



# Chloride Concentrations in Wetlands along a Rural to Urban Land Use Gradient

Alan R. Hill<sup>1</sup> · Eva K. Sadowski<sup>1</sup>

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**Abstract** Relationships between anthropogenic sources of  $\text{Cl}^-$  and wetland surface water  $\text{Cl}^-$  concentrations have received little attention. Spatial and temporal patterns of  $\text{Cl}^-$  concentration were investigated in 11 wetlands in the mid to late 1990s and in 2012–2013 along a rural to urban gradient. Chloride concentrations in wetlands located in forest watersheds were  $<3$  mg/L. Small spring-fed swamps in relatively undeveloped rural areas had elevated  $\text{Cl}^-$  concentrations ranging from 10 to 50 mg/L which originated from nearby house septic systems and salt application on secondary roads. Potassium fertilizer application on areas of intensive crop production was a major source of  $\text{Cl}^-$  in riparian wetlands where surface water  $\text{Cl}^-$  concentrations were 50–65 mg/L. The application of deicing salts caused the highest  $\text{Cl}^-$  concentrations (100–730 mg/L) which were observed in depressional wetlands in a rapidly urbanizing landscape with a denser road network. Chloride contamination in the study wetlands occurred throughout the year and diffuse surface flow paths produced a widespread pattern of elevated surface water  $\text{Cl}^-$  concentrations which have increased considerably in the past 10–15 years in some of the wetlands. Wetland  $\text{Cl}^-$  levels in the most developed landscapes reached or exceeded chronic water quality thresholds established in the USA and Canada for negative effects on aquatic biota.

**Keywords** Chloride · Road salt · Urbanization · Water quality trends · Wetlands

## Introduction

Long-term increases in  $\text{Cl}^-$  concentrations in streams and groundwater systems are raising concerns because of negative impacts on freshwater ecosystems (Kaushal et al. 2005; Findlay and Kelly 2011; Canedo-Arguelles et al. 2013). Geologic weathering and atmospheric deposition are natural sources of  $\text{Cl}^-$  to ecosystems (Mayer et al. 1999). Anthropogenic sources include potassium fertilizers in agricultural areas (Saffigna and Keeney 1977), wastewater treatment plants (Kelly et al. 2010) and septic systems in rural and urban areas (Alhajjar et al. 1990). In colder regions of Europe and North America road deicing salt often provides the major source of  $\text{Cl}^-$  contamination (Findlay and Kelly 2011).

Many studies have focused on the role of road deicing salts in relation to increasing stream  $\text{Cl}^-$  concentrations in Canada (Scott 1979; Perera et al. 2013), the United States (Demers and Sage 1990; Godwin et al. 2003; Kaushal et al. 2005; Gardner and Royer 2010; Corsi et al. 2015) and Europe (Lofgren 2001; Ruth 2003). In contrast, less attention has been paid to the impact of road salt or other sources of contamination on  $\text{Cl}^-$  concentrations in freshwater wetlands. Analysis of shallow groundwater in a fen in NE Illinois, USA revealed a discrete  $\text{Cl}^-$  plume from a house septic tank system which declined from 300 to  $<50$  mg/L approx. 40 m from the fen margin (Panno et al. 1999). At a second fen adjacent to a paved road, deicing salt applications resulted in shallow groundwater  $\text{Cl}^-$  concentrations which declined gradually from 200 mg/L at the road to 100 mg/L near a stream south of the fen. Richburg et al. (2001) reported high groundwater  $\text{Cl}^-$  concentrations (210–275 mg/L) in a calcareous fen and hardwood swamp adjacent to a major highway in Massachusetts, USA which declined gradually to background concentrations of 15 mg/L at 650 m from the highway. A similar pattern of high  $\text{Cl}^-$  in shallow groundwater that declined with distance from

✉ Alan R. Hill  
hill@yorku.ca

<sup>1</sup> Department of Geography, York University, Toronto, ON M3J 1P3, Canada

Interstate 95 was recorded in poor fen in Maine USA (Pugh et al. 1996). The effect of human impacts on wetland surface water  $\text{Cl}^-$  concentrations has not been studied in detail. Turtle (2000) recorded  $\text{Cl}^-$  concentrations of 3–7 mg/L in three woodland vernal pools and 170–225 mg/L in three roadside pools in New Hampshire, USA sampled on two dates. Pools sampled on one date in 59 wetlands near Thunder Bay in Ontario located 1 to 1000 m from the nearest road had  $\text{Cl}^-$  concentrations of 0.4 to 1030 mg/L (Sanzo and Hecnar 2006).

High  $\text{Cl}^-$  concentrations have negative effects on wetland vegetation (Panno et al. 1999; Richburg et al. 2001) and animal communities (Williams et al. 1997; Silver et al. 2009). Amphibians are particularly sensitive because they have permeable skin and some species breed in spring when road salt runoff is at a maximum. Research based on laboratory experiments indicates that the acute and long-term response to a range of  $\text{Cl}^-$  concentrations varies considerably among amphibian species. Some species such as American toad (*Anaxyrus americanus*) and green frog (*Rana clamitans*) are relatively tolerant (Karraker 2007; Matlaga et al. 2014). In contrast, wood frogs (*Rana sylvatica*), spotted salamanders (*Ambystoma maculatum*) and rough-skinned newts (*Taricha granulosa*) exhibit decreased growth and survivorship (Sanzo and Hecnar 2006; Karraker et al. 2008; Hopkins et al. 2013). Mesocosm experiments suggest that salinity may also have an indirect effect on the growth and survival of some amphibians by altering food webs (Petranka and Francis 2013).

Field studies of salt effects showed that densities of egg masses of spotted salamanders and wood frogs were two times higher in forest pools than in roadside pools (Karraker et al. 2008). A significant negative correlation between amphibian diversity and  $\text{Cl}^-$  concentrations was observed in a study of wetlands in rural and urban sites in the Don River watershed in southern Ontario (Sadowski 2002). These relationships detected in field studies may be influenced by other factors such as the presence of unmeasured aquatic contaminants and habitat fragmentation by road networks and urbanization.

Despite the growing body of evidence for the negative effects of high  $\text{Cl}^-$  levels on wetland organisms, there is an absence of detailed studies of spatial and temporal patterns of wetland surface water  $\text{Cl}^-$  concentrations in relation to anthropogenic sources of chloride. The objective of this research is to examine patterns of surface water  $\text{Cl}^-$  concentrations in 11 wetlands in watersheds along a rural to urban land use gradient that reflect varying levels of  $\text{Cl}^-$  contamination from a range of sources. Field surveys were conducted mainly in the mid to late 1990s and in 2012–2013 to assess temporal trends in  $\text{Cl}^-$  concentrations. The wetlands are located in landscapes dominated by glacial sands and gravels to reduce the effect of large differences in geology on  $\text{Cl}^-$  concentrations.

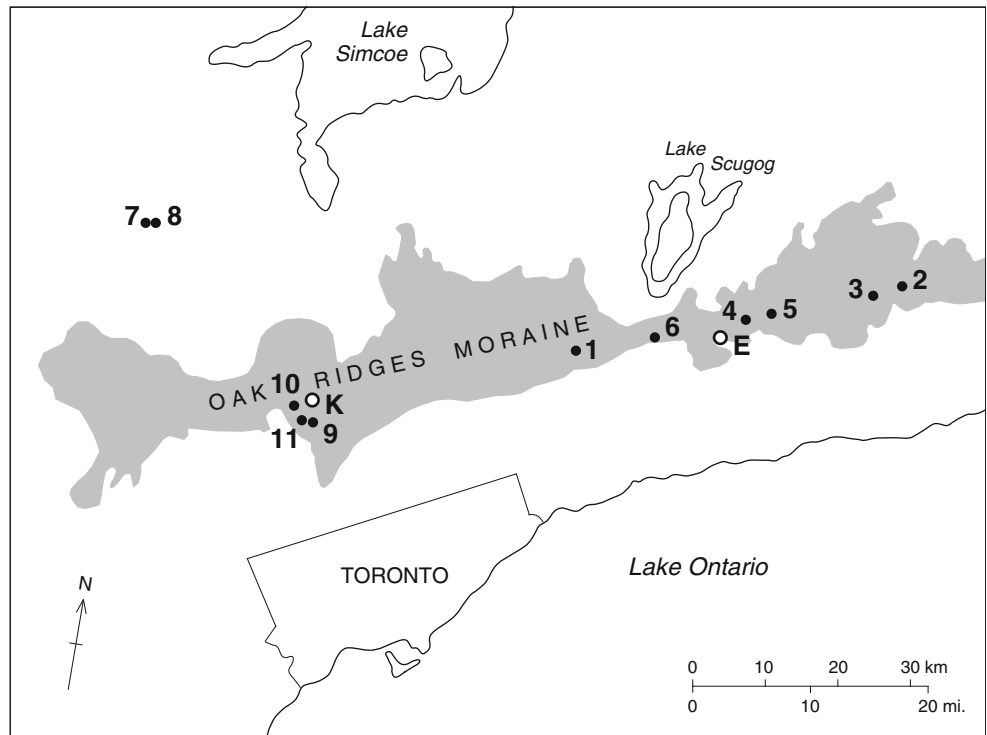
## Study Sites

The study sites are located in southern Ontario, Canada with an annual precipitation of 800–900 mm of which 120–240 mm falls as snow between December and April (Singer et al. 1997). Wetlands 1 to 6 and 9 to 11 are located on the Oak Ridges Moraine, a west-east trending interlobate moraine which is characterized by hummocky topography composed mainly of sands and gravels (Fig. 1). An extensive regional aquifer system underlies the moraine (Howard and Beck 1986). Wetlands 1 to 6 are spring-fed white cedar (*Thuja occidentalis* L.) swamps that are 20–100 m wide along small headwater streams located in areas of discharge from the regional aquifer on the southern flank of the moraine (Roulet 1990). Wetlands 7 and 8 are located 400 m apart on the flood plain of the Boyne River in a valley incised below the Alliston sand plain that forms an unconfined 9–12 m aquifer underlain by silts and clays (Devito et al. 2000). Wetlands 9 to 11 are located south of the town of King City on the Oak Ridges Moraine and form part of the King-Vaughan wetland complex which is designated as a provincially significant wetland area. These wetlands occur in kettle depressions 10–15 m below the surrounding hummocky landscape in an area of the moraine where a thin till cap is present overlying the sand and gravel deposits.

Wetlands 1 to 3 are located in landscapes that are relatively pristine. The upland portion of wetland 1 is covered with a mixed deciduous forest (Fig. 2a). Wetlands 2 and 3 occur in the Ganaraska Forest where the upland area is covered with deciduous forest dominated by red oak (*Quercus rubra* L.) and 50–70 year old red pine (*Pinus resinosa* Ait.) plantations. Wetlands 4 and 5 occur in a relatively undeveloped section of the Oak Ridges moraine east of the hamlet of Enniskillen (Fig. 1). A lightly travelled gravel road extends along the upslope area to the east of wetland 4 (Fig. 2b). A house with an adjacent constructed pond was present prior to 1994 on the northern edge of the wetland and a second house was constructed after 1994 near the western edge of the wetland. These houses are serviced with septic tank systems. A paved secondary road extends along the eastern side of wetland 5 (Fig. 3a).

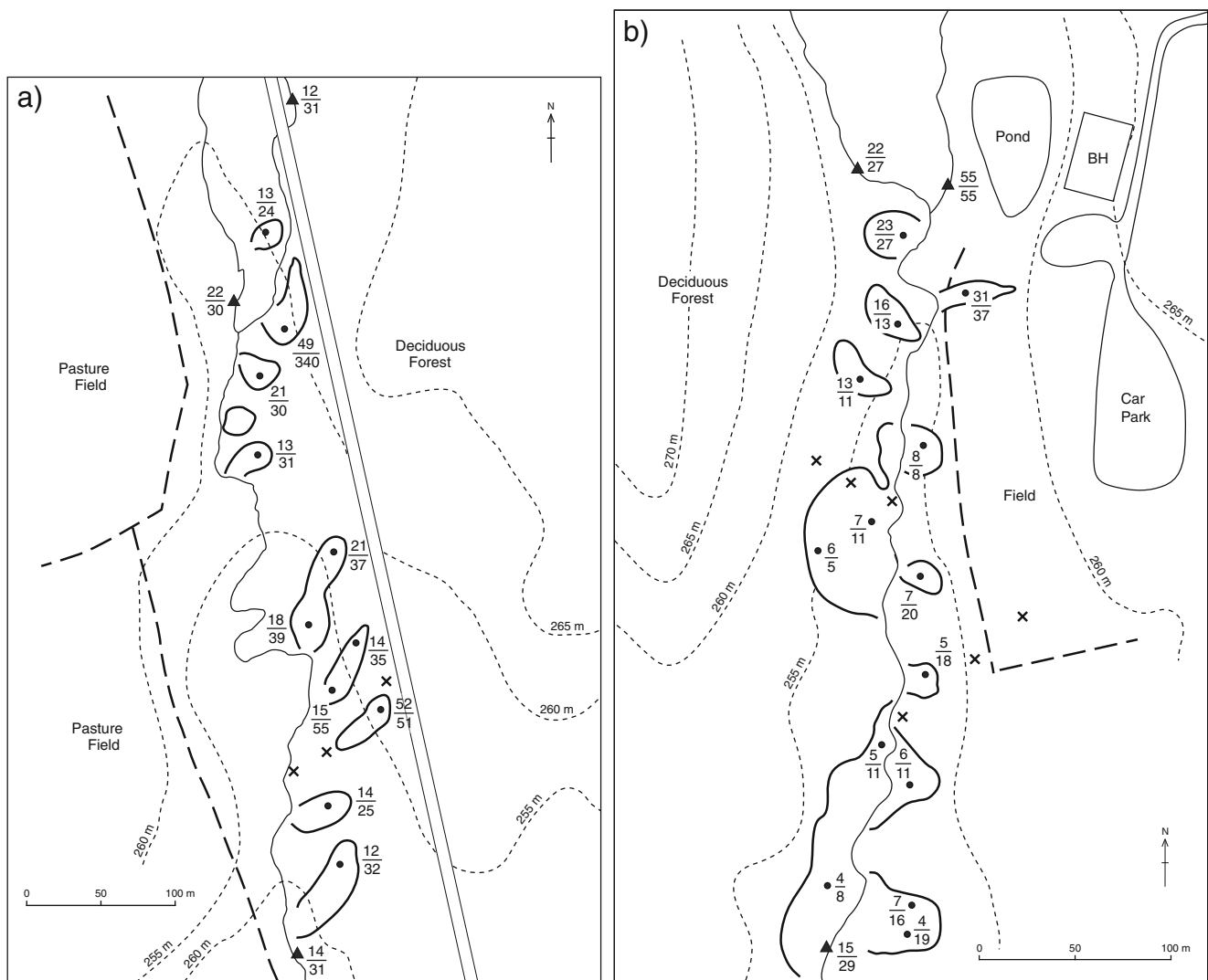
Wetland 6 is located west of Enniskillen in a rural area of increased human activity. A large banquet hall is situated near the eastern edge of the wetland (Fig. 3b). An area of residential homes on large lots is located on the eastern upslope area extending 400 m to a paved two-lane road which runs in a north-south direction. The banquet hall and upslope housing are serviced with septic tank systems. Wetlands 7 and 8 on the Boyne River floodplain are covered with white cedar near the hillslope base (Fig. 4). White cedar interspersed with deciduous species and an area of marsh occur near the river. The sand plain to the north of wetlands 7 and 8 is agricultural with potatoes as the dominant crop. A two-lane paved road running

**Fig. 1** Location of the study wetlands in southern Ontario. *E* indicates Enniskillen. *K* indicates King City



**Fig. 2** Spatial variations in mean chloride concentrations (mg/L) in surface water on saturated areas (●) and streams (▲) of (a) wetland 1 in June–August 1985–90 (upper value) and in June–August 2005 (lower

value) of (b) wetland 4 in June–August 1994 (upper value) and in June–August 2013 (lower value). *X* indicates location of piezometer nests. The thick solid line indicates the boundary of the saturated area



**Fig. 3** Spatial variations in mean chloride concentrations (mg/L) in surface water on saturated areas (●) and streams (▲) of (a) wetland 5 and (b) wetland 6 in June–August 1994 (*upper value*) and June–August

2013 (*lower value*). X indicates location of piezometer nests. BH indicates banquet hall. The *thick solid line* indicates the boundary of the saturated area

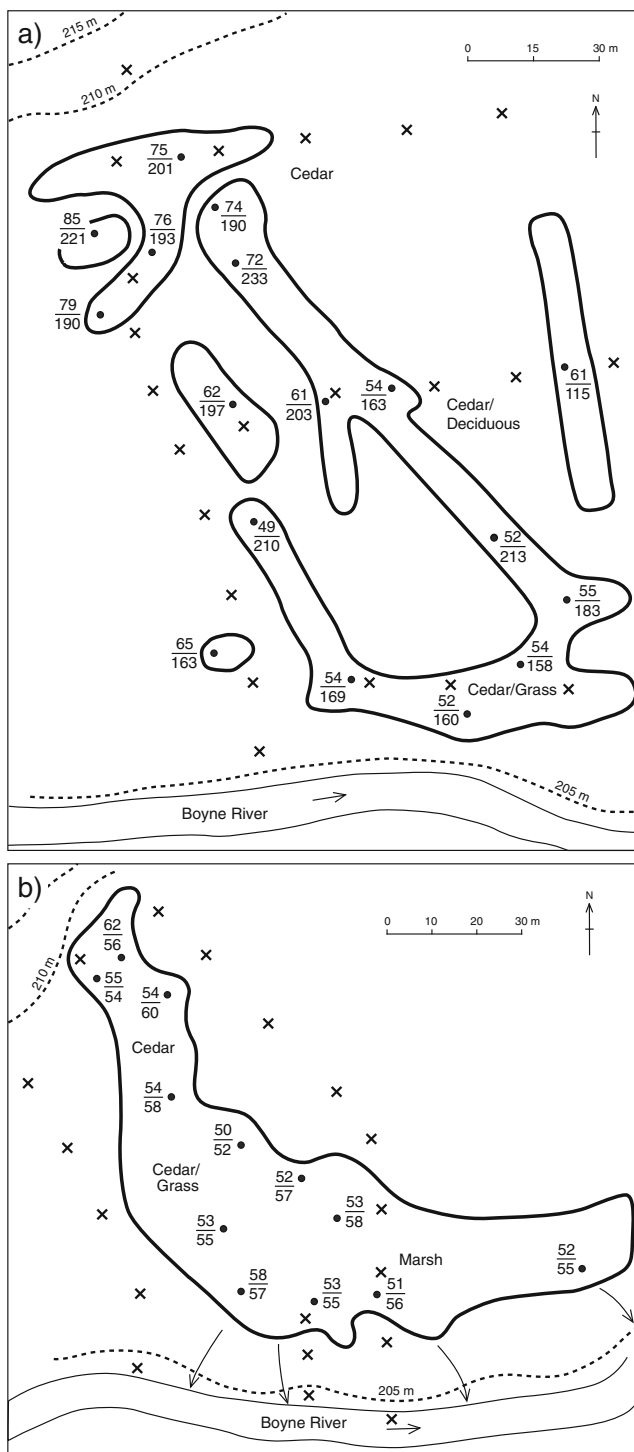
in a north-south direction is located on the sand plain approx. 200 m upslope from wetland 7.

Wetlands 9–11 near King City are covered with dense cattail marshes and mixed swamp forest including red maple (*Acer rubrum* L) red osier dogwood (*Cornus stolonifera*) and willow (*Salix* spp). Wetland 9 is bisected by the King-Vaughan road, a busy two-lane paved road (Fig. 5). A small stream flows through wetland 10 into an open pond (0.8 ha) near King Road, a four-lane paved highway. Wetland 11 is located between the King-Vaughan Road and Keele Street, a well-travelled four-lane paved highway (Fig. 5). A railway running parallel to Keele Street crosses a portion of the wetland. Surface water in the areas of wetland 11 east of Keele Street and between Keele Street and the railway is isolated from the rest of the wetland by an absence of culverts under the road and the railway. Pasture farmland is present on higher elevations surrounding wetland 9. An area of estate residential

development on large lots was present prior to 1999 on the upland between wetlands 10 and 11 (Fig. 5). This residential area was serviced by septic tank systems prior to 2006. After the construction of a trunk sewer system most properties were connected to the sanitary sewer system by 2013. In 2013 additional residential development was under construction on the upland to the east of wetland 10 and south of King Road as well as in the area east of the section of wetland 11 beyond Keele Street (Fig. 5).

## Methods

One or more transects of wells and piezometer nests were installed extending from the upland margin to the stream at all wetlands except wetlands 9 to 11 where one or two piezometer nests were installed. Piezometers were made from



**Fig. 4** Spatial variations in mean chloride concentrations (mg/L) in surface water on saturated areas (●) of (a) wetland 7 in April–June 1996–98 (upper value) and April–June 2012 (lower value) of (b) wetland 8 in April–November 1996–98 (upper value) and April–November 2012 (lower value). X indicates location of piezometer nests. The thick solid line indicates the boundary of the saturated area

1.27 cm ID PVC pipe with 20 cm slot zones installed at depths between 0.5 and 5.5 m depending on sites. Groundwater level and hydraulic heads were measured on several dates to

examine groundwater flow paths. Water samples were collected for chloride analysis from the piezometer transects and from areas of surface saturation at 10–25 sites in each wetland using various sampling regimes. Water samples were collected at approximately monthly intervals at wetland 1 in 1985–1990 and in June–August 2005. Water sampling occurred in wetlands 2–6 on three dates in June–August 1994. Wetlands 4–6 were also sampled on three dates in June–August 2013. Groundwater chloride was not measured in these wetlands in 2013. In wetlands 7 and 8 groundwater was sampled several times each year in 1994–2004 and 2007–2012 and surface water was collected at monthly intervals in April–December 1996–1998 and 2012. In wetlands 9–11 water was collected on four dates in April–May 1999 as well as in mid-March and mid-July 1999. Sampling was also done in December 2012, on four dates in April–May 2013 and in mid-November 2013. Groundwater samples were not collected in 2012–2013. Water samples were analyzed for chloride using standard techniques for automated wet chemistry on an autoanalyzer (Environment Canada 1979).

## Results and Discussion

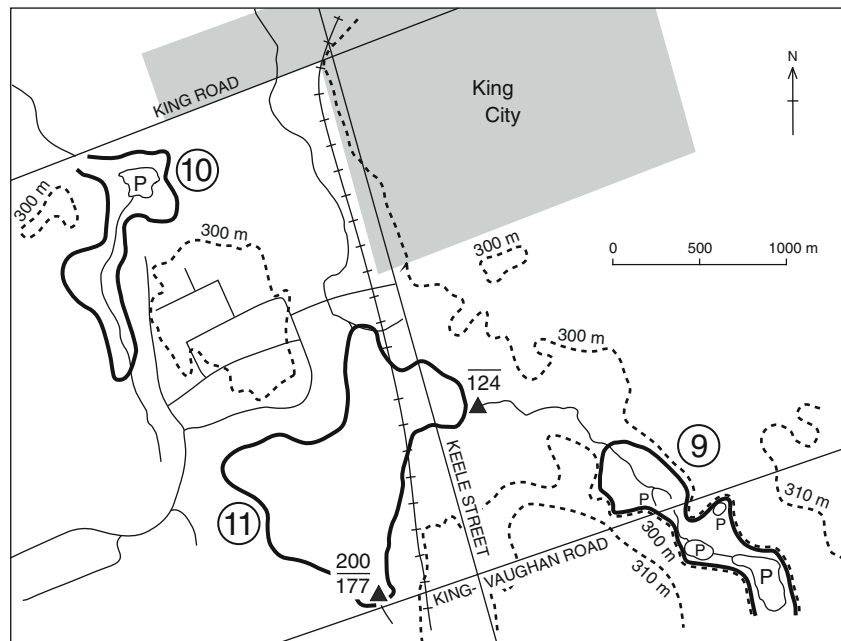
### Wetland Hydrogeology

Organic soils in wetlands 1–6 vary in thickness from a few cms at the upland margins to >2 m at some locations within the wetlands. These organic soils are underlain by glacial sands and gravels. Flow nets showing the distribution of hydraulic heads indicate a constant annual groundwater flow pattern with upward movement of water towards the surface at most locations within each wetland. Hydraulic heads in shallow piezometers at 0.5–1 m depths in wetlands 2, 3 and 4 indicate the occurrence of groundwater recharge near the stream channel which was incised 1 to 1.5 m below the wetland surface. The water table is frequently at or within a few cm of the surface in these wetlands creating areas of permanent saturation with small water filled hollows and diffuse rivulets which drain to the stream channel.

Organic deposits that range up to 3 m in depth are present at wetlands 7 and 8 and are underlain by sands containing gravel lens which extend to the silt and clay aquitard at a depth of 4–6 m. Groundwater flow at wetland 7 is generally horizontal, whereas at wetland 8 upward flow occurs at the upland perimeter. Groundwater flow is horizontal in the mid-section of wetland 8 and recharges to deeper sediments near the river. In wetland 7 springs and groundwater seeps at the upland perimeter form a large area of surface saturation with water depths of 2 to >15 cm in diffuse water flow tracts that extend across the wetland during high water table conditions in late March to early June and in late fall months. As the water table declines in mid-summer areas of surface saturation are



**Fig. 5** Wetlands 9, 10 and 11 showing location of roads and urban areas. P indicates location of ponds. Mean chloride concentrations (mg/L) in streams ( $\blacktriangle$ ) in April–May 1999 (*upper value*) and April–May 2013 (*lower value*). The thick solid line indicates the boundary of the saturated area



restricted to the base of the hillslope. The water table remains adjacent to the surface throughout the year in wetland 8 and spring flows maintain a large area of surface saturation which shows little seasonal contraction.

Organic soils in the kettle depression wetlands 9–11 extend to depths of  $>2$  m and are underlain by glacial loam till. Hydraulic heads in piezometers located at depths of 0.5 and 1.5 m indicated that surface water recharges to underlying sediments in the three wetlands. These wetlands receive water inputs from small streams as well as direct precipitation and near-surface runoff from adjacent slopes. Surface water depths range up to 30–40 cm in early spring, but decline particularly during extended dry periods in summer when areas of the wetlands have no surface water.

#### Wetland Chloride Concentrations in Rural Landscapes

Mean  $\text{Cl}^-$  concentrations in groundwater and in areas of surface water in the Glen Major forest wetland 1 were  $<2$  mg/L during June–August 1985–90 and 2005 (Fig. 2a). Similar low  $\text{Cl}^-$  values ( $<3$  mg/L) were also present in groundwater and surface water in the Ganaraska Forest wetlands 2 and 3 in June–August 1994 (data not shown). These low  $\text{Cl}^-$  levels provide an indication of background concentrations in relatively undisturbed forest landscapes located in areas of sand and gravel glacial deposits in southern Ontario.

Wetlands 4 and 5 are situated in a relatively undeveloped rural landscape. In wetland 4, elevated groundwater  $\text{Cl}^-$  concentrations ranging from 24 mg/L in early June 1994 to 64 mg/L in mid-August were only recorded in shallow groundwater adjacent to the gravel road on the eastern side of the wetland (Fig. 2b). Groundwater recharging towards the

surface elsewhere in wetland 4 had low mean  $\text{Cl}^-$  concentrations of 1–6 mg/L in 1994 indicating that the road had little effect on the adjacent wetland. Road deicing salts are not applied to gravel roads in winter. However, these roads generally receive two applications of liquid calcium chloride in the summer months to reduce dust formation.

Surface water mean  $\text{Cl}^-$  levels in wetland 4 were low in 1994 except in saturated areas downslope from the house at the northern edge of the wetland where values were 14–15 mg/L (Fig. 2b). Surface water  $\text{Cl}^-$  concentrations in June–August 2013 remained low in several locations. However, concentrations in saturated areas downslope from the northern house had increased to 30–34 mg/L and surface water downslope from the house on the western side of the wetland, which was constructed after 1994, showed an increase from mean values of 4 mg/L in 1994 to 23–28 mg/L in 2013. Mean  $\text{Cl}^-$  concentrations in the wetland streams increased from 4 to 6 mg/L in 1994 to 16–19 mg/L in 2013. The spatial pattern of elevated surface water  $\text{Cl}^-$  concentrations in wetland 4 suggests that the leach-field septic tank systems of the two houses located at the margin of the wetland are the source of the contamination. It is noteworthy that elevated  $\text{Cl}^-$  concentrations were observed in saturated surface areas downslope from the house on the west side of the wetland in 2013, whereas concentrations were low in 1994 prior to the construction of this house. The elevated  $\text{Cl}^-$  concentrations recorded in 2013 in the two tributaries at the north edge of the study site may also be attributable to the septic systems of several houses located adjacent to the wetland further upstream.

Groundwater flowing upwards towards the surface adjacent to the road at wetland 5 east of Enniskillen had mean  $\text{Cl}^-$

concentrations of 8–10 mg/L in June–August 1994. Mean surface water Cl<sup>-</sup> concentrations on two saturated areas near the paved road ranged from 49 to 52 mg/L (Fig. 3a). Elsewhere wetland surface water Cl<sup>-</sup> levels were 12–21 mg/L in June–August 1994. Similar Cl<sup>-</sup> concentrations were present at depths of 0.5 and 1 m near the stream bank where surface water recharged into the peat. Surface water samples collected in June–August 2013 showed a considerable increase in mean Cl<sup>-</sup> values throughout the wetland with a very high concentration of 340 mg/L in one location adjacent to the road. Mean Cl<sup>-</sup> values in the stream draining the wetland also increased from 12 to 22 mg/L in 1994 to 30–31 mg/L in 2013 (Fig. 3a). These Cl<sup>-</sup> concentration patterns suggest that deicing salts enter saturated areas adjacent to the road in runoff and salt spray. Wetland surface rivulets transport these elevated Cl<sup>-</sup> concentrations downslope towards the stream. The wetland streams at the northern edge of the study site which showed an increase in Cl<sup>-</sup> concentrations between 1994 and 2013 flow alongside the secondary road for several kilometers to the north.

Wetland 6 is located in an area of increased human impact with the adjacent banquet hall, an area of residential housing and a paved highway 400 m to the east. Mean groundwater Cl<sup>-</sup> concentrations discharging towards the surface increased from 2 mg/L at the perimeter of the transect on the western edge of wetland 6 to 10–11 mg/L near the stream in June–August 1994 (Fig. 3b). Much higher mean Cl<sup>-</sup> levels of 30–57 mg/L were recorded at depths of 1–2 m in upward flowing groundwater at the perimeter and mid-point of the transect on the eastern side of the wetland. In contrast, groundwater discharging to the surface adjacent to the stream had lower mean concentrations of 8 mg/L in 1994. Surface water mean Cl<sup>-</sup> concentrations in June–August 1994 were 23–31 mg/L in the upstream area of wetland 6 and decreased gradually in a downstream direction to 4–7 mg/L (Fig. 3b). In June–August 2013 mean Cl<sup>-</sup> levels on saturated surface areas in the upstream portion of wetland 6 remained similar to 1994, however concentrations showed an increase to 11–19 mg/L in the downstream area particularly on the eastern side of the stream. The streams entering wetland 6 from the north had similar high mean Cl<sup>-</sup> concentrations of 22–55 mg/L in 1994 and 2013. In contrast, stream Cl<sup>-</sup> values at the southern edge of the study area increased from 15 mg/L in 1994 to 29 mg/L in 2013 (Fig. 3b).

Road salt applications and septic tanks systems are probably the sources of the elevated Cl<sup>-</sup> concentrations in surface water near the banquet hall and in groundwater on the east side of wetland 6. Labadia and Buttle (1996) have demonstrated that winter applications of road salt to a major highway on the Oak Ridges Moraine were transported rapidly through sandy soils to depths of >2.5 m, where Cl<sup>-</sup> concentrations which exceeded 1000 mg/L by the following autumn could contaminate underlying groundwater systems. The high Cl<sup>-</sup> concentrations observed in groundwater discharging towards the

ground surface at the margin and mid-point on the east side of wetland 6 in 1994 is consistent with rapid recharge on the upland area and groundwater transport to the adjacent wetland. Surface water chloride concentrations which increased in the downstream portion of the wetland between 1994 and 2013 suggest that Cl<sup>-</sup> contaminated groundwater has extended to the south in this area where upward flowing groundwater adjacent to the stream had low Cl<sup>-</sup> concentrations in 1994. Deicing salt applications on a paved east-west road located a kilometer to the north are the likely source of the elevated Cl<sup>-</sup> concentrations recorded in the streams at the northern edge of the wetland site.

The elevated Cl<sup>-</sup> concentrations recorded in wetlands 4–6 are of concern because the large constant groundwater input from the Oak Ridges Moraine aquifer system to headwater spring-fed swamps is an important source of base flow for numerous streams that drain to Lake Ontario (Gerber and Howard 2002). In contrast to the low Cl<sup>-</sup> concentrations recorded in wetlands 1–3, headwater stream base flow Cl<sup>-</sup> concentrations of 12–30 mg/L in wetlands 4–6 reduce the dilution effects of these base flows on large sources of Cl<sup>-</sup> contamination from urban areas with dense road networks in the downstream areas of the watersheds.

### Wetland Chloride Concentrations in a Landscape of Intensive Crop Production

Groundwater Cl<sup>-</sup> concentrations of 50–90 mg/L were observed along subsurface flow paths from the upland perimeter of wetland 7 to the river in 1996–2004, whereas in 2007–2012 higher groundwater concentrations of 130–240 mg/L were recorded. Chloride concentrations in groundwater flowing upwards and laterally beneath wetland 8 ranged from 45 to 65 mg/L in 1996–2004 and in 2007–2012. Mean surface water Cl<sup>-</sup> concentrations in wetland 7 ranged from 74 to 85 mg/L near the upland margin to 49–65 mg/L near the river in April–June 1996–98 (Fig. 4a). Much higher mean Cl<sup>-</sup> concentrations which generally ranged between 160 and 233 mg/L were recorded in 2012. Further downstream at wetland 8, areas of surface water had similar mean Cl<sup>-</sup> concentrations of 50–62 mg/L in April–November 1996–1998 and 2012 (Fig. 4b).

Potato crops on the sand plain adjacent to wetlands 7 and 8 receive annual fertilizer applications of 150–250 kg/ha as potassium chloride and considerable amounts of Cl<sup>-</sup> enter the aquifer during major episodes of soil drainage in autumn and in the early spring snowmelt period (Hill 1986). High Cl<sup>-</sup> concentrations (30–60 mg/L) have been recorded to depths of 10 m in the sand plain aquifer beneath cropland (Hill 1982; Starr and Gillham 1993). These data suggest that crop fertilizer applications represent the main source of elevated surface water Cl<sup>-</sup> concentrations in wetland 8. The higher Cl<sup>-</sup> concentrations in groundwater entering wetland 7 from the upland aquifer reflect the influence of deicing salt

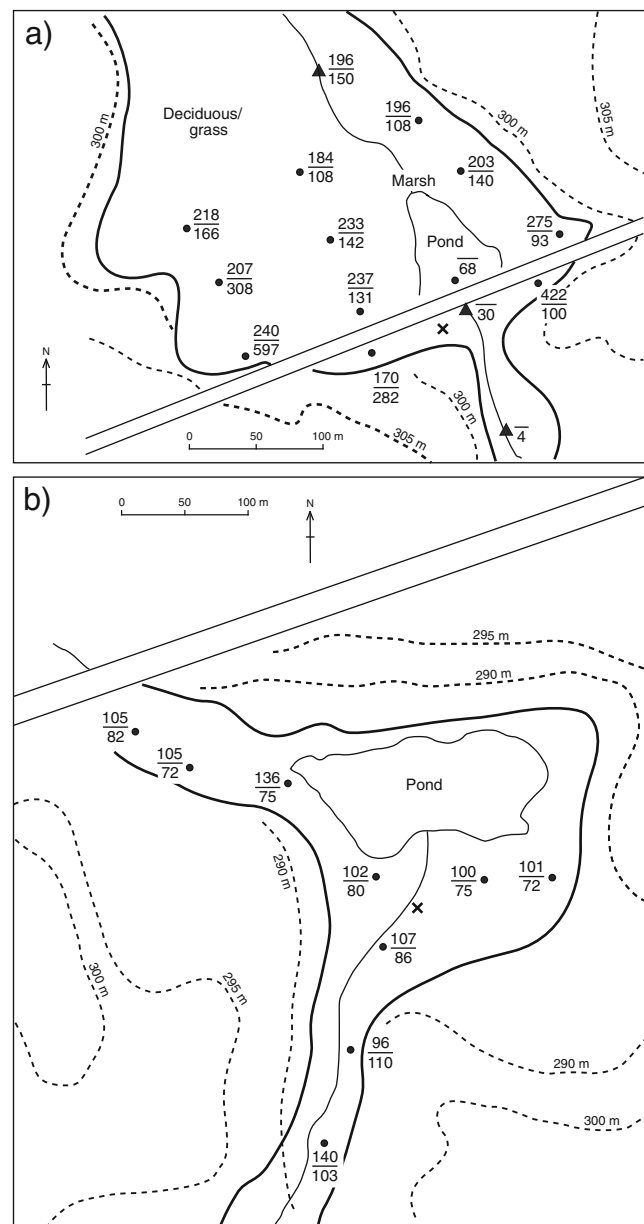
applications on the adjacent road as well as fertilizers. Hill (1982) reported high  $\text{Cl}^-$  concentrations of 100–495 mg/L in sand plain wells adjacent to highways in contrast to lower levels of <60 mg/L in wells adjacent to crops. The large increase in groundwater  $\text{Cl}^-$  observed in wetland 7 in the years after spring 2007 and the higher surface water  $\text{Cl}^-$  levels in 2012 compared to 1996–98 probably resulted from increased use of deicing salts on the adjacent highway.

### Wetland Chloride Concentrations in a Landscape of Increasing Urbanization

Groundwater recharging to deeper sediments in the three depressional wetlands near King City had elevated  $\text{Cl}^-$  concentrations in 1999 which ranged from 132 mg/L, 185 mg/L and 480 mg/L at 0.5 m depths to 110 mg/L, 132 mg/L and 156 mg/L at 1.5 m depths in wetlands 9, 10 and 11 respectively. In April–May 1999 surface water mean  $\text{Cl}^-$  concentrations in wetland 9 ranged from 170 to 422 mg/L, while in the same months in 2013 mean values varied between 93 and 597 mg/L (Fig. 6a). The small wetland stream 100 m upslope from the King–Vaughan road had a low mean  $\text{Cl}^-$  concentration of 4 mg/L in April–May 2013 which increased to 30 mg/L at the upstream edge of the road and to 68 mg/L in the pond. The stream flowing from wetland 9 to the northwest had a mean April–May  $\text{Cl}^-$  concentration of 196 mg/L in 1999 and 150 mg/L in 2013 (Fig. 6a). Surface water mean  $\text{Cl}^-$  concentrations in wetland 10 varied from 96 to 140 mg/L in April–May 1999 and were slightly lower in 2013 (Fig. 6b).

In April–May 1999, surface water mean  $\text{Cl}^-$  concentrations in wetland 11 ranged from 70 to 180 mg/L in most locations (Fig. 7). Several sites adjacent to the four-lane highway had higher concentrations of 200–256 mg/L. In April–May 2013 surface water  $\text{Cl}^-$  levels in the wetland west of the railway were similar to 1999. The stream which flows in to this portion of the wetland from the south had a mean  $\text{Cl}^-$  concentration of 200 and 177 mg/L in 1999 and 2013 respectively (Fig. 5). Chloride concentrations were generally lower in the section of the wetland east of Keele Street in 2013 in comparison to 1999. The stream which flows into this part of the wetland from wetland 9 had a mean  $\text{Cl}^-$  concentration of 124 mg/L in 2013 (Fig. 7). Chloride concentrations in the section of the wetland between the road and railway showed a large increase in 2013 to values of 400 to 728 mg/L at many sites.

Although surface water sampling in wetlands 9–11 focused on the spring months of April and May, surface water was also analyzed at other seasons of the year. In mid-March 1999 an extensive ice cover was present in wetlands 9–11. Chloride concentrations measured in a few patches of surface water were generally lower (< 50 mg/L) than in the April–May period. By mid-July 1999 wetland water levels had declined and  $\text{Cl}^-$  concentrations in the remaining areas of surface water

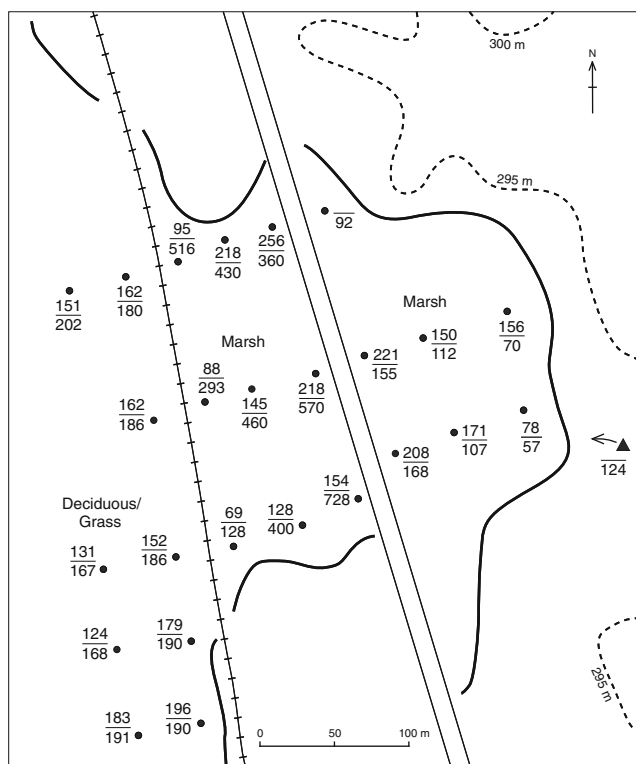


**Fig. 6** Spatial variations in mean chloride concentrations (mg/L) in surface water on saturated areas (●) and streams (▲) of (a) wetland 9 and (b) wetland 10 in April–May 1999 (upper value) and April–May 2013 (lower value). X indicates location of piezometer nest. The thick solid line indicates the boundary of the saturated area

were generally higher than at the same locations in April and May. Water samples collected at surface sampling sites throughout the three wetlands in early December 2012 and mid-November 2013 had elevated  $\text{Cl}^-$  concentrations that were similar to values recorded in the spring months.

The patterns of high surface water  $\text{Cl}^-$  concentrations in the three depressional wetlands 9–11 which are located in a rapidly urbanizing area adjacent to Toronto suggest the influence of road deicing salts. The small stream flowing through wetland 9 has low  $\text{Cl}^-$  concentrations 100 m upslope from the paved road which increase rapidly in the wetland adjacent to





**Fig. 7** Spatial variations in mean chloride concentrations (mg/L) in surface water on saturated areas (●) and streams (▲) of wetland 11 in April-May 1999 (upper value) and April-May-2013 (lower value). X indicates location of piezometer nest. The thick solid line indicates the boundary of the saturated area

and down-gradient from the road (Fig. 6a). Wetland 10 which has lower surface water  $\text{Cl}^-$  concentration than wetlands 9 and 11 does not receive drainage from a major road, however the headwater area of the small stream flowing through this wetland is adjacent to several residential streets which are salted in winter (Fig. 5). Drainage ditches on the sides of the four-lane Keele Street highway which bisects wetland 11 transport road runoff and salt spray downslope from both the north and south into this wetland. Stream flow with high  $\text{Cl}^-$  levels flowing from wetland 9 also drains into the area of wetland 11 to the east of the road (Fig. 5). The area of wetland 9 west of the railway which displays high surface water  $\text{Cl}^-$  levels is isolated from Keele Street to the east. However, this section of the wetland is affected by the King-Vaughan road to the south where high  $\text{Cl}^-$  concentrations in stream flow enter the wetland and flow in a diffuse manner across the surface.

### Spatial and Temporal Patterns of Wetland Chloride Concentration

Previous studies which have focused on  $\text{Cl}^-$  contamination in wetland groundwater systems have reported high concentrations adjacent to highways or septic systems with a decline towards background levels further from the sources of

contamination (Pugh et al. 1996; Panno et al. 1999; Richburg et al. 2001). However, most of the wetlands analyzed in this study show little evidence of a decline in surface water  $\text{Cl}^-$  concentrations with distance from contamination sources. Water transport by diffuse surface flow paths produce widespread dispersal within these wetlands that result in relatively uniform patterns of  $\text{Cl}^-$  concentration. Most sampling in our study focused on the spring and summer period. However, sampling at other seasons of the year in wetlands 7–11 recorded  $\text{Cl}^-$  concentrations that are in the same range as spring and summer values. Research on stream  $\text{Cl}^-$  concentrations have also reported elevated values in summer and autumn, as well as spikes in concentration following road salt applications in winter months (Findlay and Kelly 2011). The maintenance of high  $\text{Cl}^-$  concentrations throughout the year in streams has been linked to the slow release of  $\text{Cl}^-$  from subsurface soils and groundwater storage (Kelly et al. 2008; Kincaid and Findlay 2009). The considerable retention of  $\text{Cl}^-$  evident in the sediments of depressional wetlands 9–11 and in the groundwater systems which discharge to other wetlands in the present study reduces seasonal  $\text{Cl}^-$  fluctuations.

Many long-term studies have shown increasing  $\text{Cl}^-$  concentrations in streams in recent decades. Temporal trends in  $\text{Cl}^-$  concentrations over the period from the 1990's to 2012–2013 are also evident in several of the southern Ontario wetlands impacted by human activities. Considerable increases in  $\text{Cl}^-$  levels were observed in wetlands 4–7. The area of wetland 11 that was isolated between the railway and Keele Street to the east showed a 2–3 times increase in  $\text{Cl}^-$  concentration between 1999 and 2012–2013. Despite increasing urbanization, wetland 9 showed no clear trend and the area of wetland 11 east of Keele Street and wetland 10 had a small  $\text{Cl}^-$  decline. In contrast to wetlands 1–8 where large groundwater inputs maintained surface saturation, temporal trends in water levels and  $\text{Cl}^-$  in the three depressional wetlands 9–11 are influenced by annual variations in precipitation. Precipitation in April–May 1999 was only 60–75 % of the long-term average for these months, whereas April and May 2013 precipitation was 135 and 200 % above the long-term mean. Evaporative enrichment may have increased  $\text{Cl}^-$  concentrations at some surface sampling sites in 1999, whereas dilution resulting from greater surface water depths and increased surface flows in 2013 may have produced lower  $\text{Cl}^-$  concentrations.

Prolonged exposure to  $\text{Cl}^-$  concentrations of  $>240$  mg/L is considered to be harmful to 10 % of aquatic species (Environment Canada 2001). The water quality threshold in Canada established in 2011 for long term exposure to chloride has been set even lower at 120 mg/L (Canadian Council of Ministers of the Environment 2011). The chronic freshwater quality criterion for  $\text{Cl}^-$  developed by the US Environmental Protection Agency suggests that concentration should not exceed 230 mg/L (USEPA 2002). Chloride concentrations in this study frequently ranged between 150 and 700 mg/L in

wetlands 9 and 11 and between 160 and 230 mg/l in 2012 for wetland 7 which may have negative impacts on some aquatic species in these sites. The egg and tadpole stage of spotted salamander (*Ambystoma maculatum*) are impacted by relatively low  $\text{Cl}^-$  concentration of 145 mg/L (Turtle 2000; Karraker et al. 2008). The survival of wood frog (*Rana sylvatica*) eggs and tadpoles may decline between 145 and 628 mg/L  $\text{Cl}^-$  (Sanzo and Hecnar 2006; Karraker et al. 2008). Despite generally high  $\text{Cl}^-$  concentrations in wetlands 9–11, low  $\text{Cl}^-$  values were recorded in mid-March in some surface water patches isolated by an ice cover. This may allow the early life stage of spring breeding species such as the wood frog to occur before diffuse surface flow paths spread high  $\text{Cl}^-$  concentrations throughout the wetlands.

## Conclusions

The data collected for the 11 wetlands in this study suggest a gradient of increasing surface water  $\text{Cl}^-$  concentrations in relation to several anthropogenic sources of contamination along a rural to urban land use gradient. Our data indicate that even in rural areas of low population density, domestic septic systems and road salt applications on secondary roads can result in moderate increases of surface water  $\text{Cl}^-$  in adjacent wetlands in comparison to background values in forest watersheds. Fertilizers are also a source of wetland chloride contamination in areas of intensive crop production. The highest  $\text{Cl}^-$  concentrations were observed in several wetlands in a rapidly urbanizing area with a denser road network. These elevated concentrations frequently exceeded water quality recommendations suggesting the potential for negative effects on wetland biota. Spatial patterns in  $\text{Cl}^-$  concentrations indicated widespread contamination in the study wetlands and an absence of any large decline in concentration with distance from nearby sources. Temporal trends in  $\text{Cl}^-$  concentrations over the period from the 1990's to 2012–2013 reveal considerable increases in several of the wetlands. These results and future studies in other regions should improve our understanding of land use effects on wetland surface water  $\text{Cl}^-$  concentrations patterns. Increased knowledge of these concentration patterns can be used to assess the extent to which these concentrations lie within ranges that have been shown in laboratory studies to result in direct or indirect effects on aquatic organisms.

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