MODELLING THE TRANSPORT AND RETENTION OF CHLORIDE USING INCA-CL IN AN URBANIZING WATERSHED

By

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List of Abbreviations

Cl	Chloride
INCA-Cl	Integrated Catchment Model - Chloride
HER	Hydrological effective rainfall
ET	Evapotranspiration
LSPP	Lake Simcoe Protection Plan
LSW	Lake Simcoe watershed
OFAT	Ontario Flow Assessment Tool
PERSiST	Precipitation, evapotranspiration and runoff simulator
SMD	Soil moisture deficit
SOLRIS	Southern Ontario Land Resource Information System
TDS	Total Dissolved Solids

1.0 Introduction

In northern environments such as Canada, road salt (e.g. sodium chloride, NaCl) has been used as a de-icing agent to improve winter driving conditions since the 1950's (Godwin et al., 2003). While research has shown that the application of salt to roadways can reduce accident rates by up to 88%, the use of road salt has been linked to increasing concentrations of chloride (Cl) in ground and surface waters in urbanized watersheds (Godwin et al., 2003). A recent study (Dugan et al., 2017) which tested 371 lakes in north eastern North America found that 44% trended towards long term salinization – levels at which Cl concentrations may begin to impact freshwater ecosystems. High Cl concentrations have been found to be potentially lethal to aquatic organisms, and long-term exposure can have detrimental effects on human health (Howard and Beck, 1993; Kelly et al., 2008). Keeping lakes and rivers "fresh" is important for the maintenance of ecosystem services associated with freshwater resources such as drinking water, fisheries and aquatic habitat.

Baseline levels of salinity have been on the rise in urbanizing watersheds in Eastern Canada and the Northeastern United States (Kelly et al., 2008). Rapid urbanization can come with a host of watershed impacts, including an increase in impervious surfaces and roadways, leading to an increase in the level of Cl input from road salt application (Meriano et al., 2009). Dugan et al. (2017) found that as little as 1% impervious surface within a watershed can increase the chances of long-term salinization. Additional sources of Cl may include water softeners, sewage treatment, and natural geological sources (Kelly et al., 2008). Once applied to roadways, Cl can make its way into rivers and lakes via surface run off, transport via sewer systems, or through seepage into soil and groundwater systems (Kincaid and Findlay, 2009).

It was previously believed that the majority of Cl from road salts would wash through the hydrological system with snowmelt and storm water runoff. However, recent research has shown that as much as 55% of Cl may be retained within the watershed in soil or groundwater reservoirs (Bastviken et al., 2006; Howard and Beck, 1993). Additional work in Cl mass balance suggest this number may be as high as 90% depending on surficial geology and groundwater trends. This is supported by high summer baseflow concentrations found in many urbanized watersheds, and Cl concentrations that continue to rise even after road salt application is reduced or ceased entirely (Kelly et al., 2008; Kincaid and Findlay, 2009). As Cl can have such a profound impact on freshwater ecosystems, and long-term exposure can have ill effects for humans, understanding how Cl concentrations in freshwater are linked to road salt application, and identifying where salt vulnerable areas may be can have important implications for watershed management.

The Lake Simcoe watershed is one such region in which rising Cl concentrations have been identified (Eimers et al., 2005). Several of Southern Ontario's fastest growing cities (Barrie, Newmarket and Aurora) fall within the watershed boundaries. The Lake Simcoe Protection Plan was released in 2009, with Cl listed as a pollutant of concern, and a water quality indicator. It is anticipated that if current salt application practices continue, Cl concentrations within Lake Simcoe will exceed the Canadian Water Quality Guidelines by 2120 (*Lake Simcoe Protection Plan*, 2015). Several tributaries, such as Lover's Creek in Barrie have already demonstrated concentrations that exceed these guidelines in recent testing years – coincident with an increase in development within the Barrie catchment area (Winter et al., 2011).

In order to address concerns and help inform further management decisions about Cl in the Lake Simcoe watershed, it is important to be able to predict the behaviour of Cl concentrations across multiple spatial and temporal scales. The INCA-Cl model was developed in 2011 by Jin *et al*. It aims to provide daily time step predictions of in-stream Cl concentrations and flow. The model will be used in East Holland – a sub-watershed within the Lake Simcoe region which contains two of the fastest growing urban areas in Canada (Newmarket and Aurora (Winter et al., 2011), and is expected to experience further urbanization as part of Ontario's "Room to Grow" initiative (Places to Grow, 2017). Previous modelling work in urban-specific areas has focused on developing mass balance budgets and predicting retention on annual or longer basis. INCA-Cl will be applied to an urbanizing watershed for the purpose of testing if the model is capable of:

- *Modelling mass balance.* Is the model capable of replicating the annual retention of Cl as reported by recent mass balance studies in the region?

- *Modelling Cl concentrations and flow on a monthly or daily basis*. Is the model capable of producing accurate simulations of flow and concentrations on a finer time scale, such as seasonally, monthly, and daily? Can the model be used to forecast concentrations on these same time scales for future scenarios related to increasing urbanization and salt management regimes.

- *Modelling Cl concentrations on a temporal scale fine enough to inform toxicology and biota related research.* Is it possible for the model to be used in studies related to the timing of Cl pulse events and associated toxicity to aquatic organisms? Research such as this requires Cl concentration data that is accurate on an hourly time scale.

Determining if the model is appropriate for use in urban environments is important for modelling the specific processes at play in East Holland sub watershed related to Cl retention. Namely – is

Cl being retained, is the retention in the soil or ground water, and how long is it being retained. As Lake Simcoe moves towards implementing better salt management practices, this information will prove crucial, as any policy enacted today may take decades to show effect. The ability to predict Cl concentrations under a range of different potential application futures is an important tool for future watershed management.

2.0 Literature Review

2.1 Chloride and Freshwater Ecosystems

Salinization relates to an increase in the concentration of total dissolved solids (TDS) in water (Kaushal et al. 2005). At higher latitudes, an increase in Cl (an anion of salt) is most often attributed to runoff from the application of salt to roads, however alternative sources such as water softening systems and waste treatment plants can also contribute (Jin et al., 2011; Kelly et al., 2008). Chloride dissolves readily in water and can easily be propagated large distances – causing widespread effects to water quality and ecosystems (Winter et al. 2011). Soils in close proximity to roads are often found to have elevated concentrations of Cl, and levels as low as 30 mg/L can be damaging to vegetation (Kaushal et al. 2005). High concentrations of Cl (>1000 mg/L) can be lethal to aquatic life, and chronic exposure (as low as 250 mg/liter) has been shown to be harmful to humans (Kincaid and Findlay, 2009).

General assumptions in the past were that the majority of the Cl being applied to roads was flushed from the system during precipitation events and annual snow melt, and environmental impacts were minimal (Howard and Haynes, 1993). However, recent research suggests that Cl may be retained on an annual basis within catchments within subsurface waters

(Howard and Haynes, 1993), soil micropores (Mason et al., 1999), and as organic chlorine compounds via incorporation into soil organic matter (Öberg and Sandén, 2005). A study of a typical urban catchment in Southern Ontario (Howard and Haynes, 1993), found that only 45% of the Cl applied to the catchment annually was being removed, with the remainder stored. Average concentrations of Cl within both groundwater and as discharge to streams steadily increased despite road salt application rates remaining constant.

2.1.1 Transport and Retention of Chloride

Although Cl is naturally found in freshwater at low concentrations (Dugan et al., 2017), elevated concentrations of Cl are often found in storm water runoff and snow melt in cold regions where salt is applied to roads (Winter et al., 2011). Cl is considered highly soluble, and highly persistent. Thus, once in solution it may transported along three pathways - rapid surface runoff facilitated by impervious surfaces, shallow subsurface transport through soils, and deeper transport through groundwater and aquifers. The method of transport is dictated by soil permeability, vegetation cover, topography and sewer and other drainage infrastructure (Novotny et al., 2009). The degree of urbanization is additionally an important factor in dictating method of transport, as studies on urban and suburban streams in the Northeast United State (Dugan et al., 2017; Kaushal et al., 2005) closely linked the concentration of Cl to the amount of impervious surface coverage within the watershed. Impervious cover of less than 1% within a watershed increased the likelihood of long-term salinization (Dugan et al., 2017). Developed areas with greater than 40% impervious surface coverage consistently demonstrated mean annual Cl concentrations which were potentially lethal to sensitive freshwater taxa.

Environment Canada (2001) suggests that 50% of salt applied to roadsides is removed via direct runoff or drainage and sewer systems, while the remaining 50% is accumulated on roadsides throughout the winter. Snow dumps, and roadside snow packs can show pollutant concentrations 5 times greater than typical storm water runoff, as Cl accumulates in the pack over the winter to be released in large quantities over a short period during snow melt events in early spring (Center for Watershed Protection, 2003). As Cl concentrations are largely driven by export from soil and groundwater to streams and rivers, it is to be expected that they would peak during times of snow melt and high precipitation – namely late winter and spring. However, Cl concentrations that peak in the late winter and then remain elevated throughout the summer and fall months have been recently observed in several urbanizing watersheds (Kelly et al., 2008; Kincaid and Findlay, 2009). This suggests a retention of Cl within the reservoir. Specifically, Cl may not be exported proportionally with surface and groundwater flow, with high concentrations during higher-flow months. Rather, it may be retained within the system during times of high flow, to supply elevated concentrations during lower flow months in the summer.

Kincaid and Findlay (2009), attempted to identify the mechanism by which Cl is retained in catchments for long term or later release. Both soil retention, and accumulation in groundwater have been proposed as Cl reservoirs, acting as both a sink and eventual source for summer baseflows. Cl is largely considered a conservative substance, wherein it moves through the hydrological cycle with little interaction with vegetation or soil. This is why it has historically been used as a tracer to calculate water fluxes and other ions (Svensson et al., 2012). However, recent research (Bastviken et al., 2006; Öberg and Sandén, 2005) suggest that small amounts of Cl may participate in some form of biogeochemical cycling involving the formation of organically bound chlorine. Bastviken et al., (2006) performed lysimeter experiments in which artificial rain was used to irrigate soil cores over a period of 4.5 months. They found that the Cl added via the irrigation did not act in a conservative manner. Cl measured in the leachate from the soil cores decreased for the initial months of the study period, and additionally was lower than the concentration of Cl being added to the cores. This suggests some retention of Cl, likely caused by ion exchange, or chlorination. In latter half of the study period, the net retention shifted to net release of Cl. This suggests that there is a mechanism at play for which soil can act to both retain and release Cl. It is suggested that the release of Cl may be triggered when easily accessible organic material for the purpose of chlorination is depleted.

As well as retention within the soil, mechanisms of retention and storage may include soil micropores, soil water, and ground water. To test which mechanism was at play, ground and stream water concentrations were tested by Kincaid and Findlay (2009). Groundwater concentrations were consistently below or equal to stream water concentrations. Soil samples taken from a variety of locations and across several soil types were irrigated with artificial rainwater with a known concentration of Cl. The concentration in the leachate was tested, and a mean retention across all samples was shown to be 20-60%. Whether the Cl was physically retained in porewater, or via chlorination of soil organic matter is unknown. The study showed soil retention and release was the most likely source of summer stream Cl concentrations, as levels of Cl were too low in the groundwater to maintain summer stream Cl concentrations. It was acknowledged that the two potential reservoirs might in fact not work exclusively, with the gradual release of Cl from soils in wetter spring months moving Cl into groundwater pools for summer stream recharge in dryer months. Additional studies have found long-term accumulation of Cl in groundwater aquifers (Howard and Maier, 2007; Kelly et al., 2008; Meriano et al., 2009; Novotny et al., 2009)

Storage of Cl in groundwater is a serious concern for drinking water quality, and suggests that Cl concentrations can continue to increase in stream water even after road salt application has been reduced or ceased. Understanding the mechanism that drive long-term retention and release of Cl is important for developing salt management best practices, and helping to mitigate some of the potential impacts high concentrations of Cl can have on freshwater ecosystems.

2.1.2 Potential Environmental and Health Impacts

Multiple studies have shown the impact of road salt or Cl on water quality and freshwater flora and fauna. Kaushal et al. (2005), have shown that levels of baseline salinity at the regional watershed level in Eastern Canada and the Northeastern United States are approaching a threshold at which the availability of drinking water and health of freshwater ecosystems will be permanently impacted. Both lethal and sub-lethal effects to aquatic organisms have been described (Findlay and Kelly, 2011). Potential effects can be considered direct, or indirect. Direct impacts are caused by altering the osmotic balance between the surrounding environment and the organism such that the threshold level for a given organism is surpassed. Indirect effects are caused by the altering of the physical environment, changing the physical process at work.

Direct impacts to organisms can be either acute or chronic. Acute impacts are generally lethal and can be caused by short term pulse events in which Cl concentrations rapidly rise after snow melt or a period of high temperatures. The lethality of the impact is dictated by the concentration and length of exposure. For example, a high concentration can be lethal after a short time, while a lesser concentration can also be lethal if exposed for a longer period. Each organism will have unique tolerance to Cl concentrations, however threshold levels for developing or larval forms of organisms are generally lower, and thus impacts have most commonly been described at these life stages. The adult form of some freshwater fishes may not experience lethal effects until levels of over 2000 mg/L (Findlay and Kelly, 2011), while juvenile forms of the same species may exhibit negative effects at less than 500 mg/L. The source of the exposure is also important, as direct exposure via road splash etc. will be different than exposure to a contaminant laden plume to a lake.

Sub lethal effects, or those which occur when organisms are exposed to a lower concentration of Cl for an extended period of time can have similarly devastating impacts to an ecosystem. Some of the effects which have been described include a reduction in reproductive ability of some fish species, loss of mobility, degradation of RNA and inhibited egg development (Evans and Frick, 2001). If the reproductive ability of a species is impacted, eventually that population will suffer long term decline.

Indirect impacts to surface waters as described by Ramakrishna and Viraraghavan (2005), include an alteration of water densities (Winter et al., 2011). Inflow that is higher in Cl concentrations may be denser. If levels are high enough, the inflow will sink to the bottom of the lake and prevent spring overturn. Spring mixing is important for the purpose of distributing oxygen and other nutrients within the lake. If mixing is prevented for long enough, salt induced stratification can occur, wherein oxygen is depleted at the bottom of the lake causing “dead zones” where no plants or animals are able to exist.

High concentrations of Cl can also cause increases in invasive species which are more salt tolerant, as well as encourage growth of microbial communities and algae (Richburg et al., 2001). While higher levels of Cl are required to encourage the growth of blue green algae, as little as 5 mg/L are required for *Anabaena cylindria* to thrive (Ramakrishna and Viraraghavan, 2005).

Cl concentrations are generally much higher closer to roads, and therefore streams located closer to roads are more vulnerable to impacts. This can also been seen in the terrestrial environment as studies have described permanent alteration of soil chemistry (Nelson et al., 2009), and tree death and damage (Bryson and Barker, 2002; Munck et al., 2010).

Potential impacts to human health come mostly in the form of chronic exposure. Unlike surface waters which have the power of dilution due to flow and precipitation inputs, groundwater aquifers are generally confined to a specific volume (Ramakrishna and Viraraghavan, 2005). These are also often the source of drinking water in urban areas. In addition to causing a salty taste, long-term exposure to drinking water with elevated concentrations of Cl has shown to cause increased risk of hypertension (Daley et al., 2009). Private drinking water wells are not required to be tested for Cl concentrations, and thus those regions where wells are more common are at higher risk for this effect.

2.1.3 Chloride Dynamics in Lake Simcoe Watershed

Chloride was identified as a pollutant of concern within the LSW in 2009 by the Lake Simcoe Protection Plan. Since then, some efforts have been made to assess changing Cl concentrations and the potential impacts to the broader ecosystem.

Winter et al. (2011) compiled data on Cl levels within the LSW over the past 36 years, and has found that concentrations measured at the outflow of the lake in 2007 have increased 3 times beyond the levels recorded in 1971. Additionally, 8 of the tributaries to the lake had also experienced significant increases in concentration – with the highest increases found in those tributaries with the greatest proportion of urban areas. As previously mentioned, two sub-watersheds within the Lake Simcoe watershed have greater than 25% urban area.

Unsurprisingly, tributaries within these sub-watersheds also demonstrated the highest increase in Cl concentrations. It is estimated if current trends in Cl levels continue, concentrations within the Lake will exceed national guidelines before the year 2120.

In 2015, a report was released summarizing the efforts of the local conservation authority to develop a model for identification of salt vulnerable areas within the Lake Simcoe region. This was in response to Environment Canada's Code of Practice for the Environmental Management of Road Salts. The policy recommends the identification of areas which may be vulnerable to high Cl concentrations. Salt vulnerable areas are defined as catchments where more than 5 taxa are impacted by exposure to high Cl concentrations. Betts et al. (2014) developed a method by which modelled concentrations were compared to watercourses with published aquatic sensitivities. Much of the urban region of Lake Simcoe, including the areas surrounding Newmarket, Barrie and Aurora was found to be "salt vulnerable," with between 20-40 potential species at risk. Work such as this is made possible through the use of mass balance and hydrological models which help to predict regions in which Cl will be highest. The LSRCA has made it a priority to address salt application in this region going forward.

2.2 Hydrological modelling of Chloride

Initial modelling of Cl began in the 1970's as a series of simple mass balance studies which calculated the total Cl inputs to a given watershed and compared it to measured outputs. Paine (1979), first suggested that Cl may be retained within the watershed by creating a coarse mass balance model of the Don River watershed in the Greater Toronto Area (GTA) which showed as little as 50% of the total Cl applied annually may be exported. Several follow up studies by Pilon and Howard (1987) and Eyles and Howard (1988) confirmed the widespread contamination of the shallow groundwater aquifer, with measured Cl concentrations of up to 14 000 mg/L. Howard and Haynes (1993) expanded on this work this by conducting the most robust mass balance modelling on the watershed to date. Three years worth of Cl inputs were calculated for the years 1988-1991, including estimates of private inputs and those from sources other than road salting. These inputs were compared to concentration data collected via conductivity probes installed in Highland Creek. It was found that only 45% of the Cl being applied annually was removed via either overland flow or summer discharge. This confirmed the accumulation of large amounts of Cl within the watershed.

Additional studies in other urban areas focused on the mass balance approach to determining retention rates. Studies in Boston (35% retention (Huling and Hollocher, 1972)) Helsinki (50% retention (Ruth, 2003)) and New York (59% retention (Bubeck et al., 1971)) used similar methods by which estimated inputs were compared to measured outputs to assess the degree of accumulation within the watershed. Novotny et al. (2009), expanded on the scale of the mass balance model by studying the entire Twin Cities Metropolitan Area (TCMA) of Minneapolis/St. Paul. This encompassed an area of over 4150 km^2, and included over 6 years of sampling work across multiple stream locations within the region. An extensive Cl input budget was developed, including road salt application, private inputs, natural sources, wastewater and septic treatment, atmospheric deposition and agricultural sources. Retention was found to be nearly 77%.

The majority of mass balance studies on Cl attempt to model current in stream concentrations in order to assess the degree to which Cl may be retained in the hydrological system. Kelly et al. (2008) produced a simple model which estimated groundwater and stream-water Cl concentrations trends for future years in addition to net retention over an extended period of time, using 20 years of data reflecting Cl and sodium concentrations in rural streams in Duchess County, New York, to The model was calibrated via measured precipitation and Cl inputs, with 10% of the road salt application used as a "bypass fraction" which will flow directly into the stream, and a fixed groundwater pool which composes all subsurface Cl pools. It is assumed that the concentration of Cl in the groundwater pool is the same as what will be exported via subsurface runoff, which is calculated as 50% of annual precipitation. It was found that the concentration of Cl in the stream water increased steadily over the 20-year period modeled, and the increase was observed in both winter and summer. An increase in the export of Cl was also observed over the study period, however the increase was evident in the winter months only. The model predicted that 91% of total Cl input was from roadway salt application. The model suggested that with a steady input of Cl, export and concentration will steadily increase before eventually leveling off. In the watershed modeled, the increase in stream water Cl concentration could not be accounted for by an increase in urbanization, and thus suggests the retention of Cl in groundwater or soils due to long-term road salt use. Increases in the summer concentration in tributaries are additional evidence of a storage effect in subsurface systems with slow release year-round.

The model by Kelly et al. (2008) was found to do a reasonable job of modeling Cl concentrations, however fluctuations due to abnormal precipitation or road salt applications were missed. As these are common in the urban environment due to the influence of impervious surfaces, the model left something to be desired for use in urbanizing watersheds. Jin et al. (2011) sought to improve on this issue by developing the Integrated Catchment Model for Chloride (INCA-Cl) to answer questions about how changes in road salting behavior will be reflected in long term Cl concentrations within watersheds. The model built upon the Integrated Catchment Model (INCA) first developed for nitrogen (Whitehead et al. 1998).

2.2.1 The Integrated Catchment Model & Chloride

Since development in 1998 by Whitehead et al. (1998), INCA has been used to model a variety of hydrological and nutrient related factors such as nitrogen (Langusch and Matzner, 2002; Whitehead et al., 1998), phosphorus (Wade et al. 2002) and carbon (Futter et al. 2007) with the purpose of determining impacts on water quality from land use changes and climate change (Jin et al. 2011). The model functions as a semi-distributed simulation, and is process-based. The model attempts to track temporal variations in hydrological flows, transformations and stores across both the land and stream portions of the catchment using reaction kinetic equations. The INCA Cl module was first developed as a means to provide estimates of Cl concentrations based on multiple input sources. The purpose was to develop a simple model that could be easily transferable to similar watersheds and which could address questions about how future Cl concentrations would reflect changes in road salt regimes, including increases in the use of salt due to urbanization. The development of this model was deemed necessary to help inform watershed management questions related to the rapid urbanization of certain population centres.

To date, the model has only been applied once, during development, in Fishkill Creek, New York by Jin et al. (2011). This is a small watershed currently experiencing slow transition from small scale agriculture to residential land use. Necessary data was land use area percentages, daily rainfall, daily temperature, soil moisture deficit, and hydrologically effective rainfall. Daily flow and Cl concentration were simulated for each reach within the modeled tributary. A small continuous data set on Cl concentrations available via a USGS gauge was used for model validation.

The model did a reasonable job of modelling flow, with slight over and underestimation of extreme high and low flow events. Similarly, Cl concentrations were well modelled, however measured concentrations were consistently slightly lower than modelled – suggesting a process by which Cl is retained within the ground or soil water. Basic scenarios related to increasing and decreasing salt application produced reasonable changes in modelled concentrations, suggesting that the model functions well as a potential management tool for road salt.

2.3 Summary & Significance

Chloride from road salt application is increasingly becoming an issue for water quality and watershed health in many areas of Canada and the Northeastern United States despite its utility in improving winter driving safety. Owing to the possibility of lethal effects to freshwater ecosystems, and impacts to human health, developing an understanding of how Cl moves within the hydrological system has become a focus for watershed management (Kaushal et al. 2005).

Lake Simcoe is an area where high Cl concentrations have been observed in several areas, and increasing urbanization may lead to an increase in road salt application. The Lake Simcoe Protection Plan, published in 2009, lists Cl as a pollutant of concern. If current trends in concentration continue, Lake Simcoe may reach levels that exceed the Canadian Water Quality Guidelines by 2120.   Previous Cl modelling work completed in urban areas has focused on developing mass balance budgets to determine retention of Cl. The application of the INCA-Cl model to an urbanizing environment will allow for the determination if the model is appropriate for use in modelling future Cl concentrations in these urban areas.

3.0 Modelling Chloride Transport and Retention Using INCA-Cl in the East Holland River Watershed

3.1 Abstract

In northern environments such as Canada, road salt (e.g. sodium chloride, NaCl) has been used as a de-icing agent to improve winter driving conditions since the 1950's. While research has shown that the application of salt to roadways can reduce accident rates, the use of road salt has been linked to increasing concentrations of chloride (Cl) in ground and surface waters. High Cl concentrations have been found to be potentially harmful to freshwater organisms, and long-term exposure can have detrimental effects on human health. The Integrated Catchment Model for Chloride (INCA-Cl), is a sub-watershed scale model that requires land cover, meteorological, and Cl surface application data as inputs to model the transport of Cl through a watershed. Here, we apply INCA-Cl to the rapidly urbanizing East Holland River sub-watershed located within the Lake Simcoe watershed in Southern Ontario, Canada. Results showed good agreement between measured and modelled stream flow, however the model fails to capture the in-stream Cl concentration dynamics. We reworked the spatial aspect of the model in an attempt to more accurately target Cl inputs to appropriate areas of land use, and still failed to obtain a satisfactory simulation. A comparison of modelled and measured Cl inputs, show that the model is able to balance mass on an annual basis, however, looking at the modelled results on a seasonal basis shows a strong negative relationship in summer months, suggesting that that the model is failing to capture the timing of the low-concentration summer flows. This is likely due to inadequacies in the model structure, such as an inability to model impervious surfaces, or to constrain salt application to specific land covers. Further work will be necessary to make INCA-Cl a viable option for Cl modelling in urban environments.

3.2 Introduction

Salinization of freshwater as a result of the widespread use of road salts is an emerging threat to water quality in Northern environments (Findlay and Kelly, 2011; Kaushal et al., 2005; Kelly et al., 2008) While the use of road salts has been shown to reduce winter driving accidents by up to 88% (Godwin et al., 2003), it has been linked to increasing concentrations of Cl in ground and surface waters (Dugan et al., 2017). High levels of Cl can be potentially lethal to aquatic organisms and long term exposure can damage freshwater ecosystems and have harmful effects on human health (Howard and Beck, 1993; Kelly et al., 2008). Baseline levels of salinity in surface waters have increased in urbanizing watersheds in Eastern Canada and much of the Northeastern United States (Kelly et al., 2008) due to the expansion of roadways and other impervious surfaces which require winter road salt applications (Meriano et al., 2009). Dugan et al. (2017) tested 371 freshwater lakes across Northeastern North America and found that as low as 1% impervious surface area in a watershed significantly increased the long-term chances of salinization Additional sources of Cl to receiving waters may include water softeners (Müller and Gächter, 2012), sewage treatment (Nimiroski and Waldron, 2002), and natural geological sources (Kelly et al., 2008); however, the dominant source in northern latitudes is road salt (Kaushal et al., 2005) .

Once applied to impervious surfaces, Cl is transported to receiving waters, such as rivers and lakes, via surface runoff and storm infrastructure, and via infiltration into soil water and percolation to groundwater systems (Kincaid and Findlay, 2009). While the conservative nature of Cl and the fact that it applied to impervious surfaces might suggest that it would be completely flushed from a watershed during snowmelt , research since the 1990s has shown that as much as 55% of Cl may be retained annually in soil water or groundwater aquifers (Bastviken et al., 2006; Howard and Haynes, 1993; Kelly et al., 2008; Kim and Koretsky, 2013; Perera et al., 2013), resulting in elevated Cl concentrations in surface waters year-round. These findings are supported by the high summer baseflow concentrations found in many urbanized watersheds (Findlay and Kelly, 2011; Howard and Maier, 2007), and Cl concentrations that continue to rise even after road salt application is reduced or stopped entirely (Kincaid and Findlay, 2009). Higher concentrations in the growing season are more likely to have impacts on freshwater ecosystems, as larval stages of aquatic organisms are typically more susceptible to toxic effects from exposure to even low Cl concentrations (Evans and Frick, 2001). Additionally, increased salinity can influence the stratification of lake ecosystems. Dense saline water sinks to the bottom, and prevents the turnover that is necessary to preserve ecosystem functions including the replenishment of deep water dissolve oxygen (Findlay and Kelly, 2011). Chloride retained in soil and groundwater may mean that historical salt application will have future consequences that remain to be seen. In addition to the short-term ecological implications of elevated salinity, changes made to salt application rates now may not result in a reduction of in-stream and lake Cl concentrations for several decades to come.

Howard and Haynes (1993), was one of the first to attempt to quantify Cl retention via a simple mass balance study in Highland Creek - a sub watershed within the Toronto area. It was found that the total input of Cl (an estimated 10 000 tons/season) far exceeded the amount of Cl leaving. Additional mass balance work by Kelly et al. (2008) used 20 years of data reflecting Cl concentrations in rural streams in Duchess County, New York to estimate ground and stream-water Cl concentrations in addition to net retention over time. It was found that the concentration of Cl in the stream water increased steadily over the 20-year period modeled, and the increase was observed in both winter and summer.

The need to develop a better understanding of Cl dynamics within the watershed has given rise to work which attempts to simulate the movement of Cl from application at roadside to waterways. The use of models which can better predict retention and release of Cl can help to inform salt management and application techniques. The Integrated Catchments Model (INCA) was first developed for use with Nitrogen (Langusch and Matzner, 2002; Whitehead et al., 1998) and has since grown to also include modules focused on phosphorus (Jackson-Blake et al., 2014; Jin et al., 2013; Wade et al., 2002) carbon (Futter et al., 2007), Cl (Jin et al., 2011), and mercury (Futter et al., 2012). All INCA models are designed to track temporal variations in hydrological flows, transformations and stores across both the land and stream portions of a catchment and can be used to investigate the impacts of climate and land use change on water quality.

The Integrated Catchment Model for Chloride (INCA-Cl) was first developed as a means to provide estimates of Cl concentrations based on multiple input sources (Jin et al., 2011), but could also be used to answer questions about how changes in road salt application rates, for example, increases due to urbanization or decreases due to better management or changing climatic conditions, would manifest in freshwater Cl concentrations. The goal was to develop a simple model which makes use of meteorological, streamflow and Cl application data, which are often easily accessible to watershed managers. To the best of our knowledge, there is only one published application of INCA-Cl to a small, suburban watershed (15% urban) in New York State for a period of one year (Jin et al., 2011). Given the growing concerns over increasing Cl concentrations in streams and lakes across the northern U.S. and southern Canada, the application of this model to an urbanizing watershed over an extended period of time will help determine if INCA-Cl is suitable for predicting future Cl concentrations in urban regions.

In this study, INCA-Cl will be used to model in-stream Cl concentrations and annual loads for the East Holland River, a sub-watershed of the Lake Simcoe watershed in Southern Ontario, Canada. Several of Southern Ontario's fastest growing cities (Barrie, Newmarket and Aurora) fall within the East Holland River sub-watershed and the Lake Simcoe watershed is a region in which rising stream Cl concentrations have been identified (Eimers et al., 2005; Winter et al., 2011). The Lake Simcoe Protection Plan was released in 2009, with Cl listed as a pollutant of concern, and a water quality indicator. Winter et al. (2011) compiled data on Cl levels within the Lake Simcoe Watershed over the past 36 years, and has found that concentrations measured at the outflow of the lake in 2007 have increased 3 times beyond the levels recorded in 1971. Additionally, 8 of the tributaries to the lake had also experienced significant increases in concentration with the highest increases found in those tributaries with the greatest proportion of urban areas. It is estimated if current trends in Cl levels continue, concentrations within the Lake will exceed national guidelines before the year 2120. Using the INCA-Cl model and data available from a federal gauging station near the outlet of the East Holland River, this study will model in-stream Cl concentrations at Holland Landing in East Holland, compare model output to measured Cl concentrations at the outlet site, and identify the parameters that the model results are most sensitive to.

3.3 Study Area

After the Laurentian Great Lakes, Lake Simcoe is the largest lake in Ontario (722 km^2), with a watershed area of 2914 km^2 and 22 sub-watersheds draining into it (Figure 1a,b). The lake itself is an important source of freshwater for the surrounding communities of Barrie, Kawartha, Newmarket and Orillia, and supports a thriving freshwater fishery that provides over $100 million in economic support to the area (Eimers et al., 2005). Owing to its proximity to the City of Toronto, the population of the Lake Simcoe region increased by 25% between 2000 and 2011 (Places to Grow, 2017) and concomitantly urban impervious area increased by 200% (Winter et al., 2011). Additionally, the East Holland area has been identified as a priority area for further development by the 2017 Growth Plan for the Greater Golden Horseshoe (Places to Grow, 2017), and a further population increase of up to 65% is expected by 2031. As of 2017, urban lands accounted for ~8% of the total land area within the watershed, with two sub watersheds, Lover's Creek and East Holland River having between 25 and 30% urban land use. As part of the previously mentioned Places to Grow plan, approximately 10 000 km^2 of the watershed has been identified for intensive urban development prior to 2031.

The East Holland River sub-watershed is located in central-southern portion of the Lake Simcoe watershed (Figure 1b) and flows northwards from its headwaters on the Oak Ridges Moraine until it meets the West Holland River approximately 5.5 km upstream of the outlet into Cook's Bay at the southern end of the lake (Figure 1c). Watershed boundaries and reach length were derived via the Ontario Watershed Flow Assessment Tool (OFAT). The drainage boundaries were drawn from Holland Landing where a Water Survey of Canada gauge is located, providing daily measurements of streamflow, as well as Cl concentrations at the outflow of the sub-watershed. Additional data on groundwater Cl concentrations is available from the Provincial Water Quality Monitoring Network (PWQMN) well in the same location. The catchment is approximately 173 km^2 and the total reach length is 39 km. East Holland river is characterized by high gradient slope and fast flow in the upstream reaches, (associated with the Oak Ridges Moraine), with flow that slows and lower gradient in the downstream reaches. It merges with the West Holland river approximately 5 km before the outflow to Lake Simcoe (Jin et al., 2013).

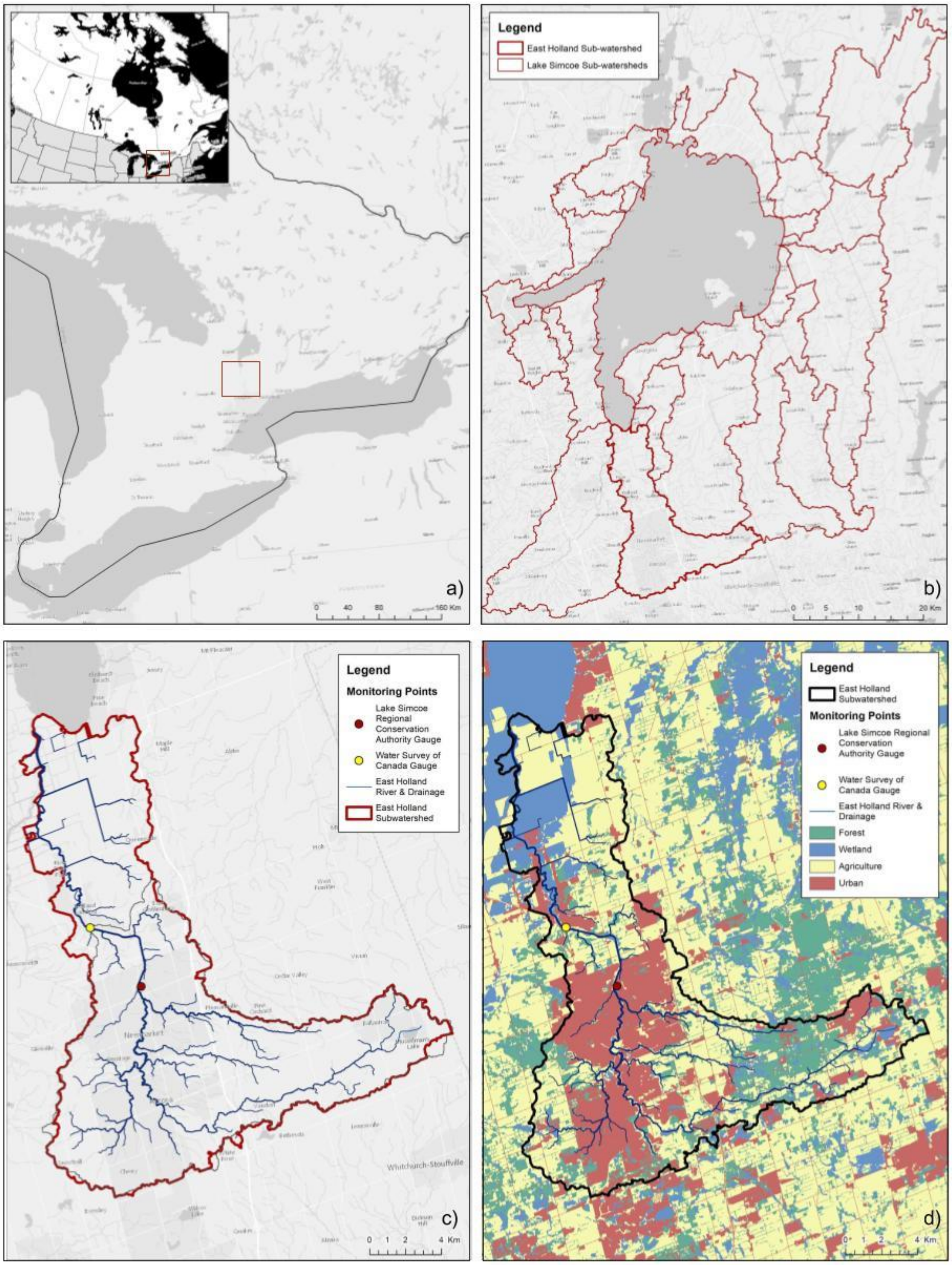


Figure 1: Maps of a) Lake Simcoe Region location, highlighted in red, b) sub-watersheds of Lake Simcoe, c) drainage and monitoring locations in East Holland sub-watershed (derived from OFAT, 2017) and d) land use in East Holland sub-watershed (derived from SOLRIS, 2017).

Data on the land cover characteristics of the catchment were derived from the Southern Ontario Land Resource Information System (SOLRIS). SOLRIS is a Government of Ontario raster product which provides detailed information on 23 land class uses at a 10 m resolution. The 23 land cover classes were condensed into four relevant classes – urban, agricultural, forest and wetland. Land cover is variable across the central-southern portion of the Lake Simcoe watershed and the East Holland River sub-watershed, as delineated from the Water Survey of Canada gauging station at Holland Landing (Figure 1c), is considered moderately urbanized (40%) containing both the Town of Aurora and the City of Newmarket. Agricultural and natural (e.g. forest and wetland) land cover make up 36% and 24% of the sub-watershed, respectively.

Mean annual temperature at the Richmond Hill meteorological station is 8°C and total annual rainfall is ~900 mm (with 16% falling as snow) (EC, 2017). Mean annual streamflow measured at the Holland Landing federal gauge (Figure 1c) is 1.35 m^3/s and Cl concentrations (recorded between 1993 and present as part of the Lake Simcoe Region Conservation Authority Monitoring Program (2017)) range between 7.2 and 1540 mg/L at peak magnitude, with an annual average of 212 mg/L. Concentrations have been increasing an average of 15% per year (LRSCA, 2017).

3.4 INCA-Cl Implementation and Data Sets

3.4.1 General description of INCA-Cl

INCA-Cl models the transport of water and Cl from surface application to the river via a semi-distributed approach, wherein the river or stream is split into reaches with associated sub-catchments (Jin et al., 2011). Each sub-catchment is further divided into land cover types – similar to the idea of a hydrologic response unit (HRU) (Devito et al., 2005), in which the soil type and topography is the same within the unit. In previous INCA-based studies, these HRUs have been distinguished via land-cover types (Jin et al., 2011; Wade et al., 2002; Whitehead et al., 1998). Inputs, flow, and storage of water and Cl are calculated for each land cover class within each sub-catchment and added to the associated reach (Figure 2). The total inputs for the reach then move to the downstream reach segment wherein inputs for that sub catchment are added. There is no flow simulated between land cover types within the sub-catchment (Jackson-Blake et al., 2014).

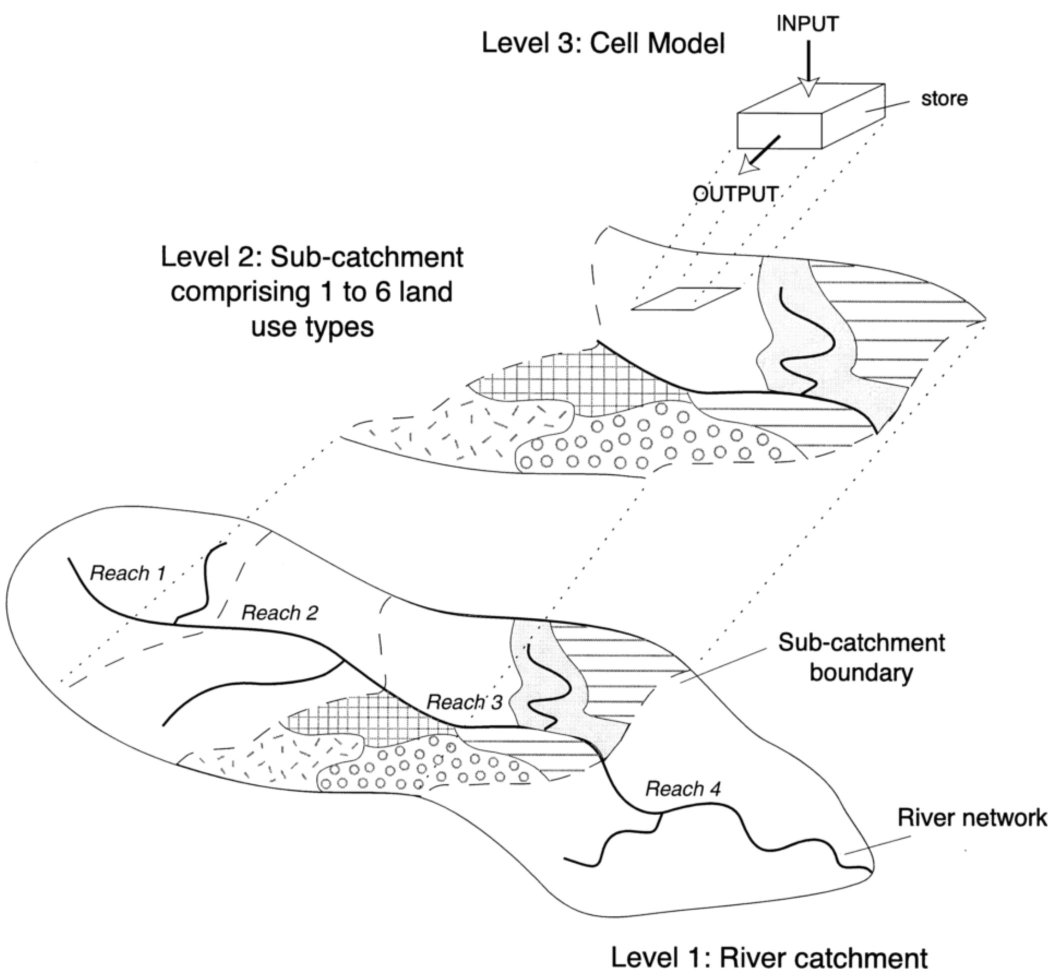


Figure 2: The spatial hierarchy of the INCA-Cl model (Wade et al., 2002).

A bucket-type approach is used to model the flow of water and Cl through the various stores and to the reach (Figure 3). Two zones exist within the bucket – the soil zone and groundwater zone. Precipitation enters the soil zone as hydrologically effective rainfall (the portion of precipitation which contributes to discharge), and can move laterally through the soil water zone to the stream, or can percolate down to the groundwater zone.

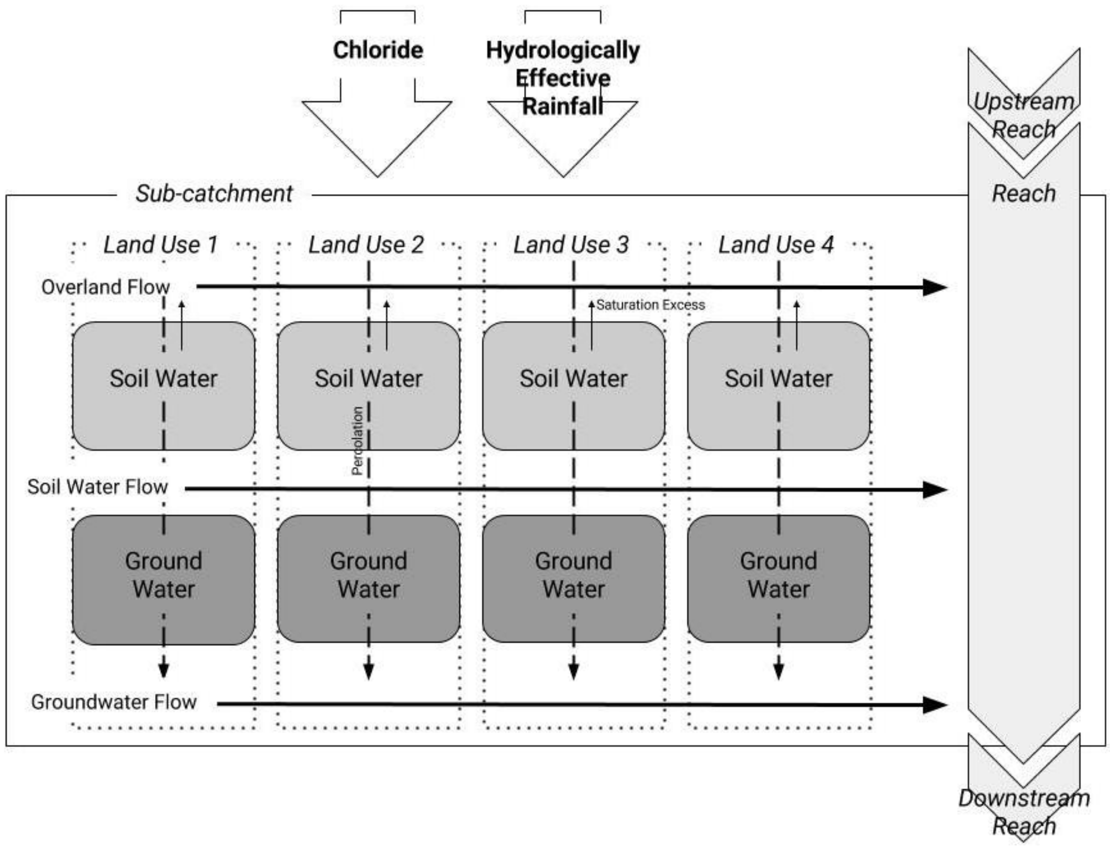


Figure 3: Conceptual model of INCA-Cl.

The flow models for each zone are:

Soil Zone (1)

$$\frac{dx_1}{\mathrm{d}t} = \frac{1}{T_1}(U_1 - x_1)$$

Groundwater Zone: (2)

$$\frac{dx_2}{\mathrm{d}t} = \frac{1}{T_2}(U_2\, x_1 - x_2)$$

Where U_1 is the HER (m^3/s) which drives inputs through the soil zone, U_2 is the baseflow index (the proportion of water which moves to the groundwater zone from the soil water zone), x_1 and x_2 are the output flows (m^3 s^{-1}) from each zone respectively, and T_1 and T_2 are the residence time, measured in days, in each zone. A third zone, the "surface zone," is modelled via the use of a "quick flow box," which accounts for overland flow and direct runoff and is supplied via saturation excess flow. Data on flow rate and residence time within each zone is necessary for accurate calibration of the model, as Cl can enter the stream system via any of the three zones. Additional parameters for calibration can be found in Table 1. The model produces daily simulation of streamflow and Cl concentration at the outflow of each reach which can be compared to observed data for validation.

Table 1: Parameters necessary for calibration of INCA-Cl.

Process	*Parameter*	*Unit*	*Description*
Reach	Flow a	n/a	Velocity flow multiplier
	Flow b	n/a	Velocity flow exponent
	Initial value flow	m^3/s	Starting value of streamflow in the reach
	Initial value Cl	mg/l	Starting value of Cl concentration in the reach
*Land-Phase**	Initial Cl concentration*	mg/l	Starting value of Cl concentration in soil and groundwater zones
	Initial flow*	m^3/s	Starting value of flow in soil and groundwater zones
	Drainage volume*	m^3	Amount of water leaving soil and groundwater zones
	Maximum soil retention value	m	Maximum amount of water soil can hold
	Residence time*	days	Number of days water is retained in soil and groundwater zones
Sub-catchment	Base flow index	n/a	Portion of water moving to groundwater
	Initial water volume	m^3	Starting value of
	Initial Cl concentration	mg/l	Starting value of Cl concentration in sub-catchment

*Land-phase parameters must be calibrated for each land cover class. Additional starred parameters are required for both the soil and groundwater zones.

3.4.2 Model inputs and data sources

Model Inputs. Necessary inputs for use in the INCA-Cl model include meteorological data, spatial data, Cl inputs, and observed streamflow and Cl concentrations for model validation (Table 2). Hydrologically effective rainfall (HER), and soil moisture deficit (SMD) are used to drive the model, and can be derived via a second hydrological model - PERSiST. The model is structured to allow multiple time-series data sets of meteorological data to be uploaded which correspond to different sub-catchments. As our interest is primarily in the changes related to the total Cl concentrations being exported via the East Holland River to Lake Simcoe, the entire sub-watershed was treated as a single catchment and reach, as opposed to being broken up into multiple reaches.

Table 2: Data required as inputs to INCA-Cl.

Process	*Data*	*Description*	*PERSiST*	*INCA-Cl*	*Source*
Meteorological	Precipitation	Daily time series	x	x	EC
	Temperature	Daily time series	x	x	EC
	Soil Moisture Deficit*	Derived using PERSiST	-	x	PERSiST
	Hydrologically Effective Rainfall*	Derived using PERSiST	-	x	PERSiST
Spatial	Land Cover	% of sub-catchment area	x	x	SOLRIS
	Sub-catchment Area	km^2	x	x	OFAT
	Reach Length	m	x	x	OFAT
Inputs	Non-point Cl application	Total Cl inputs in kg/ha/day	-	x	Giberson (2016)
	Atmospheric Cl inputs	Wet/dry inputs in kg/ha/year	-	x	N/A
In-stream processes	Cl concentrations	In-stream concentrations in mg/L	-	x	WSG
	Flow	In-stream flow in m^3/s	x	x	WSG

Data sources: hydrological. INCA requires daily air temperature, precipitation, hydrologically effective rainfall (HER), and soil moisture deficit (SMD) data. Precipitation and temperature data are available via Environment Canada weather stations. Not all stations have continuous data so a complete dataset was compiled from sensors in Newmarket (Station number 615N002, 625501.15 E, 4878619.39 N) and Aurora (Station number 6150398, 624235.62 E, 4874891.85 N). HER and SMD were obtained via the hydrological model Precipitation, Evapotranspiration and Runoff Simulator for Solute Transport (PERSiST) model, developed at the Swedish University of Agricultural Sciences (Futter et al., 2014). PERSiST is a semi-distributed rainfall-runoff model, which simulates flow at one or more points within a river network. It is built on the same framework as the INCA model, conceptualizing water stores in the same method - and having the ability to export files for direct use within INCA. As such, it has similar data requirements, outlined in Table 2. Daily streamflow data is available from 1965 onwards from the Water Survey of Canada gauge located at Holland Landing (Station number 02EC009, 620915.11 E, 4883502.74 N).

Data sources: water quality. Multiple sources of data are available for Cl concentrations through several water quality monitoring programs. Continuous Cl concentration data is available on a daily time step through the LSRCA from the previously mentioned gauge at Holland Landing. The Provincial Stream and Ground Water Quality Monitoring Networks as administered through the Ontario Government provides point source samples in wells for groundwater and at Holland Landing for in stream concentrations. These data are available from 2000 onwards.

Data sources: terrestrial Cl inputs. Chloride can be applied in the model via annual wet/dry atmospheric input as well as a daily mass application (kg/ha/day). The main sources of Cl in the East Holland River sub-watershed are application of NaCl (rock salt) to roads, parking lots and other impervious surfaces. Giberson (2016), used a geospatial approach to estimate the total annual input of road salt to the East Holland River sub-watershed for 2007-2011 using a combination of provincial and municipal (voluntarily reported to Environment Canada) datasets. Inputs on to commercial, industrial, institutional and residential parking lots were estimated using published average application rates (Fu et al., 2013). The data was transformed from an annual applied mass to a daily applied rate and used as the input in salting months (October-March). Each salting year stretches from October of the year to March of the following year. Compiled data was available only for years 2007-2010 as seen in Table 3. For any additional years modelled (2000-2007) an average salting rate was applied.

Table 3: Cl inputs to East Holland sub-watershed.

Year	*Annual Mass (Tonnes)*	*Daily Salting Rate (kg/ha/day)*
2007	26932	8.6
2008	69565	22.2
2009	42767	13.6
2010	35532	11.3
Average Annual Rate	43698	13.9

3.4.3 Issues with Cl application and subsequent simplification of the model

Initial calibration runs of the model uncovered an issue with the initial set up of the spatial component of the model. As seen in Figure 3, Cl is applied to the sub-catchment evenly over the entire area, including all land cover classes. There is no way to limit the application of Cl to on urban land cover, thus, Cl is routed through land covers which likely receive little in the way of Cl input in the real world, such as wetlands and forest. This results in artificially inflated soil and groundwater Cl concentrations in these land cover classes, and underestimates the amount of Cl input to the urban land cover class.

In previous applications of the model (Jackson-Blake et al., 2014; Jin et al., 2011), a multi-reach model with associated sub-catchments was used. The sub-catchments were divided in such a way that allowed for Cl to be applied only to reaches which were mostly urban. Typically the reaches are divided in a manner which corresponds with existing water gauge and quality monitoring stations so as to provide data for calibration. As appropriate data to further divide East Holland River was unavailable due to the existence of only one monitoring station, the model was implemented using a more low-resolution approach which would allow for Cl inputs to be applied only to the urban area. Using the previously determined geometries of the sub-catchment, a two-reach model was implemented in which the first reach would include the agriculture, wetland, and forest land cover classes. The second reach is composed only of the urban land cover. In this way, the model does not function in a spatially explicit manner, but it allows for the Cl to applied only to the land cover (urban) in which it is applied in reality. This is not a complete departure from the spatial reality of the watershed, as the East Holland River sub-watershed is, to an extent, naturally divided with most the urban land cover (Newmarket, Aurora) located closer in the latter half of the catchment (Figure 1d). The low-resolution division was devised to replicate this as much as possible (Table 4).

Table 4: Low-resolution model geometries breakdown.

Reach	*Reach Length*	*Sub Catchment*	*Forest*	*Wetland*	*Urban*	*Agriculture*
1	23588 m	103.8 km^2	60%	10%	-	30%
2	15724 m	69.3 km^2	-	-	100%	-
Total	39314 m	173.1 km^2	18%	6%	40%	36%

3.5 Results

3.5.1 Catchment hydrology

The hydrology of the East Holland River was modelled using PERSiST for the purpose of generating HER and SMD to input into INCA-Cl. Additionally, a good simulation of stream water flow is necessary for the accurate modelling of Cl concentrations. The model was calibrated to observed flow measured by the Water Survey of Canada Survey Gauge at Holland Landing. The PERSiST model was calibrated to the years 2005-2012 with a 5 year spin up period between 2000 and 2005. Manual calibration was completed to obtain a credible parameter range (the model is simulating stream flow with an adequate r^2 value) before a Monte Carlo analysis was carried out. The Monte Carlo analysis selects a random starting point within the parameter space and tests model performance. This process is repeated a user-determined number of times to determine the best possible parameter set for the model. A combination of r^2 and Nash-Sutcliffe statistic (NS) (Nash and Sutcliffe, 1970), was used to determine which parameter set performed best. The final streamflow calibration in PERSiST demonstrated a satisfactory fit between observed and simulated daily flow values, with an r^2 value of 0.74 and a NS value of 0.47 (Figure 4).

A comparison of the observed versus simulated values (Figure 5) suggest that the model consistently neither over nor underestimated the magnitude of streamflow. Once the calibration was finalized, PERSiST was used to generate a direct input file of HER, SMD, as well as the previously input temperature and precipitation for use in INCA-Cl.

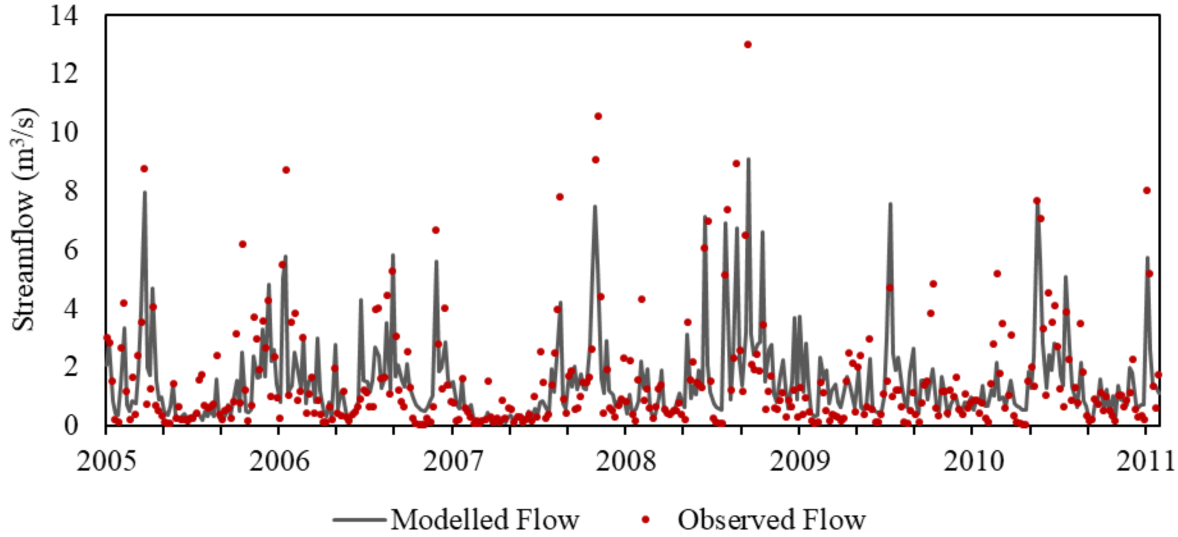


Figure 4: Weekly averaged time series of modelled and observed flow (m^3/s) at Holland Landing.

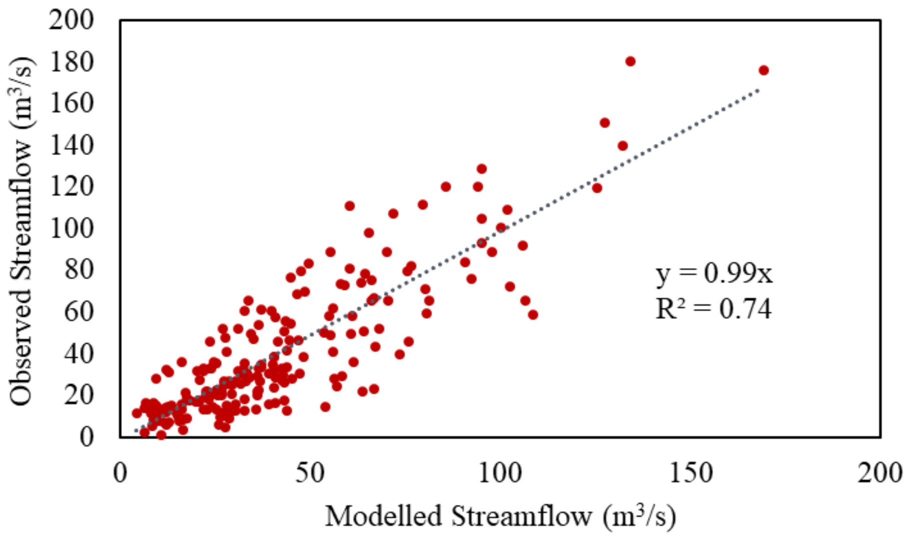


Figure 5: Observed vs. modelled flow as summed on a monthly bases at Holland Landing for years 2005-2011.

3.5.2 Initial chloride simulation results

The PERSiST generated-inputs for INCA-Cl were initially used to model streamflow and Cl concentrations at Holland Landing for the years 2000-2012 with the years 2000-2004 used as a spin up period. INCA-Cl produces daily simulated values of streamflow and Cl concentration at the outflow of each reach, as well as daily values of soil and groundwater Cl concentrations. Under the initial parameterization, the INCA-Cl simulations are not accurately capturing in-stream Cl concentrations, with an r^2 of only 0.17 and a NS of 0.38. A visual inspection of the time series data (Figure 6) suggests that peak Cl concentrations are consistently being underestimated and minimum simulated Cl concentrations are occurring earlier than observed in 2005-2008.

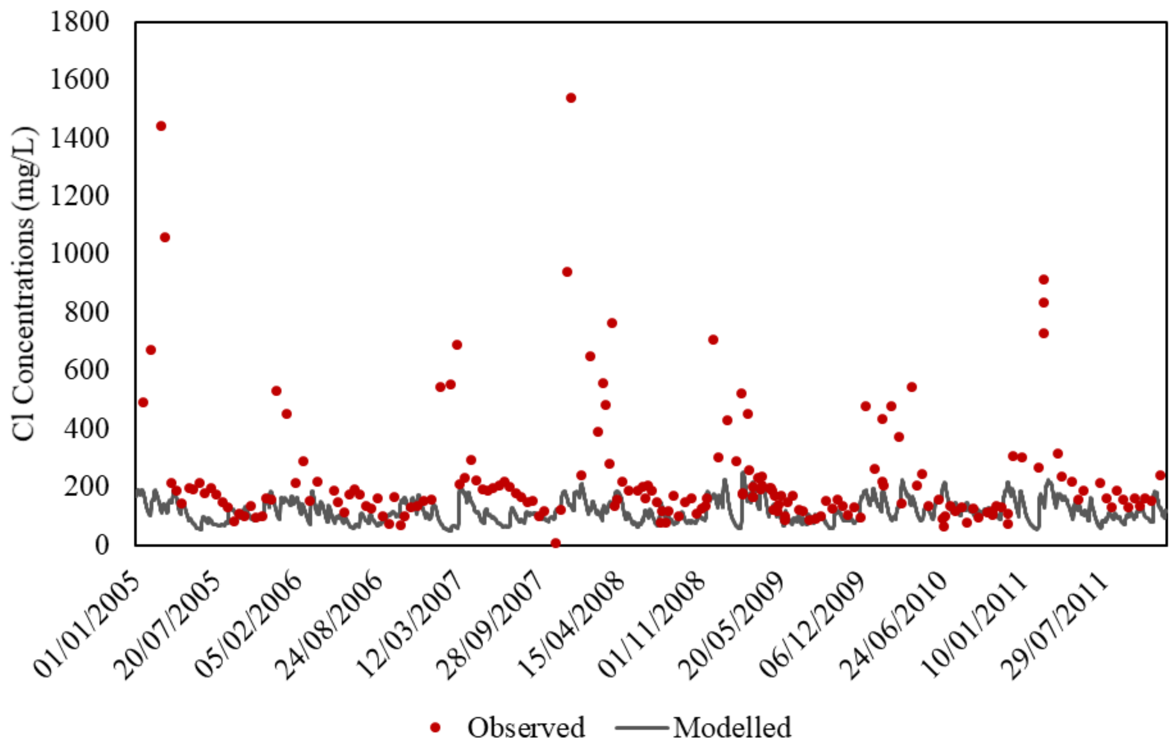


Figure 6: Time series comparison of in-stream modelled vs. observed Cl values with initial calibration.

A local analysis method (van Griensven et al., 2006) used to test parameter sensitivity shows that the only way to introduce more Cl into the stream is to increase the initial values of the soil and ground water Cl concentrations for each land cover. Although no data on concentrations within the soil reactive zone in the area is available for comparison, the PGWMN well at Holland Landing show that groundwater concentrations in 2005 were approximately 0.04

mg/L, which is four orders of magnitude lower than the 200 mg L^{-1} required to simulate a detectable Cl concentration in the stream.

A comparison of the distribution of the input Cl (Figure 7) shows that the applied Cl is being evenly distributed over all the land covers, including forest and wetland, where we wouldn't expect significant Cl application. In this initial model setup, Cl applied in these natural areas is retained in sub-surface reservoirs as evidenced by elevated soil and groundwater concentrations. The Cl is thus delayed in moving to the stream – delaying the timing and dampening the magnitude of simulated Cl concentration peaks. Currently, there is no method to manually assign Cl input mass to a specific land cover, causing excess sub-surface storage in the natural and agricultural land covers, and reducing the amount of Cl available to the urban land class.

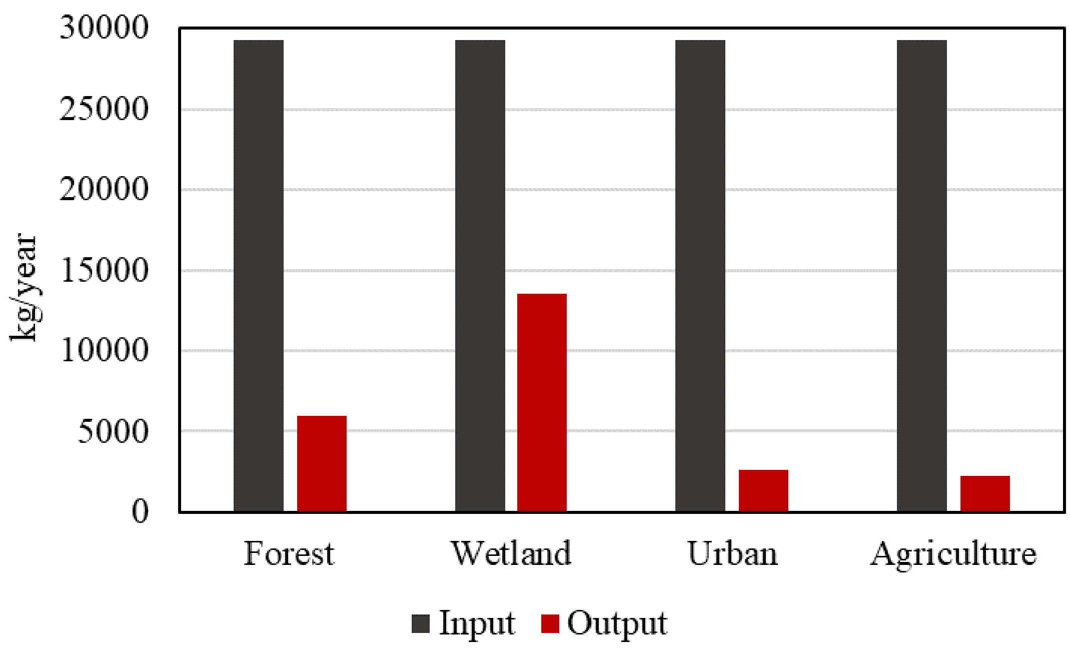


Figure 7: Comparison of input mass vs. output mass of Cl with initial calibration.

3.5.3 Chloride simulation with simplified model

The simplest approach to mitigating the issues related to how INCA-Cl applies input Cl mass would be to implement a multi-reach model where individual reaches divide the sub-catchment in a way that matches the land cover divisions. However, in the absence of sufficient data by which to divide and calibrate multiple reaches, the spatial aspect of the model was framed in a more conceptual manner, in which the East Holland River watershed was split into two reaches, one entirely urban and one entirely non-urban land cover (see section 3.4.3). In dividing the watershed this way, it was possible to apply the Cl only to the urban land class, thus more closely replicating the real-world application of salt during the winter season and avoiding a build-up of Cl in the subsurface.

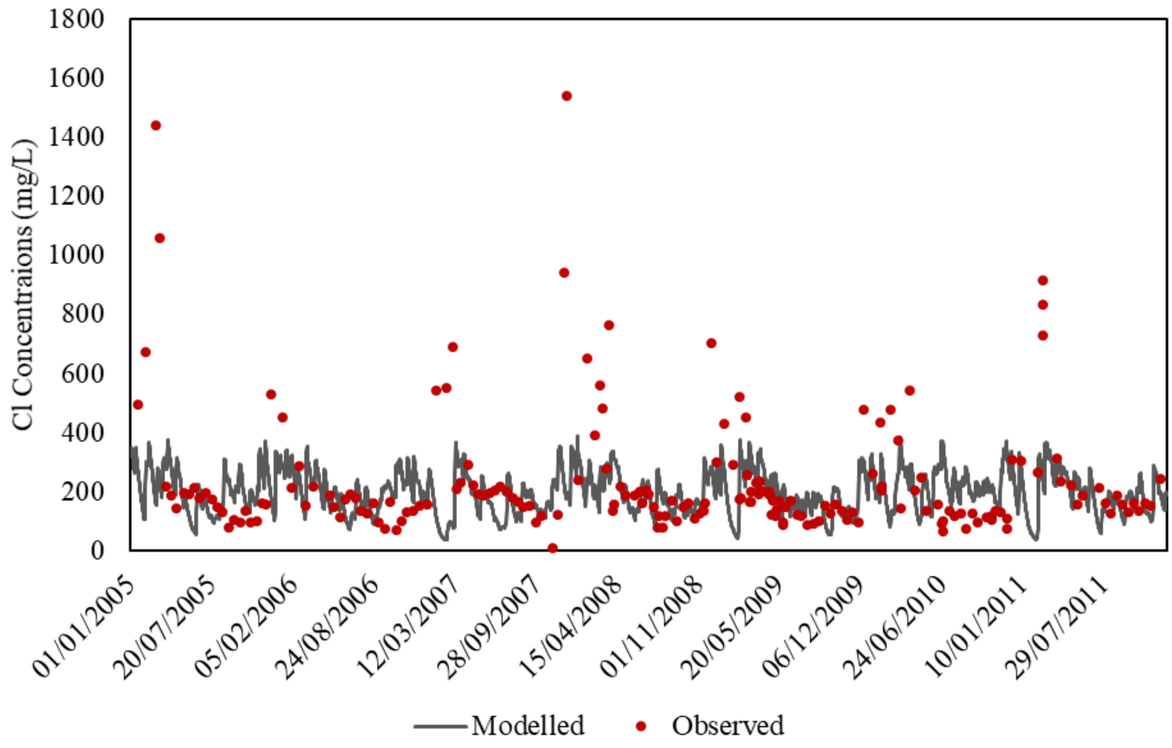


Figure 8: Comparison of modelled vs. observed Cl concentrations at Holland Landing.

Re-conceptualizing the spatial aspect of the model did provide a more reasonable estimate of soil and ground water estimates (decreases of approximately 800 mg/L and 40 mg/L respectively). However, the model still fails to simulate daily in-stream Cl concentrations accurately, and in fact the simulation was worse than in the previous model structure with an r^2 value of 0.002 and NS value of -3.1. Figure 8 shows that peak values are consistently underestimated, and in the case of observed events, the model predicts a decrease in Cl concentrations (or dilution) – the opposite of what should be expected in wintertime. Averaging the Cl concentrations on a monthly basis did not significantly improve the model predictions ($r^2 = 0.02$) (Figure 9). This suggests the model isn't properly simulating Cl concentrations on longer time scales either.

Figure 10 underscores the timing issue – pulling the last year of simulation (2011) out of the data shows that the model is unable to match the annual pattern of Cl concentrations. Simulated values respond in a reverse fashion to what is being observed – with rising concentrations in the growing season, and decreasing concentrations where spring peaks should occur. Pulling these values out for comparison (Figure 11) shows that there is a strong negative relationship which increases in strength when comparison is limited to July and August. The model is failing to capture the low concentration summer baseflows, in which the majority of Cl in the stream is being exported from groundwater. There are two possibilities for the negative summer relationship. The first is that little to no available HER in the summer months means that there is no overland flow to the reach – preventing the dilution of the concentrations in-stream. The second is that the model is routing the majority of the summer flow through the soil water zone rather than the ground water zone.

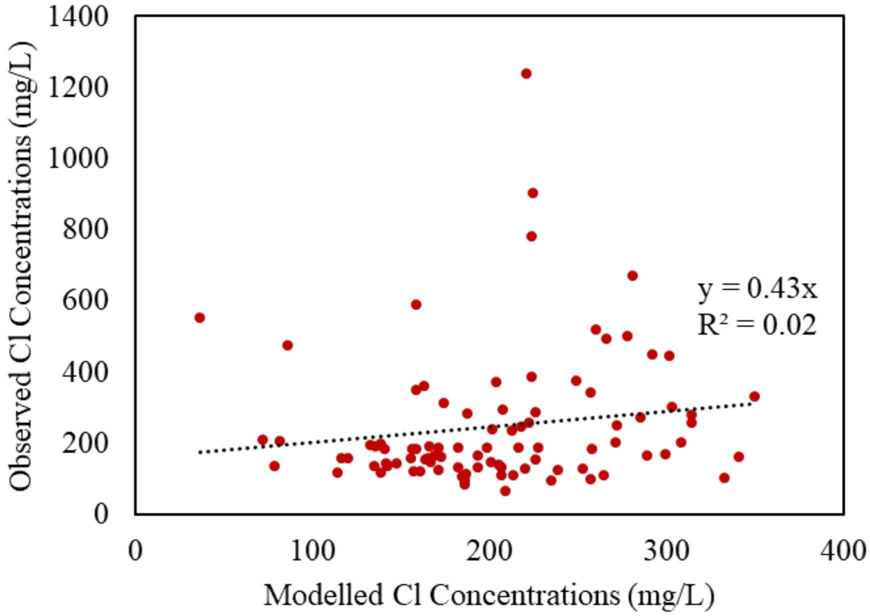


Figure 9: Comparison of monthly averaged observed and modelled Cl concentrations

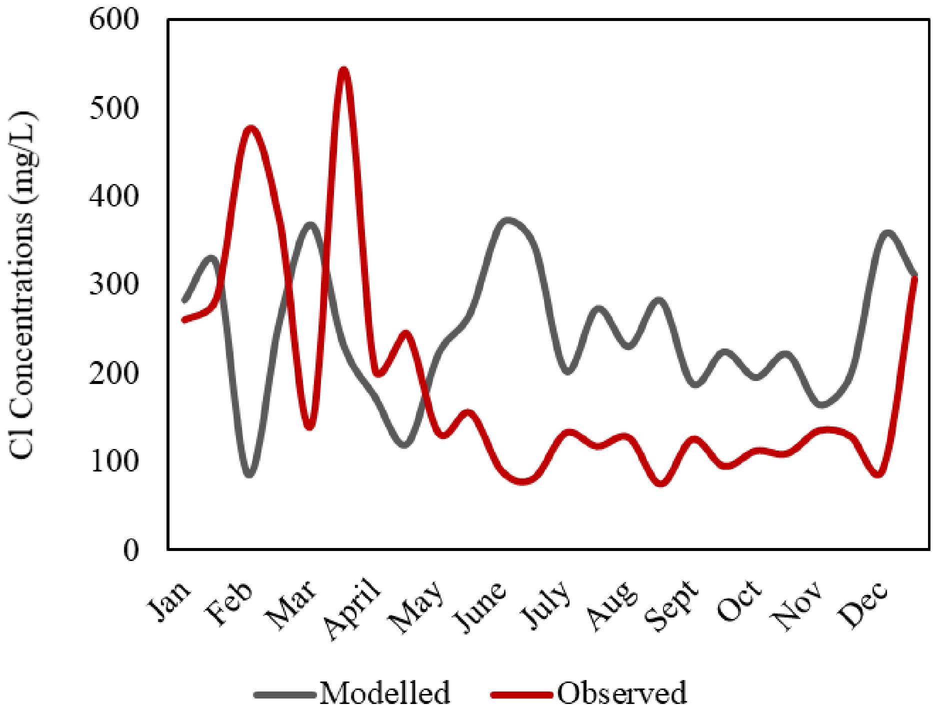
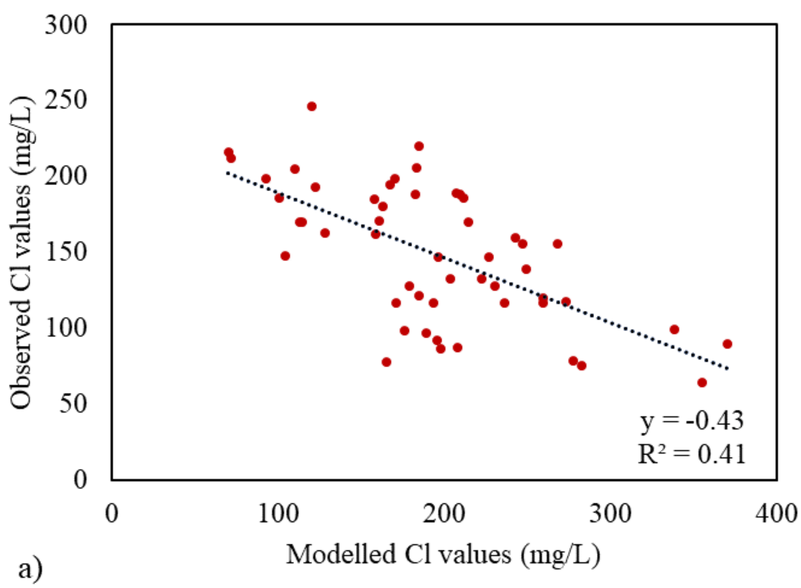


Figure 10: Time series of weekly averaged observed and modelled in-stream Cl concentrations for the year 2011.

Modelled concentrations of Cl are significantly higher in the soil water zone than in the groundwater zone – if summer concentrations are fueled by lateral movement in the soil zone rather than groundwater baseflow, this could explain the high summer concentrations.

HER is used as the method by which Cl is driven through the system in the INCA-Cl model – HER being the percentage of actual precipitation which eventually contributes to runoff. PERSiST calculates HER as actual precipitation minus interception and evapotranspiration (ET). Cl concentration in the stream is governed by runoff from soil and groundwater reservoirs, and overland flow. Overland flow in INCA-Cl is supplied by saturation flow excess, which is in turn influenced by soil moisture. A deficit of soil moisture as calculated by the model can reduce the amount of water available for overland flow – wherein Cl applied to the surface may move directly to the stream as it does in many spring melt pulse events. Instead, the Cl would move into the soil and groundwater reservoirs rather than into the stream. There is no way in the model to a) simulate the effect of frozen ground, and b) manually calibrate the percentage of available water which will move through each bucket (i.e. how much water moves from soil to groundwater reservoirs, and how much will leave the system as direct runoff).



a)

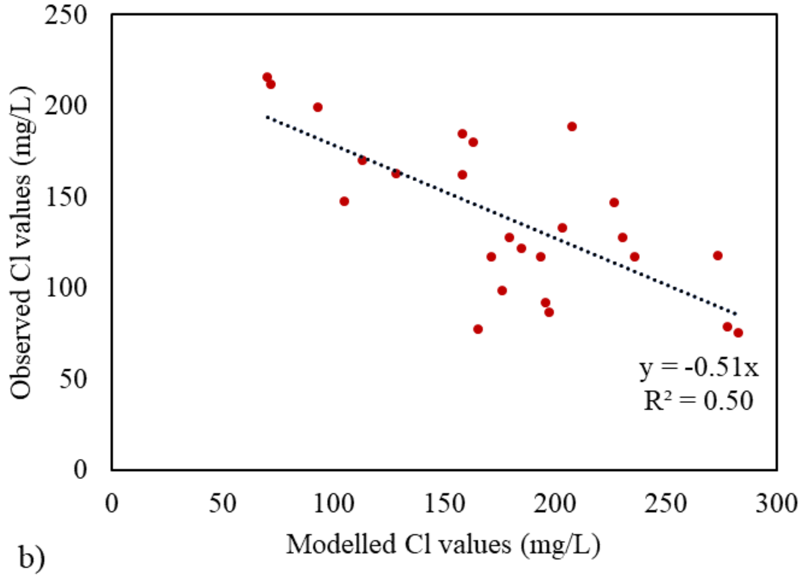
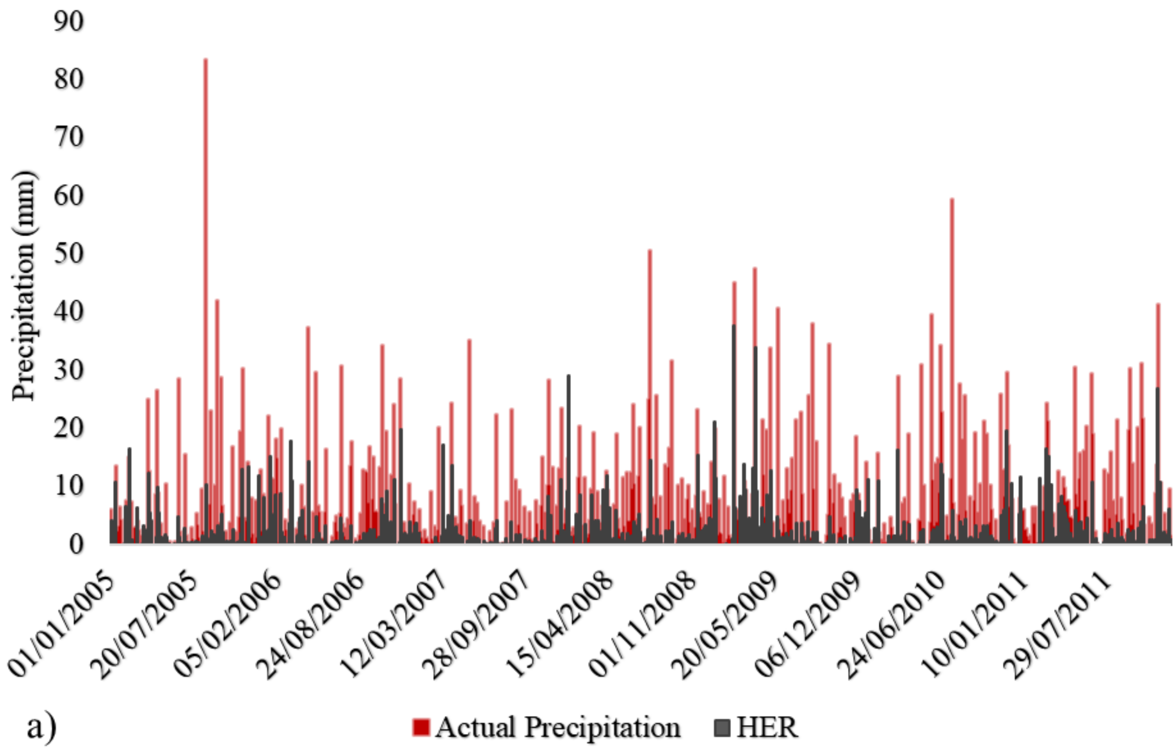


Figure 11: Linear regressions of modelled vs. observed values in (a) the growing season (May-August) and (b) late summer months (July-August).

In a comparison of modelled HER vs. actual precipitation (Figure 12). While minor underestimations of precipitation and associated events may be overlooked in the broader hydrology calibration, consistent underestimation of precipitation can ultimately impact the availability of water within the model. Additionally, HER often misses precipitation events – particularly in the summer. This reduces the magnitude of corresponding in-stream discharge, and may be the reason for the elevated summer Cl concentrations found in the modelled values – lack of dilution of the high concentrations found in summer baseflow. Additionally, a major component of this may be the lack of ability to define impervious surfaces and model sewer systems within INCA-Cl.



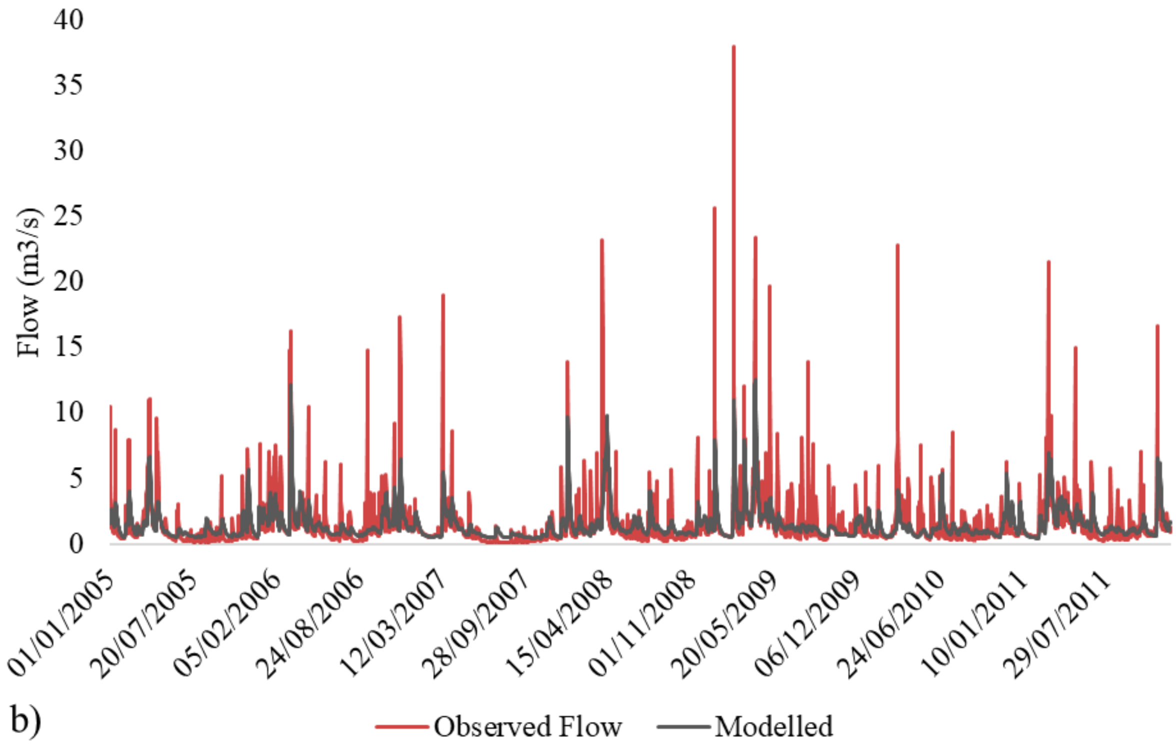


Figure 12: a) Comparison of HER vs. actual precipitation and b) corresponding observed and simulated streamflow.

3.5.3.1 Annual Cl mass balance

Although the model is not correctly simulating the timing and magnitude of in-stream Cl concentrations, it does appear to be capable of modelling retention and mass balance. Total output of Cl was calculated on an annual (salting year) basis by averaging daily flow-weighted Cl concentrations. They were compared to recent mass balancing work completed in the region. Giberson (2016) used data made available from the Ministry of Environment and Environment Canada to calculate total Cl inputs to several Lake Simcoe regional sub-watersheds. A later study (Oswald et al. *in prep.*) additionally calculated the inputs from private sources including parking lots, as seen in Table 3. These four years of data were used to assess the ability of the model to balance mass. The specific values for comparison are found in Table 5. As can be seen in Figure 13, the model is balancing annual mass quite well, with an r^2 value of 0.9.

Table 5: Annual sum of observed and simulated Cl export (tonnes/year)

Year	*Input (tonnes/year)*	*Observed output (tonnes/year)*	*Observed retention (%)*	*Simulated output (tonnes/year)*	*Simulated retention (%)*
2007	26932	7965	70%	5749	78%
2008	69565	13060	82%	12079	82%
2009	42767	14560	66%	12330	70%
2010	35532	9693	72%	9332	73%
Average	43699	11319	73%	9873	75%

The model is predicting an average retention rate of 75% - well in line with the literature (Betts et al., 2014; Howard and Maier, 2007; Perera et al., 2013, 2009; Winter et al., 2011) on Cl retention in Southeastern Ontario watersheds.

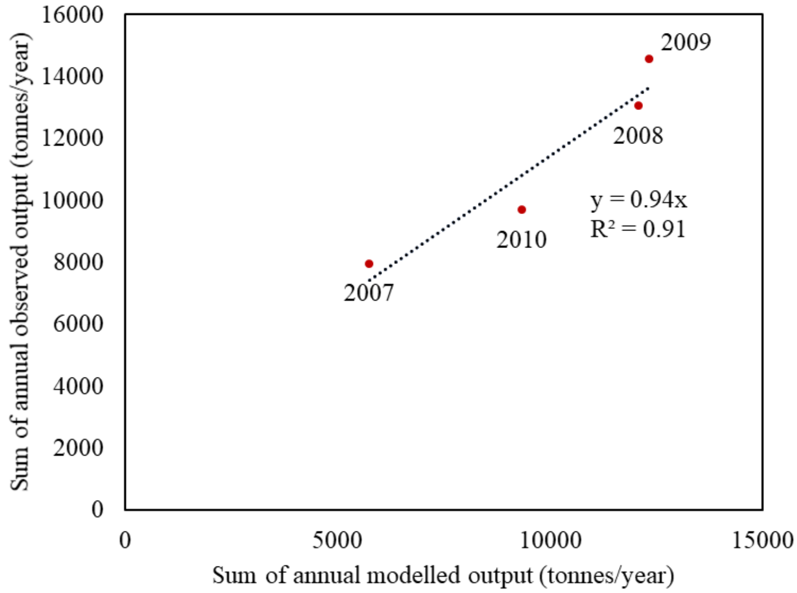


Figure 13: Comparison of annual observed vs. simulated Cl load at for the East Holland sub-watershed.

The ability of the model to balance mass in it's original spatial arrangement was also tested. The model was able to replicate the observed levels of retention across the four years in a passable manner (r^2=0.74), albeit not as well as the low-resolution model was able to. As seen in Table 6, and Figure 14, the original calibration of the model consistently overestimates retention by 10-15% per year. This may be a result of the extra retention modelled in the land covers which do not typically receive Cl input such as wetland and forest.

Table 6: Annual sum of observed and simulated Cl export (tonnes/year) as modelled by initial INCA-Cl calibration.

Year	*Input (tonnes/year)*	*Observed output (tonnes/year)*	*Observed retention (%)*	*Simulated output (tonnes/year)*	*Simulated retention (%)*
2007	26932	7965	70%	3904	85%
2008	69565	13060	82%	7222	90%
2009	42767	14560	66%	7699	82%
2010	35532	9693	72%	6639	81%
Average	43699	11319	73%	6365	84%

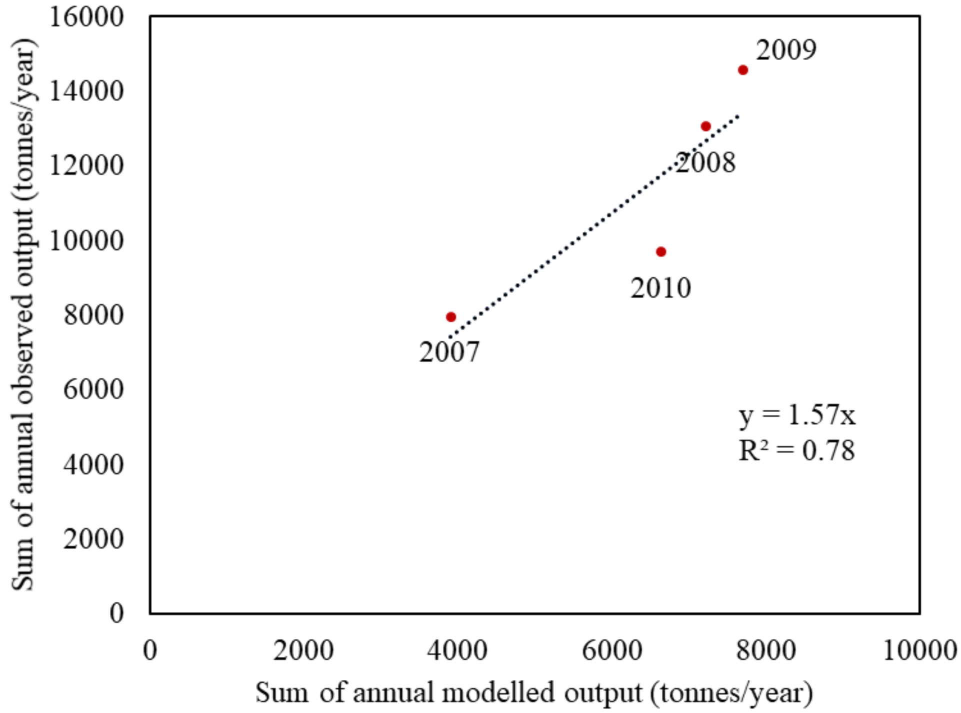


Figure 14: Comparison of annual observed vs. simulated Cl load at for the East Holland sub-watershed as modelled by the initial calibration of INCA-Cl.

3.6 Discussion

Several previous studies in the Lake Simcoe and Southern Ontario regions have focused on balancing the mass and quantifying the retention of Cl in sub-surface reservoirs (Howard and Maier, 2007; Perera et al., 2013; Winter et al., 2011). Going forward, the ability to predict Cl concentrations in the face of increasing urbanization and changing salt application regimes will be important for ensuring the availability of freshwater resources and the health of aquatic ecosystems. INCA-Cl has been presented as a potential solution for modelling Cl concentrations in an urbanizing watershed, and was previously used to model one year of Cl concentrations in the sub-urbanizing watershed of Fishkill Creek (Jin et al., 2011). Initial presentation of the model suggested it as a method by which to predict future Cl concentrations and test potential salting scenarios with data that should be easily accessible to watershed managers. While INCA-Cl performed adequately in Fishkill Creek (a watershed which is only 15% urban), it did not perform in a similar manner in the more urban East Holland river sub-watershed (40% urban). The current structure of INCA-Cl does not appear to be suitable for use in urban and urbanizing environments as it is not modelling Cl concentration dynamics in a significant way.

Jackson-Blake et al., (2014) developed a checklist (Table 7) for identifying the cause of poor model performance based on Krueger et al., (2007) with four key categories of assessment.

Table 7: Criteria for model performance assessment - adapted from Jackson-Blake et al. (2014) and Krueger et al. (2007).

	Description
Calibration	Was the calibration undertaken as thoroughly as possible? Are the statistics being used to assess the model appropriate?
Data	Is all the input data appropriate? Are there any issues or uncertainty associated with the input data? Is data available to constrain all the parameters? Is enough data available for calibration and validation?
Structural	Is the model conceptually a reflection of reality? Are there any key processes that the model is failing to address?
Conceptual	Is the model reflecting the most current understanding of processes?

The categories of this checklist can help to identify some of the over arching issues with the INCA-Cl model of the East Holland River watershed.

a) *Issues with calibration*: Manual calibration is necessary for a model as complex as INCA-Cl, but comes with its own challenges. A tool like Monte Carlo analysis can ease the difficulty of searching the complete parameter space – a feat which is not possible manually. This leaves the possibility that there is in fact an alternate parameter set which may provide a better calibration, particularly when taking into account equifinality. Jackson-Blake et al., (2014), encountered a similar problem when using INCA-P, wherein automated calibration would be preferable, but the complexity of the model did not allow for this possibility. This is a common problem with distributed and semi-distributed models (Refsgaard, 1997), wherein the number of parameters necessary for representation of the physical space within the model makes calibration difficult.

   Jackson-Blake et al., (2014) additionally suggested that the lack of phosphorus-centric models did not allow for the development of an understanding of what a "good" simulation of phosphorus would be considered – the complexity of modelling the movement of contaminants such as phosphorus means that a "good fit" by traditional measures may not always be possible. A similar issue could be considered with INCA-Cl, wherein a lack of literature regarding catchment-style modelling of Cl does not allow for a base for comparison of what satisfactory modelling of Cl dynamics is. A suggested solution to this, and one which serves to remove some of the uncertainty in modelling is to use two models to simulate concentrations in the same region over the same time period.

b) *Data availability and uncertainty:* INCA-Cl was built to make use of what is considered readily accessible data for any watershed manager. This includes meteorological, spatial, hydrological and Cl input data. Data is required on a long enough time frame to encompass both calibration and validation (ideally several years of continuous data for both (Refsgaard, 1997)). Data on streamflow and stream Cl concentration is required for validation at each reach. Wherein the model had to be divided into two reaches for accurate Cl input, there was no data available for validation of the first reach – thus all calibration and validation had to be completed at the endpoint of the reach. Ideally data would have been available that reflects Cl concentrations in urban land use areas as well as natural and agricultural land uses. Additional issues come with the necessary data for parameterization. Specific values related to internal processes including concentrations in the soil reactive zone, maximum water volume, etc. are difficult to measure; however accurate numbers are necessary to constrain the model.

Beyond the difficulties associated with procuring the necessary data, there were issues with the data once input into the model. As previously mentioned, although hydrology calibration was satisfactory, the way by which HER and SMD were calculated damped the amount of water that was available to drive Cl concentrations. Additionally – accurate Cl input data was only available for four years, so an average salting rate was used for the remaining years. This may not reflect the true salting behaviour on these years, as even within the four years of data, salting mass varied by up to 50% year to year. Additionally, as the data available was an annual mass of input Cl, the total mass was divided by the number of days in the salting season and applied on a daily basis. In reality, Cl would only be applied on days for which precipitation is predicted. Thus, the annual mass would be applied in larger amounts on fewer days. If event-scale salting data was available, it may help to better model the magnitude of observed Cl peaks.

c) *Structural:* The first issue encountered with the model has been previously described in section 3.4.3, wherein there is no way to constrain salt application to specific land covers such as urban. This resulted in an even application of salt across all land covers, causing input of Cl to non-urban land covers. Subsurface retention in non-urban land covers delayed the movement of Cl to the stream, causing underestimation of in-stream concentrations, and reducing the magnitude of peak events. The way the model was previously implemented (Jin et al., 2011) to deal with this issue is through the use of a multi-reach model in which salt application can be varied by sub-catchment – those sub-catchments with higher urban land cover would accordingly receive more salt. Again, the lack of data for effectively defining reaches prevents the use of the multi-reach model. This was dealt with by developing a low-resolution model wherein two sub-catchments divided by land cover rather than spatial setting were created in order to force salt application to the appropriate land cover class. While this provided a temporary solution, it also a) removes the spatial aspect of the model and b) may cause problems for the hydrology, wherein the model structure differs from the real-world geography of the reach. Additionally, data is only available to calibrate at the furthest downstream point.

d) *Conceptual:* An additional, and potentially larger issue with the model structure is that is does not fully represent impervious surfaces and storm drainage systems. Impervious surfaces disrupt normal hydrological processes in a manner which can cause significant changes to peak flow event timing and magnitude. They prevent infiltration, and often come with sewering and other drainage systems which can direct water in manners other than through the soil and ground water reservoirs. While it is possible to parameterize the urban land class in a manner which may partially reflect the impact pavement and sewers have water and solute transport, there is no method by which to manually set the amount of water input to each box (e.g. increase the amount of water that remains in the quick flow box as overland flow or allot a percentage of water to groundwater without percolating through the soil (as may occur in the case of soil macropores, or drainage systems). Additionally, a common function of impervious surfaces is a process called Hortonian overland flow wherein water from precipitation flows laterally across surfaces rather than infiltrating. As the model only accounts for saturation excess flow when calculating overland flow, the additional water which would move directly to the reach is not accounted for.

The majority of these issues may stem from the fact that INCA-Cl was built on a framework which was used to simulate nitrogen inputs from agricultural sources, and it attempts to treat Cl in the same manner. The model has not received as much attention or use as INCA-N or INCA-P and has lagged behind in implementing some of the structural upgrades such as multi-reach simulation. The only previously published use of INCA-Cl (Jin et al., 2011) modelled only one year of Cl concentrations in a small, sub-urbanizing watershed. Currently, INCA-Cl is not effectively simulating Cl in urban environments on a time scale long enough to be useful for scenario analysis and prediction of future Cl concentrations. It is important to note that despite the fact that the model was able to balance mass, it is obviously not simulating internal processes correctly. For this reason, it would not be an effective tool for the purpose of predicting Cl export from the sub-watershed to Lake Simcoe.

Recently noted increases in Cl concentrations in freshwater streams and lakes in Northeastern North America have brought Cl to the forefront of pollutant and contaminate concerns (Dugan et al., 2017; Gardner and Royer, 2010; Godwin et al., 2003; Gutchess et al., 2016; Perera et al., 2013; Winter et al., 2011). Much of the previous research has focused on quantifying retention within sub-surface reservoirs – finding that as much as 75% of Cl is remaining within the system. Any changes made now will likely take decades to impact in-stream Cl concentrations as built up Cl moves slowly through groundwater aquifers to streams. This is even more challenging in the face of increasing urbanizing such as the 65% population growth expected in Lake Simcoe Region. An increase in impervious surfaces and/or Cl application rates in rapidly urbanizing regions are a strong rationale for developing models which accurately represent both urban and non-urban areas. INCA-Cl will require some basic functional changes before it can be used effectively in this manner.

3.7 Conclusions

In Northeastern North America, Cl concentrations in surface waters have been increasing at a rate which is beginning to threaten the availability of freshwater resources and the health of aquatic ecosystems. Road salt, applied as a de-icing agent in winter months to improve driving conditions is the source of the majority of the Cl input to watersheds. The ability to model in-stream Cl concentration is important for the purpose of developing salt management regimes, particularly in areas facing rapid urbanization, and thus an increase in impervious surfaces.

INCA-Cl is a semi-distributed, process based model built to simulate Cl dynamics using meteorological, spatial, and hydrological data easily accessible to most watershed managers. It was applied to the sub-watershed of East Holland – an area in the Greater Golden Horseshoe region of Ontario which is anticipated to undergo a rapid expansion of urban areas in the next 30 years. East Holland drains to Lake Simcoe – a large freshwater lake in which rising Cl concentrations have already been identified as pollutant of concern. The simulation results showed generally good agreement between modelled and measured streamflow, however the Cl concentration simulation did not perform as well. The model was re-worked to attempt to better target input Cl mass to relevant land covers, with little improvement in model results. The model was found to balance mass of input and output Cl well – suggesting the issues with the model are in the timing of the Cl release, and/or the routing that the water may take through the soil and groundwater zones to the reach. This may be a reflection of problems with the driving meteorological data. HER and SMD are modelled separately using a separate hydrological model, and resulting data are used to drive Cl through the INCA-Cl system. Values were shown to considerably be dampened, resulting in a large amount of Cl sub-surface storage, and delaying the export of Cl to the stream. Additionally, the INCA-Cl model has no way by which to model urban infrastructure such as impervious surfaces, sewering and other drainage systems. These urban characteristics considerably alter the functioning of hydrology in these areas, and the associated impacts cannot be accurately simulated in INCA-Cl. If INCA-Cl is to be an effective tool for monitoring and predicting Cl concentrations in urbanizing watersheds, it will be necessary to make some structural and conceptual changes to the model.

4.0 Summary

Increasing Cl concentrations in freshwater streams and lakes has become a concern for the health of aquatic ecosystems and the availability of freshwater resources. By far the most common contributor to elevated Cl concentrations in Northeastern North America is the use of road salt in winter months. As road salt is a valuable tool for safe winter driving – expanding urban centres and an increase in roadways will make the responsible use of salts an important goal for watershed management. The ability to model in-stream Cl concentrations, and quantify retention and release of Cl within watersheds will help to inform best management practices for salt application techniques.

Current literature on modelling Cl has mostly focused on mass balance and quantifying retention. INCA-Cl is a semi-distributed, process based model which uses easily accessible data to provide daily estimates of flow and Cl concentration. It was applied to East Holland sub-watershed. East Holland is located in Lake Simcoe region, and contains two of Ontario's fastest growing urban areas within the watershed boundaries – Newmarket and Aurora. Elevated Cl concentrations have been identified as a potential threat to Lake Simcoe, as it both functions as a source of freshwater to several small cities, and supports a fishery worth over 100 million in economic benefits to the area. The Lake Simcoe protection plan was released in 2009, and Cl was identified as a pollutant of concern.

In addition, East Holland is included in the Ontario governments "Growth plan" which outlines regions which can expect to experience further urbanization in the next 10 years. With increased urban areas comes an increase in impervious surfaces and thus an increase in road salt application. With that in mind, INCA-Cl was used to simulate in-stream Cl concentrations and flow in the East Holland river. Data from a gauge maintained at Holland Landing by the LRSCA was used to calibrated the model, and annual Cl application calculated by a previous mass balance study was used to quantify inputs. The model was tested to determine if it could model three elements of Cl dynamics within a watershed.

Is INCA-Cl capable of:

- *Modelling mass balance.* The model was able to accurately simulate the rates of Cl retention within the East Holland sub-watershed. A comparison of observed and simulated annual outputs correlated well – with an r^2 value of 0.9. There was only four years of calculated Cl inputs and outputs, so there was not enough data by which to complete a validation of the mass balance data for the purpose of running scenario analysis.
- *Modelling Cl concentrations and flow on a monthly or daily basis.* While the model was able to simulate flow on a reasonably accurate basis ($r^{2 =}$ 0.74) there were some

small issues with the way the hydrological model calculated HER and SMD – which are the driving inputs for INCA-Cl. While these issues seemed minor during hydrology calibration, they became apparent during the Cl calibration when high soil moisture deficit and low HER reduced the amount of water available to the system. The model failed to model Cl concentrations on either a daily or monthly basis in a satisfactory manner, and in fact, the timing issues with the simulation meant that in-stream concentrations often reacted in the opposite manner than observed.

- *Modelling Cl concentrations on a temporal scale fine enough to inform toxicology and biota related research.* INCA-Cl is not suitable for modelling Cl concentrations on a time scale that would be useful for toxicology purposes, as it models simulations on a daily time step.

Unfortunately, INCA-Cl did not perform in a satisfactory manner to provide accurate predictions for two of these elements. A lack of ability to model impervious surfaces, issues with the input driving data, and no way to constrain salt application to specific land covers and regions contributed to the failure of the model. Future directions for modelling Cl concentrations can take two directions, a) working within INCA-Cl to fix the model deficiencies and improve Cl simulations, and b) testing other contaminants models such as SWAT to determine if they are more suitable for use in an urban environment.

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