2003; Environment Canada, 2004; CCME, 2011). The US EPA has established toxicity thresholds for chloride, which sets chronic freshwater quality criterion at 230 mg/L and the acute freshwater quality criterion at 860 mg/L (US EPA, 1988). The Canadian Council of Ministers of the Environment (CCME, 1998) established Canadian drinking water standards for chloride and sodium based on aesthetic objectives at 250 mg/L and 200 mg/L, respectively.

A primary concern regarding road salt application is contamination of drinking water sources such as groundwater. Chloride that infiltrates through surface soil layers and into aquifers has the potential to migrate towards drinking water wells (e.g. Huling and Hollocher, 1972; Eisen and Anderson, 1979; Jones et al., 1986; Howard and Beck, 1993; Thunqvist, 2004; Bester et al., 2006; Meriano et al., 2009; Iqbal et al., 2014). Runoff that percolates into the soil, transporting chloride to groundwater, will ultimately resurface through discharge (e.g. seeps or springs) into the surface water network (D'Itri, 1992; Williams et al., 2000; Howard and Maier, 2007; Perera et al., 2009, 2010, 2013; Kilgour et al., 2013; Trenouth et al., 2015; Trenouth and Gharabaghi, 2015).

The extent of the impact that road salts have on groundwater depends to a large extent on the road salt loading, climate conditions, surface and subsurface soil conditions and position of the site within the hydrogeologic environment. As examples of



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Nomencl	ature
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А	contributing area (m ²)	SVA	salt vulnerable areas (-)
BFI	Baseflow index (-)	Theta (θ) recharge fraction that discharges through interflow
CGVD28	Canadian geodetic vertical datum 1928 (–)	UAR	Unit Chloride Application Rate (g/m ²)
CAD	Chloride Application Density (–)	MAF	mean annual flow (flow volume per unit drainage area)
CCME	Canadian Council of Ministers of the Environment (-)		(m/yr)
GIS	Geographical Information System (–)	MOE	Ontario Ministry of the Environment (-)
GPS	Global positioning system (–)	MTO	Ontario Ministry of Transportation (–)
Phi (φ)	Recharge fraction from non-salted areas	PGMN	Provincial groundwater monitoring network (-)
Q	mean annual flow rate (m ³ /s)	US EPA	United states environmental protection agency (–)
RCC	mean annual groundwater recharge chloride concentra-	WHPAs	Wellhead Protection Areas (-)
	tion (mg/L)		

magnitudes, chloride attributed to road salt applications has been measured at concentrations up to 10,800 mg/L in groundwater in the New York Mohawk River Basin (Godwin et al., 2003), over 1200 mg/L (Williams et al., 2000) and up to 3000 mg/L (Eyles and Howard, 1988) in spring water near Toronto, Canada, and over 300 mg/L in municipal wells in Kitchener, Canada (Bester et al., 2006).

Groundwater quality is at greatest risk for chloride contamination in urban areas due to heavy salt application practices (Environment Canada and Health Canada, 2001). Howard and Haynes (1993) estimated that chloride concentrations in baseflow will reach upwards of 400 mg/L in some urban streams in the Greater Toronto Area in the near future. A follow-up study in the heavily urbanized Highland Creek area in Toronto, Canada found that, as predicted, average chloride concentrations in baseflow has reached 275 mg/L and continue to increase, with discrete measurements reaching as high as 600 mg/L (Perera et al., 2013). Perera et al. (2013) also determined that up to 40% of road-salt applied chloride was transported into the shallow aquifer.

Environment Canada (2012) concluded that attention to saltvulnerable areas was significantly lacking in provincial and municipal salt management plans (SMPs) in Canada, since less than 30% of the SMPs had inventoried salt vulnerable areas. Vulnerable areas to road salt are defined as any area susceptible to adverse impacts to the health of the aquatic species or quality of drinking water sources as a result of the application of road salts during winter maintenance activities on roads and parking lots (Environment Canada, 2012). The low rate of participation of agencies responsible for road maintenance in identifying salt vulnerable areas is attributed to a lack of clear guidance on the methods and to the concern that the process of identifying vulnerable areas to road salt may require expensive and advanced data collection and analysis (Environment Canada, 2012). It is important to identify salt vulnerable areas because these areas would benefit most from Beneficial Management Practices (BMPs) outlined in SMPs.

Groundwater vulnerability maps are useful tools as part of effective land use planning and implementation of best management practices. Previous studies have presented a variety of statistical, process-based, and index-based groundwater vulnerability mapping models. Of all the techniques developed so far, indexbased techniques remain the most widely used method due to ease of implementation (Kumar et al., 2015; Aliewi and Al-Khatib, 2015; Chenini et al., 2015).

Index-based techniques usually employ geographic information systems (GIS) methods to determine the sensitivity of the drinking water well capture zone to infiltration of surface contaminants, but with little field validation (groundwater quality observations) for the calculated vulnerability scores. The main limitation of the index-based methods is that the weights that are assigned to hydrogeological factors in the calculation of the risk scores are

arbitrarily chosen (Dedewanou et al., 2015; Enzenhoefer et al., 2015; Ghazavi and Ebrahimi, 2015; Marin et al., 2015).

This paper describes a methodology, using commonly-available Geographical Information System (GIS) data, to identify areas vulnerable to road salts through evaluation of the impact of road salt application to drinking water quality. However, to address the above concern of the key limitation of the index-based methods, this paper uses a GIS-based mass balance technique that takes into account salt application rates, Chloride Application Density, and recharge rates to determine chloride concentrations/loadings in each of the three pathways: surface runoff, shallow interflow and baseflow. A risk score is calculated based on the steady-state mean annual recharge chloride concentrations (RCC), which depends on the land use and salt management plans within the respective municipal supply well capture zone.

If we do nothing and keep applying salt at the current rate for foreseeable future, eventually, after many decades, steady-state groundwater chloride concentrations will be reached; our risk score is based on the eventual steady-state groundwater chloride concentrations and not the current transient values; that is why we have based our risk score calculations on the steady-state recharge chloride concentration. The methodology quantifies the relative vulnerability to identified areas in order to prioritize implementation of beneficial management practices for road salt application for reduced water quality impact on groundwater resources.

2. Study areas

The Grand River watershed encompasses an area of approximately 6800 km² and contains a population of over 800,000 people (Grand River Conservation Authority (GRCA), 2008). A comprehensive understanding of the hydrological and hydrogeological characteristics of the study areas is essential for developing a methodology to estimate the chloride loading from road salt application and how chloride impacts the drinking water supply within each study area.

Twenty municipal water supply wells within the Grand River watershed in Ontario were used in the chloride mass balance study described herein to estimate the vulnerability to road salt application. Seven wells are located within the Region of Waterloo and fifteen are within the City of Guelph (Fig. 1). In general, the climate of the Grand River watershed is considered moderate to cool temperate (LESPR, 2008). The area experiences four distinct seasons, including winters where most of precipitation is in the form of snowfall. Precipitation is fairly uniformly distributed throughout the year, i.e. there is no rainy season, and the annual average precipitation in this catchment ranges from approximately 800 to 1025 mm/yr (Environment Canada, 2005). Snowfall typically



Fig. 1. Site location map.

begins in late October or November and ends around April, with average annual snowfall (liquid water equivalent) ranging from 98 to 245 mm/yr.

The geology of the watershed is not uniform, resulting in changing hydrologic conditions within the watershed. In general, the watershed is relatively flat with a total elevation change of approximately 180 m along the 300 km of the Grand River. The northern section of the watershed is comprised mainly of till plain, which typically leads to high surface runoff and little infiltration. The central section of the watershed contains moraines and sand/gravel deposits, which leads to high infiltration (i.e. greater than 400 mm/year) and relatively low surface runoff (outside of the highly urbanized sections). The southern section of the watershed consists mainly of Haldimand Clay Plain, which creates high surface runoff with little to no infiltration (i.e. less than 50 mm/year) (LESPR, 2008). Background (natural) groundwater chloride concentrations in the study area and southern Ontario are generally low, ranging from about 5 to 20 mg/L (Bester et al., 2006). Anthropogenic sources of chloride in the study area include road salt application, water softener discharge, septic tanks and wastewater treatment plants.

2.1. Data

Approximately 82% of the population within the Grand River watershed relies on groundwater as a source of drinking water (GRCA, 2008). As such, water quality data are collected and interpreted for municipal drinking water wells to ensure it is a safe source for public water supply. Chloride concentration data for each of the selected municipal supply wells were obtained from the Region of Waterloo and the City of Guelph. The municipal supply wells were chosen to cover a wide range of land use types to ensure the vulnerability assessment methodology was broadly applicable. The land use types covered by the selected municipal supply wells ranged from rural to urban sites. Table 2 presents a summary of the land use types in the study areas.

3. Methodology

Chloride ions are transported from roads and parking lots to surface and groundwater resources along three pathways: (1) rapid runoff to stormwater drainage systems; (2) shallow soil infiltration through interflow; and (3) a deeper and slower pathway through aquifers (Novotny et al., 1999). The temporal and spatial variations in chloride concentrations in groundwater recharge are related to source availability and hydrogeologic setting (Novotny et al., 2009). As such, a chloride mass balance approach which accounts for the spatial application rates of road salt, not the subsurface heterogeneity, is the basis for the improved vulnerability assessment approach presented in this paper.

Three key assumptions were considered in the road salt mass balance calculation: (i) road salts applied in a study area are transported by either surface runoff or groundwater recharge (infiltration); (ii) chloride concentrations in surface runoff are the same as the chloride concentrations in groundwater recharge when spatially averaged for a given watershed. This is premised on groundwater recharge originating from surface runoff in urban areas; and (iii) the volume of water in groundwater recharge is, on an annual long-term average, equal to the volume of water discharged into the stream as baseflow.

In this study, groundwater recharge refers to surface contributions from precipitation and runoff only, and does not consider groundwater recharge from surface water bodies (e.g. rivers). Mean annual recharge chloride concentration is calculated using the following equation:

$$\operatorname{RCC} = \frac{(1-\varphi)*(1-\theta)*\operatorname{BFI}*\operatorname{CAD}*\operatorname{UAR}*A}{(1-\varphi)*(1-\theta)*\operatorname{BFI}*A*\operatorname{MAF}+\varphi*\operatorname{BFI}*A*\operatorname{MAF}}$$
(1)

$$\operatorname{RCC} = \frac{\operatorname{CAD} * \operatorname{UAR}}{\operatorname{MAF}} * \frac{(1-\varphi) * (1-\theta)}{(1-\varphi) * (1-\theta) + \varphi}$$
(2)

where RCC is mean annual groundwater recharge chloride concentration (mg/L); *A* is contributing area (m²); CAD is Chloride Application Density (dimensionless); UAR is Unit Chloride Application Rate (g/m²); MAF is normalized mean annual flow (m/yr); φ is the fraction of groundwater recharge originated from non-salted areas (dimensionless); θ is the fraction of groundwater recharge that discharge through interflow (dimensionless). This methodology only considers the chloride contribution from road salt application and does not account for alternative sources such as water softeners, septic tanks, and wastewater treatment plants.

This methodology ultimately assigns a risk ranking score based on the ratio between mean annual groundwater recharge chloride concentration (RCC) (Eq. (1)) and Canadian drinking water standards set at 250 mg/L, as summarized in Table 5.

3.1. Contributing area

The focus in this study is on drinking water sources and, as such, the area of influence for the groundwater component refers to the capture zones for a specific municipal drinking water supply well. A capture zone for a drinking water well is defined as the area within which groundwater will migrate to the pumped well (Seaburn, 1989) and is usually defined for a specific timeframe. A Wellhead Protection Area (WHPA) is defined as the area surrounding a wellhead where the land use activities within the capture zone have the potential to adversely impact the quality of the pumped groundwater.

Under the Clean Water Act, the Province of Ontario has amended Ontario Regulation 287/07 (MOE, 2010) to support the preparation and implementation of source water protection plans. As a result, communities in Ontario are required to develop source water protection plans to protect their municipal sources of drinking water. As part of the source water protection plan the Ontario Ministry of the Environment requires delineation of WHPAs around municipal groundwater supply wells. Conservation Authorities across Ontario have recently developed maps of the WHPAs, which this study will use as the areas of influence for groundwater recharge areas; however, the modeling behind the development of the WHPAs does not include water quality, nor take into account road salt application rates and spatial distribution salt application.

The methods presented in this paper do not aim to calculate spatial nor temporal variations of groundwater chloride concentrations but to provide a simple salt vulnerability ranking score for WHPAs based on road salt application on roads and parking lots for better salt management to protect groundwater. These methods go a step beyond just mapping WHPAs by providing a salt vulnerability ranking score to refine salt management plans for critical areas.

WHPAs are in practice delineated primarily using 3D numerical models that take into account detailed subsurface characterization of heterogeneity to inform the model parameters, simulating groundwater flow (assuming equivalent porous media parameters) to pumped wells. In the Ontario context, the delineated WHPAs encompass the well capture zone for a 25 year travel time (that is, the time it takes for water to travel from a given point within the aquifer to the pumped municipal supply well using the accepted practice that assumes equivalent porous media parameters for all hydrologic settings). Many input parameters are included in the delineation of WHPAs. These include: (1) the topography; (2) the quantity of water being pumped; (3) aquifer and soil types (i.e. geology, hydrostratigraphy, hydraulic conductivity); and (4) the direction and velocity of groundwater flow. Four different capture zones (timeframes) are calculated for each well in Ontario:

Zone A: 100 m radius around well. Zone B: 0–2 years travel time. Zone C: 2–5 years travel time. Zone D: 5–25 years travel time.

3.2. Chloride Application Density (CAD)

Land use has direct and indirect effects on the physical, chemical and biological characteristics of groundwater (Stanfield and Kilgour, 2006). Many studies, for example, have identified that the percent impervious cover can be used to predict overall stream health (Schueler, 1994; Goetz et al., 2003; Snyder et al., 2005; Sabouri et al., 2013; Sattar and Gharabaghi, 2015).

The Chloride Application Density (CAD) refers to the total area within the contributing drainage area that receives chloride applications, including roads, parking lots, driveways and sidewalks. For a given land use type, CAD is calculated as:

CAD = % Area Receiving Road Salt Application

$$\times$$
 Salt Application Weighting Factor (3)

Table 1 presents the assumed Fraction of Area Receiving Road Salt Application (based on Betts, 2013) and the Salt Application Weighting Factors (based on Perera et al., 2010) for the typical urban land use categories, including: commercial, industrial, institutional, roads, residential, and open areas.

 Table 1

 Fraction of area receiving road salt application

Land use type	Fraction of area receiving road salt application	Salt application weighting factor (Perera et al., 2010)	Chloride Application Density (CAD)
Commercial	0.560	2	1.12
Industrial	0.465	1	0.47
Institutional	0.154	2	0.31
City roads	1.000	1	1.00
Highways	1.000	1	1.00
Residential	0.240	0.5	0.12
Open	0.000	0	0.00

For a given WHPA, the area-weighted CAD is a unitless parameter based on the weighted-sum of percent land use receiving salt application multiplied by the Chloride Application Density per land use type, as:

Total CAD =
$$\Sigma_i$$
(% Area Covered by a Land Use
× CAD for the Land Use) (4)

To calculate the CAD value for a WHPA, the distribution of land use was determined using ArcGIS 9.3, within the boundary of the well capture zone, with land use and road network map shapefile layers. The land use and road network maps were clipped using the WHPA map and total areas were summed for each land use and road type.

The CAD value was calculated by multiplying the land use areas by the fraction of land use receiving road salt application and the salt application weighting factor, then dividing by the total contributing area.

3.3. Unit Chloride Application Rate (UAR)

Road authorities typically define road salt application rates on a mass per unit area basis. Quantification of total salt applications within a study area becomes difficult when multiple road maintenance agencies which employ different application rates, are within the same study area. Therefore, for the purposes of the mass balance calculation, the application rates of the municipal road maintenance agency, which is typically the largest road salt applied in urban areas, is used as a surrogate for all application agencies (with the difference being accounted for through the CAD parameter). The use of site-specific road salt application data for each road maintenance agency in a study area leads to the most reliable RCC values. The UAR can be calculated using Eq. (5):

$$UAR\left(\frac{g}{m^{2}}\right) = \frac{Annual Road Salt Application Mass (tonnes) * 10^{b} \frac{grams}{tonnes}}{Total Road Length (2 - lane km) * 1000 \frac{m}{km} * 7.0 \frac{m}{2-lane}} \\ * 60.66\% \frac{Cl^{-}}{NaCl}$$
(5)

The inputs to the UAR calculation (annual quantity of road salts applied and total road length) can typically be obtained from the annual SMP reports produced by the governmental road maintenance agency, as required as part of the Code of Practice (Betts et al., 2014).

3.4. Normalized mean annual flow (MAF)

Chloride concentration in groundwater recharge is a ratio of the mass of available chloride and the dilution from the volume of water. The methodology proposed here uses the mean annual flow (MAF) as the dilution factor for chloride concentration. The MAF is the average annual volume of stream water per unit drainage area (m/yr).

Environment Canada's Water Survey of Canada collects, interprets and distributes gauged streamflow data for over 1600 active hydrometric gauges across Canada (Environment Canada, 2014). For each gauging station, Environment Canada calculates the mean annual flow (m^3/s). The data from the gauging stations are collected under a federal–provincial joint program. There are a total of five monitoring stations within the WHPA located in the Grand River watershed. The longest data range available for each gauging station was collected and the mean annual flow (MAF) was calculated for each watershed using Eq. (6):

$$MAF (m/yr) = \frac{Q\left(\frac{m^3}{s}\right) * 3600 \frac{s}{hr} * 24 \frac{hr}{day} * 365 \frac{days}{yr}}{Drainage Area \ km^2 * \frac{10^6 \ m^2}{km^2}}$$
(6)

The average annual stream flow rate Q (m³/s) was calculated from historic records for the Environment Canada gauge stations and divided by the drainage area to produce the MAF for each of the WHPA, as shown in Eq. (6).

3.5. Recharge fraction from non-salted areas, phi (φ)

As shown in the water mass balance diagram (Fig. 2), phi (φ) represents the fraction of groundwater recharge that originates from non-salted areas within the WHPA. The area represented by φ is a dilution factor that accounts for the "clean" non-salted groundwater recharge.

To calculate the φ value for a WHPA, the distribution of land use was determined using ArcGIS 9.3, within the boundary of the well capture zone (contributing area), with land use and road network map shapefile layers (similar to the method to determine CAD). The land use and road network maps were clipped using the WHPA map and total areas that do not receive road salt application were summed and divided by the total contributing area, resulting in the dimensionless φ value. Areas that do not receive road salt application are parks, lawns, roofs, and non-salted roads. Figs. 2 and 3 illustrate how φ is determined for the two components of the mass balance calculation, mass loading and dilution, respectively.

3.6. Recharge fraction that discharge as interflow, theta (θ)

As shown in the water mass balance diagram (Fig. 2), theta (θ) represents the fraction of groundwater recharge that discharges, in a relatively short period of time, back into surface waters through interflow. Interflow is referred to the horizontal movement of water in the unsaturated soil zone (and stormwater and sanitary sewer pipes), in a relatively short period of time (in the order of days) following a storm event.

The Ontario Flow Assessment Tool (OFAT) Daily Flow Toolkit, created by the Ministry of Natural Resources, was used to calculate interflow using baseflow separation techniques built into the model (Atieh et al., 2015). OFAT uses the Environment Canada Hydrometric database (HYDAT) of stream flow data and performs baseflow separation techniques using a two parameter digital filter. A digital filter is a numerical algorithm that partitions the streamflow hydrograph into "high frequency" (quick flow) and "low frequency" (baseflow) components. Quick flow represents the direct response to a rainfall event and includes overland flow (runoff), lateral flow in the soil (interflow) and rainfall that falls directly onto the stream surface. Baseflow represents the longer-term discharge derived from natural storage.

4. Results and discussions

Twenty WHPAs, delineating the municipal drinking water supply wells recharge capture zones (25 year time of travel), were provided by the Grand River Conservation Authority. Fig. 4 presents the three influence zones (Zone B, C and D) for the City of Cambridge at the Highway 401 WHPA used in this study. The WHPAs were selected to encompass a wide range of land use distributions, such as urban areas (Waterloo Center and Cambridge 401), urban and rural mixed (Guelph) and rural (Linwood).



Fig. 2. Water mass balance.



Fig. 3. Salt mass balance.

4.1. Chloride Application Density (CAD)

Chloride Application Density (CAD) refers to the total weighted area within the study area that receives salt application as presented in Eq. (3). The salt application weighting factor for typical urban land uses are adopted from Betts (2013). In addition, each land use type may have a different percentage of land area that receives road salt. Table 2 presents the land use breakdown for each study area and the area-weighted average Chloride Application Density (CAD) for each case study WHPA.

The resulting RCC CAD values also show a wide range for all WHPAs. The highest value is in Waterloo Center (0.75) due to the dominant land use of commercial areas and the lowest value is at Calico (0.04) due to the dominant land use of open space and no commercial, industrial or institutional areas within the WHPA. This was an expected result since Waterloo Center is the most urbanized watershed in the RCC calculation with 41% of the influence area comprising commercial land use. It was also expected that Calico would result in the lowest CAD value since almost the

entire influence area is open space (98.7%) with no commercial, industrial, institutional, MTO highways or residential land use areas.

4.2. Unit Chloride Application Rate (UAR)

Table 3 presents road salt application records for the City of Toronto (1986–2011) with annual chloride application per unit area (UAR) that range from 357 to 1308 mg/L.

Fig. 5 summarizes road salt application data for the municipalities within the study area (Region of Waterloo, City of Cambridge, City of Kitchener, City of Waterloo, North Dumfries, Town of Wellesley, Town of Wilmot and Township of Woolwich). The long-term average annual chloride application per unit area (UAR) was calculated for each study area from 2004 to 2013, as shown in Table 4. This date range was selected to represent the chloride application rates that reflect the decade post adoption of the Environment Canada Code of Practice.



Fig. 4. Cambridge 401 WHPA.

Between 1997 and 2013, the chloride application rates in each of the municipalities varied considerably from year to year. The variations are a result of the variability in climate conditions. In addition to climate variations, different classes of roads have different salt application requirement based on the level of service and performance targets. In Ontario, road classes are defined according to function and traffic volume. These classifications typically include Class 1 – expressways; Class 2 – arterials (major and minor); Class 3 – collectors and Class 4 – local residential. Road class 1 and 2 receive roughly double the salt load compared to road class 3 and 4.

4.3. Normalized mean annual flow (MAF)

Using the average mean annual flow in m³/s calculated from the data range for each of the five Environment Canada gauging stations within the study area and dividing by the contributing drainage area to the gauge station (Eq. (5)), the normalized MAF was calculated for each of the WHPAs. Table 4 presents the normalized MAF results for each of the gauging stations within the study areas.

Each WHPA contained only one Environment Canada gauging station and therefore the calculated MAF value for the sole station in each of the study areas was utilized. The results in Table 4 show the MAFs within each of the study areas are similar. This is expected since all study areas are within the Grand River watershed.

4.4. Recharge fraction from non-salted areas, phi (φ)

Phi (φ) was calculated for each of the municipal supply wells. Table 4 presents the results for each of the WHPAs investigated. The WHPA with the highest φ value was Calico (0.99). This was expected because the land use within the WHPA was only open green space area (i.e. zero area receiving road salt). The WHPA with the lowest φ value was Cambridge at 401 (0.50).

4.5. Recharge fraction that discharge as interflow, theta (θ)

Theta (θ) was calculated for each of the municipal supply wells. Table 4 lists the results for each of the WHPAs investigated. The

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Chloride Application Density (CAD) for each land use type.

Well location	Study area	Percent land use type					Chloride Application Density (CAD)	
		Commercial	Industrial	Institutional	Residential	Open	City roads	
Region of Waterloo wells	Linwood	0.2	0.0	6.1	45.9	38.3	9.5	0.105
	New Hamburg	0.0	3.0	0.0	26.7	61.0	9.3	0.062
	Waterloo Center	41.0	4.8	4.8	32.4	0.4	16.7	0.747
	Cambridge West	0.0	0.0	3.0	49.3	4.4	43.3	0.501
	Bleams Road	0.0	0.0	0.0	2.4	82.9	14.7	0.150
	Cambridge 401	22.0	52.9	0.0	8.1	5.0	12.0	0.646
City of Guelph wells	Burke	3.3	0.0	0.0	43.9	50.2	2.5	0.120
	Calico	0.0	0.0	0.0	0.0	98.7	1.3	0.013
	Clythe	0.0	30.1	0.0	0.0	66.5	3.5	0.175
	Dean	17.3	0.0	1.4	44.5	28.4	8.4	0.360
	Downey	4.0	0.0	4.6	26.8	54.7	9.9	0.204
	Edinburgh	4.8	22.3	0.0	45.7	18.2	8.9	0.314
	Emma	0.0	0.0	0.0	90.5	0.1	9.4	0.211
	Helmar	0.0	0.0	0.0	8.2	89.0	2.8	0.039
	Membro	0.0	31.5	0.0	48.5	13.8	6.2	0.270
	Paisley	0.0	0.0	2.7	67.6	20.9	8.7	0.184
	Sacco	0.0	60.0	0.0	0.0	34.6	5.4	0.335
	Smallfield	0.0	51.9	0.0	8.2	34.4	5.5	0.309
	University	26.7	0.0	1.4	37.0	29.9	4.9	0.428
	Water	0.0	1.2	14.1	53.2	23.9	7.6	0.194

Table 3

Road salt application records for the city of Toronto (1986-2011).

Year	Total road salt applied (tonnes)	Total road length (2-lane km)	UAR salt (g/m ²)	UAR Cl ⁻ (g/m ²)
1986/87	124,381	12,337	1440	874
1987/88	119,621	12,337	1385	840
1988/89	128,386	12,337	1487	902
1989/90	165,312	12,337	1914	1161
1990/91	154,044	12,337	1784	1082
1991/92	112,528	12,337	1303	790
1992/93	148,473	12,343	1718	1042
1993/94	149,647	12,343	1732	1051
1994/95	95,130	12,343	1101	668
1995/96	127,977	12,343	1481	898
1996/97	157,585	12,415	1813	1100
1997/98	101,939	12,493	1166	707
1998/99	140,410	12,493	1606	974
1999/00	142,869	13,846	1474	894
2000/01	176,595	13,800	1828	1109
2001/02	56,893	13,800	589	357
2002/03	208,230	13,800	2156	1308
2003/04	108,152	13,800	1120	679
2004/05	147,433	15,052	1399	849
2005/06	94,673	15,052	899	545
2006/07	89,112	15,052	846	513
2007/08	195,645	15,052	1857	1126
2008/09	147,130	15,052	1396	847
2009/10	81,484	15,052	773	469
2010/11	158,811	15,052	1507	914
Average				868

WHPA with the highest θ was Cambridge West (0.27). Fig. 6 presents a graphical representation of the baseflow separation results obtained from OFAT for the Environment Canada HYDAT station 02GA007 Speed River near Guelph. The results indicate that interflow represents, on an annual average, approximately seven percent of total streamflow.

4.6. Groundwater recharge chloride concentration (RCC)

Using Eq. (2), Table 4 presents each of the WHPAs input values and the resulting RCC calculated values for Zone B.

Waterloo Center has the highest calculated RCC value (1423 mg/L) for the WHPAs in the Grand River watershed. This



Fig. 5. Region of Waterloo and municipalities UAR Trent 1996-2013.

was expected due to the high percentage of commercial area and low percentage of open space within the WHPA. As can be seen in Table 4 the results in the WHPAs with high calculated CAD value typically coincide with a high RCC value.

4.7. Groundwater recharge chloride concentration validation

Validation is an essential part of any model development process if a model is intended to be accepted and used to support future decision-making. Therefore, chloride concentration monitoring data were collected for the municipal supply wells in Guelph (provided by the City of Guelph) and Waterloo Region (provided by the Region of Waterloo) and used to validate Eq. (2). The monitoring data indicated that urban areas within the Grand River watershed contained the highest chloride concentrations and reached levels similar to those found in urban areas in the City of Toronto. Fig. 7 presents the validation results.

The calculated RCC value for the municipal supply wells compares favourably to the measured groundwater chloride concentration values, with an $R^2 = 0.84$, calculated on log-transformed RCC values to enhance linearity (fitting a logarithmic

Table 4
WHPAs input values and the resulting RCC calculated values for Zone B.

Well location	Study area	CAD	ϕ	θ	UAR (g/m ²)	MAF (m)	Background concentration (mg/L)	RCC (mg/L)
Region of Waterloo wells	Linwood	0.11	0.87	0.06	912	0.37	1.0	33
-	New Hamburg	0.06	0.88	0.10	990	0.37	1.0	19
	Waterloo Center	0.75	0.54	0.21	1408	0.30	10.0	1423
	Cambridge West	0.50	0.54	0.27	572	0.37	1.2	300
	Bleams Road	0.15	0.85	0.11	990	0.37	1.0	56
	Cambridge 401	0.65	0.50	0.24	1493	0.33	10.0	1302
City of Guelph wells	Burke	0.12	0.93	0.07	693	0.31	10.0	27
	Calico	0.01	0.99	0.07	693	0.31	10.0	10
	Clythe	0.18	0.83	0.07	693	0.31	10.0	74
	Dean	0.36	0.79	0.07	693	0.31	10.0	173
	Downey	0.20	0.86	0.07	693	0.31	10.0	71
	Edinburgh	0.31	0.76	0.07	693	0.31	10.0	172
	Emma	0.21	0.86	0.07	693	0.31	10.0	71
	Helmar	0.04	0.97	0.07	693	0.31	10.0	13
	Membro	0.27	0.77	0.07	693	0.31	10.0	143
	Paisley	0.18	0.88	0.07	693	0.31	10.0	58
	Sacco	0.34	0.67	0.07	693	0.31	10.0	247
	Smallfield	0.31	0.70	0.07	693	0.31	10.0	207
	University	0.43	0.77	0.07	693	0.31	10.0	221
	Water	0.19	0.87	0.07	693	0.31	10.0	63



Fig. 6. Baseflow separation for the water survey of Canada hydrometric station 02GA007 on speed river near Guelph.



Fig. 7. Calculated recharge chloride concentration versus measured supply well chloride concentration.

model $y = 64.753 \ln(x) - 162.85$ as shown in Fig. 7). In Fig. 7, the two wells with highest RCC values have reached about 33% of their respective steady-state concentrations while the wells with much lower RCC values have reached 50–70% of the steady-state

recharge chloride concentrations; it will take many more decades before all wells will reach steady-state chloride concentrations. Equilibrium is more rapidly attained at some wells due to the specifics of an individual area. As a result, the ranking score is based on calculated RCC values as they reflect the eventual groundwater chloride concentrations (GCC) assuming current salt application rates will continue for foreseeable future. The correlation between the RCC and steady-state equilibrium GCC values (after a few decades) may approach closer to a linear trend.

Despite the fact that there were no groundwater recharge monitoring data to validate the ability of Eq. (2) to accurately estimate RCC, the strong correlation between measured transient chloride concentration in municipal supply wells and calculated steadystate RCC values indicates that Eq. (2) can be used with a degree of confidence, to rank the vulnerability of one municipal supply well relative to others.

There are many factors that might contribute to the error or uncertainty of Eq. (2) to predict groundwater chloride concentration. For example, there may be additional contributing sources of chloride other than from road salt (e.g. water softeners, septic tanks, wastewater treatment plants, etc.).

Horizontal and vertical error bars (\pm one standard deviation) were added to each municipal supply well's UAR (horizontal error bars) and measured groundwater chloride concentration (vertical error bars). An error bar with one standard deviation of the mean



Fig. 8. Regional supply well G5 chloride concentration trend (1973-2012).

in both the positive and negative direction, accounts for 68.3% of the data set.

Fig. 8 illustrates the regional supply well G5 chloride concentration trend (1973–2012) due to rapid urbanization that resulted in CAD increasing from 0.21 in late 1980s to 0.65 in 2012. As evident on Fig. 7, the calculated recharge chloride concentration and measured supply well chloride concentration are not on a 1:1 correlation, which may indicate that these wells have not reached equilibrium and suggest that if current road salt application procedures continue, there is a high likelihood that chloride concentrations will continue to increase until equilibrium is reached (this may take many decades). Perera et al. (2013) also noticed similar trend towards chloride concentration equilibrium in urban areas due to road salt application in his study on the Highland Creek watershed in Toronto. Transient conditions for groundwater chloride concentrations will always exist. However, the salt vulnerability scores are calculated based on RCC values (not groundwater chloride concentrations). The long-term average groundwater chloride concentrations will be strongly correlated with RCC values.

The main change post-1990 was the land use change where the dominant land use within the WHPA that was corn fields which were suddenly turned into industrial parking lots and Chloride Application Density (CAD) increasing from 0.21 in late 1980s to 0.65 in 2012.

4.8. Groundwater recharge risk ranking score

The risk ranking score for Zone B groundwater recharge chloride concentration for each of the WHPAs in the Grand River watershed is based on the ratio between calculated RCC and Canadian drinking water guidelines set for chloride concentration (250 mg/L). A summary of the risk ranking score for all RCC WHPAs is presented in Table 5.

Table 5 ranks the calculated scores in descending order to highlight the WHPAs that would benefit most from implementation of BMPs. The WHPA with the highest score was Waterloo Center having the highest risk score of 5.69. The result is anticipated because it contains the highest percentage of commercial areas. Calico municipal supply well was estimated to have the lowest risk ranking scores of 0.04, which is expected as this study areas does not contain any commercial, industrial or institutional areas.

Table 5

Risk ranking score	for WHPAs.
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Study area	RCC (mg/L)	Risk ranking score
Waterloo center	1423	5.69
Cambridge 401	1302	5.21
Cambridge West	300	1.20
Sacco	247	0.99
University	221	0.88
Smallfield	207	0.83
Dean	173	0.69
Edinburgh	172	0.69
Membro	143	0.57
Clythe	74	0.30
Downey	71	0.29
Emma	71	0.29
Water	63	0.25
Paisley	58	0.23
Bleams Road	56	0.22
Linwood	33	0.13
Burke	27	0.11
New Hamburg	19	0.08
Helmar	13	0.05
Calico	10	0.04

5. Conclusions

Clean water is essential for potable domestic water supply and the health of rivers and lakes. Of all the previous methods developed for groundwater vulnerability mapping, index-based techniques remain the most popular due to ease of implementation (Kumar et al., 2015; Aliewi and Al-Khatib, 2015; Chenini et al., 2015). Index-based techniques usually employ geographic information systems (GIS) methods to determine the sensitivity of the drinking water well capture zone to infiltration of surface contaminants, but with little field validation (groundwater quality observations) for the calculated vulnerability scores. The main limitation of the index-based methods is that the weights that are assigned to hydrogeological factors in the calculation of the risk scores are arbitrarily chosen (Dedewanou et al., 2015; Enzenhoefer et al., 2015; Ghazavi and Ebrahimi, 2015; Marin et al., 2015).

However, to address the above concern, this paper uses a GISbased mass balance technique that takes into account salt application rates, Chloride Application Density, and recharge rates to determine chloride concentrations/loadings in each of the three pathways: surface runoff, shallow interflow and baseflow. A risk score is calculated based on the steady-state mean annual recharge chloride concentrations (RCC), which depends on the land use and salt management plans within the respective municipal supply well capture zone.

This paper presents a new, simple and practical approach for salt vulnerability assessment of drinking water wells due to road salt contamination. The main advantage of the presented model is that it is based on analysis of commonly-available geo-spatial data (GIS maps of land use, well head protection areas) and their combination with public accessible data (salt application rates, hydrometric data). This study presents a practical method for calculating a relative index of vulnerability of municipal supply wells due to the use of road salt as a management tool.

The key notable results of the study, include:

- 1. Commercial properties contain the largest percent parking lot area and typically receive the highest salt application rates of all land use types (mean annual salt application rates on commercial and industrial parking lots in Ontario is about two times higher than expressways in the same area).
- 2. A good correlation was observed between measured groundwater chloride concentration in the municipal supply wells in the study area and the calculated groundwater recharge chloride concentration RCC (R^2 = 0.84), indicating that the calculated RCC – using readily available spatial data – can be used for ranking salt vulnerable areas for municipal supply wells and to help devise a sustainable road salt management plan.
- 3. The parameter with the greatest influence on the mean annual groundwater recharge chloride concentration (RCC) equation is Chloride Application Density (CAD). This study highlights what could happen to our drinking water supply wells (e.g. Well G5) if we urbanize land in the WHPA without consideration to the potential adverse effects on the recharge chloride concentrations.
- 4. Simplistic water protection policies should be revised to reflect these findings. In Ontario, under the Clean Water Act, 2006, for example, road salt application is considered to be a "significant" threat to drinking water quality in WHPAs – A, B, C and D where "the percentage of total impervious surface area, as set out on a total impervious surface area map, is 80% or more" (Government of Ontario, 2009). However, this study presents a more accurate assessment of threat to drinking water quality for municipal supply wells due to road salt application than the 80% total impervious surface area threshold.

This study presents a practical method for calculating a relative index of vulnerability of municipal supply wells due to the use of road salt as a management tool. However, the methods presented in this paper do not aim to calculate transient groundwater chloride concentrations but to provide a simple salt vulnerability ranking score for WHPAs based on road salt application on roads and parking lots for better salt management to protect groundwater. These methods go one step beyond just mapping WHPAs beyond providing a salt vulnerability ranking score to refine salt management plans for critical areas.

Acknowledgements

This research was made possible by the funding from the Natural Sciences and Engineering Research Council of Canada. The authors would like to acknowledge generous funding and support from the City of Toronto, the City of Guelph, the City of Cambridge, the City of Waterloo, the Region of Waterloo, the County of Wellington, the Grand River Conservation Authority, Ontario Ministry of Transportation, Ontario Research Fund, G360 Centre for Applied Groundwater Research, Environment Canada, Ontario Ministry of the Environment and Climate Change and the Salt Institute. Flow data for various streams were obtained from Water Survey of Canada and Toronto and Region Conservation Authority and water quality data were obtained from the Ontario Ministry of the Environment and Climate Change.

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