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## Road Salt Impacts on Ground-water Quality — The Worst is Still to Come!

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### ABSTRACT

Throughout snow-belt regions of Canada, Europe, and the United States, millions of tonnes of road de-icing agents are applied to roads and highways each year. The problem is particularly acute in the Metropolitan Toronto area of southern Ontario, Canada, which receives well over 100 000 t (tonnes) (Mg) of NaCl annually, a rate approximating 200 g for every square metre of land. Historically, the common presumption has been that most of the applied salt is flushed from the system each season by overland flow and that impact on subsurface water is minimal and at steady state. However, there is now evidence that continued deployment of road de-icing chemicals may compromise ground-water quality for generations to come.

The results of a detailed salt budget determined for the Highland Creek basin of Metropolitan Toronto reveal that only 45% of the salt applied is being removed annually from the catchment in surface-water flow, the remainder entering temporary storage in shallow subsurface waters. The data from this study indicate that if present rates of salt application are maintained, chloride concentrations in ground waters discharging as stream base flow will eventually reach a steady-state concentration of >400 mg/L. This value represents a threefold increase over present average base-flow concentrations and well exceeds guidelines for drinking-water quality. The impact of sodium will be delayed by ion exchange, but similar calculations suggest that steady-state

sodium concentrations will reach an equally unacceptable 250 mg/L.

Although the salt balance calculations are useful in determining the average steady-state concentrations of sodium and chloride in ground-water discharge, numerical models are necessary to determine temporal and spatial changes in water quality. As expected, these models indicate that rates of ground-water degradation are highly dependent on the local hydrogeology, including catchment size. In Toronto, where Quaternary sediments form the major aquifer units, models indicate that steady state may take 200 yr, by which time average concentrations of sodium and chloride in ground-water will be similar to predicted base-flow concentrations. Locally, however, particularly within a few hundred metres of highways, concentrations three to four times the base-flow concentrations can be anticipated.



### INTRODUCTION

Throughout snow-belt regions of Canada, Europe, and the United States, many millions of tonnes of de-icing chemicals are applied to roads and highways every year. These chemicals, usually in the form of sodium chloride (NaCl), are readily mobilized in air-borne spray and surface-water runoff and usually appear in streams and lakes within months, if not weeks of their application. Although there have been many documented instances of ground-water pollution resulting from application of salt to roads (Huling and Hollocker, 1972; Diment et al., 1973; Toler and Pollock, 1974; Field et al., 1974; Wulkowicz and Saleem, 1974; Eisen and Anderson, 1980; Locat and Gélinas, 1989), it is generally assumed that relatively little salt enters the subsurface, and that when it does, only shallow road-side wells are affected.

In the Toronto area of southern Ontario, Paine (1979) first suggested that impacts of road salting on ground-water quality could be more serious. Paine performed a relatively coarse chloride mass balance determination on the Don River watershed (Fig. 1) and found that as little as 50% of the yearly application of NaCl was being removed by surface-water flow. His suggestion that the remaining salt was being stored in the shallow subsurface was strongly supported by Joy (1979), who, working in the same region, found elevated concentrations of sodium (>20 mg/L) in 141 road-side wells. It was not until the mid-1980s that follow-up studies confirmed the severity of the problem. Pilon and Howard (1987) recorded concentrations of chloride as high as 14 000 mg/L in pore waters from the unsaturated zone adjacent to highways in Metropolitan Toronto. Howard et al. (1985) found that the chloride concentration of urban springs of the Scarborough Bluffs (Fig. 1) averaged 380 mg/L, and local concentrations were as high as 2800 mg/L. Although Metropolitan Toronto ground waters are not generally used for domestic consumption, fears were raised that shallow contaminated ground waters could threaten the quality of urban streams and would ultimately affect the quality of the Great Lakes (Hodge, 1989; Duda, 1989;

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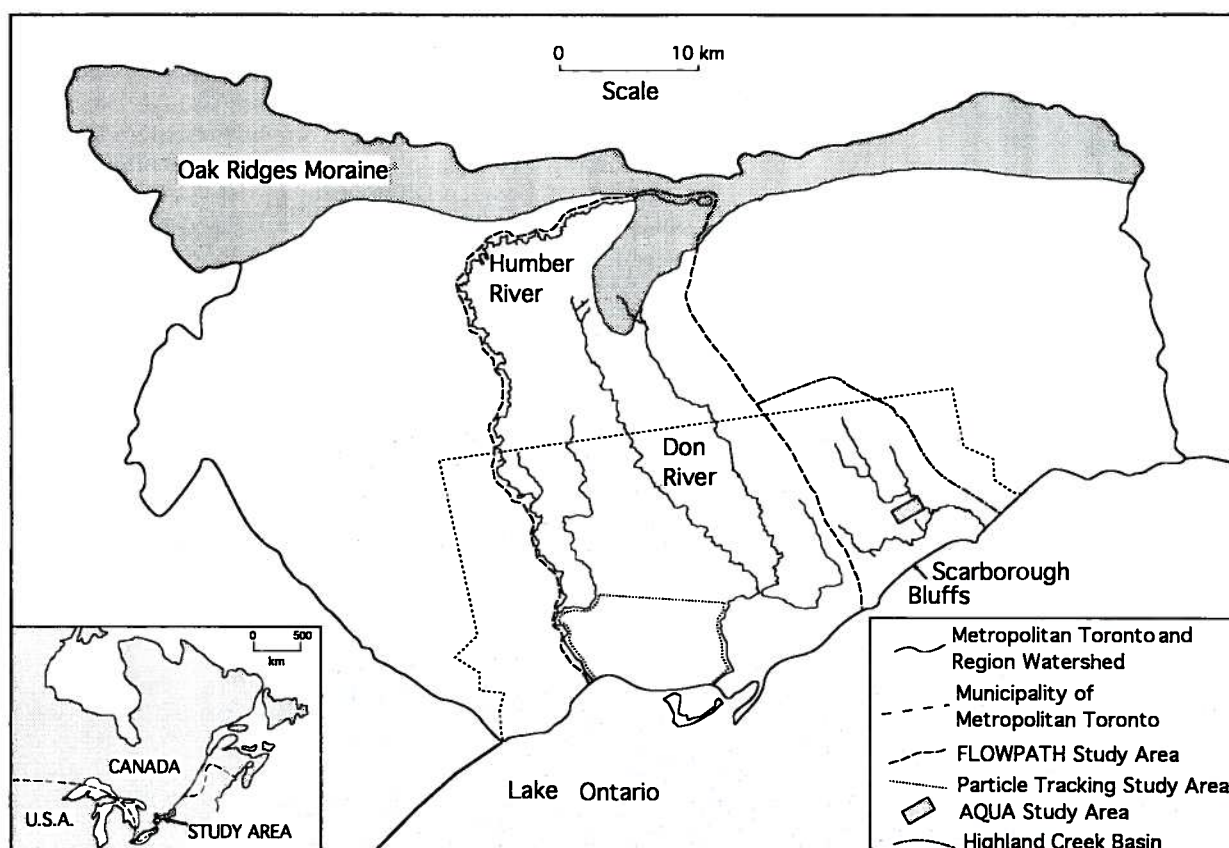


Figure 1. The Metropolitan Toronto and Region Watershed, showing locations of the study areas.

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International Joint Commission, 1988). Concerns have also been expressed that because of the explosive growth of satellite communities within the Metropolitan Toronto and Region Watershed (Fig. 1), continued road salting as now practiced may have serious implications for ground-water quality in major aquifers such as the Oak Ridges Moraine (Howard and Beck, 1986).

In recent years, the Groundwater Research Group at the University of Toronto has focused considerable attention on the issue of road de-icing chemicals as a source of sodium and chloride in ground-water. The primary aims of this work have been (1) to determine the degree to which primary and trace constituents of road de-icing chemicals and other urban sources of chloride contamination may ultimately threaten the quality of ground water; (2) to determine the chemical behavior of the contaminants and identify inorganic chemical constituents that could assist in labeling the source of contamination; (3) to predict the extent to which continued deployment of road de-icing chemicals will eventually degrade the inorganic quality of ground water; and (4) to develop models that will enable the rates of ground-water degradation to be estimated. In this paper we review the major findings of this research and, in particular, examine the value of models for predicting regional changes in water quality with time.

## HYDROGEOCHEMISTRY AND WATER QUALITY

Road de-icing chemicals take several different forms, but NaCl is the cheapest and most commonly used. It is particularly cost-effective at temperatures above -12 °C. In practice, NaCl is normally applied in pure mineral form, but it is also used in conjunction with abrasives such as sand. In Metropolitan Toronto, the preferred practice is to apply pure NaCl to main urban roads, highways, and freeways, whereas mixtures of sand and 5%–95% NaCl are used on side streets. Mixtures of sand and 5% NaCl are also used on gravel roads, because pure NaCl tends to damage the road surface during a thaw. Calcium chloride (CaCl<sub>2</sub>) is more effective than NaCl at temperatures in the range -12 to -34 °C but is less commonly used because it is two to four times more expensive and is known to make the road surface slippery when wet (Hanley, 1979).

Environmental damage due to NaCl road de-icing chemicals is well documented (Jones et al., 1986; Scott and Wylie, 1980), but most accounts concern visible impacts such as vehicle corrosion, dying vegetation, and disintegration of concrete. When NaCl is dissolved in water, the most common concern is an increase in salinity to levels that would make the water unsuitable for consumption and some industrial applications. Table 1 lists water-quality guidelines for sodium and chloride in drinking water as defined by various interested agencies. In most cases the guideline for chloride is set at 250 mg/L in recognition of a taste threshold that for most people exists between 200 and 300 mg/L. The guideline for sodium is more contentious, because the ion has been strongly linked with the development of hypertension, a condition affecting perhaps 20% of the U.S. population (Moses, 1980; Craun, 1984; Tuthill and Calabrese, 1979). Raised sodium intake has also been associated indirectly with hypernatraemia (World Health Organization, 1984). Most agencies retain a guideline of 200 mg/L for purely aesthetic purposes. However, other agencies have been more cautious, the European Economic Community, for example, setting a guideline of just 20 mg/L.

During the hydrogeochemical part of the study, major ion, minor ion, and trace-metal analysis was performed on solutions of road salt and other suspected sources of chloride in the Toronto region. These sources include fertilizers and manure piles (Hill, 1982; Poinke and Urban, 1985), septic tanks, landfill leachates, and saline waters from the underlying Palaeozoic bedrock formations. The primary purposes of this work were to screen the chloride sources for potentially hazardous major, minor, and trace inorganic pollutants and to identify inorganic chemical parameters that could provide a diagnostic indication of the chloride source. In total, chemical analysis was performed on 37 chloride source samples, including five samples of road de-icing chemical from four different suppliers. Details of the geochemical investigation are described in Howard and Beck (1993).

Analysis of 5% solutions of NaCl (30 000 mg/L chloride) revealed an unexpectedly high degree of

TABLE 1. WATER-QUALITY GUIDELINES FOR SODIUM AND CHLORIDE IN DRINKING WATER

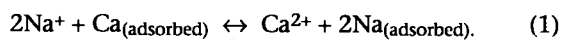
Agency	Limit	Type	Chloride (mg/L)	Sodium (mg/L)
U.S. Environmental Protection Agency (USEPA)	Secondary maximum contaminant level	Aesthetic	250	-
Health and Welfare Canada	Aesthetic objective	Aesthetic	250	200
Ontario Ministry of the Environment (MOE)	Maximum desirable concentration	Aesthetic	250	-
"	Aesthetic objective	Aesthetic	-	200
State of New York	Maximum contaminant level	Health	250	-
State of Florida	Maximum contaminant level	Health	-	160
World Health Organization (WHO)	Guideline value	Aesthetic	250	200
European Economic Community (EEC)	Guideline level	Aesthetic	-	20
"	Maximum admissible concentration	Aesthetic	-	150

Note: Data after Ontario Ministry of the Environment (1991). Dashes indicate no guideline given.

chemical purity. Sulfate and nitrate were found to be the most important secondary constituents, but they contributed less than 0.4% each to the solutions' total dissolved solids. Of the trace metals, only iron, aluminum, copper, and barium were detected, normally at concentrations in the range 0.1% to 0.3%. From a water-quality perspective, it is apparent that only sodium and chloride, the primary inorganic components, constitute a serious threat to ground-water potability.

A comparison to the chemical characteristics of all potential chloride sources revealed that it is the absence rather than the presence of certain ions that offers greatest potential for distinguishing NaCl road salt from other sources of chloride contamination. For example, NaCl road de-icing salts are characterized by extremely low levels of iodide and fluoride (~20 µg/L and 100 µg/L, respectively, in a 5% solution). In contrast, most natural sources of saline ground water are considerably more enriched in iodide and fluoride, commonly by several orders of magnitude.

When minor ion data are unavailable, the depletion of sodium with respect to chloride is a common characteristic of recent, active contamination by NaCl road salt. The depletion is attributed to an ion exchange reaction that has been observed during seawater invasion of coastal aquifers (Howard and Lloyd, 1983). The reaction takes the form:



Although this reaction has been responsible for lowering sodium concentrations in aquifers on the fringe of Metropolitan Toronto (Howard and Falck, 1986), the capacity of soils and sediments to perform ion exchange appears to have been exceeded in heavily urbanized areas that have received large influxes of NaCl over extended periods of time. As a result, saline ground waters from the central area rarely show a depletion of sodium.

## SALT BALANCE

A prerequisite for modeling subsurface salt transport is an understanding of the rate at which the applied salt is retained in the subsurface on an annual basis. This was achieved using a catchment-mass-balance approach, in which chloride input, represented by the mass of chloride applied to the catchment during a specified time frame, is budgeted against chloride output in the form of chloride loading in the

exiting stream. The net difference represents the mass of salt that is stored (retained) within the catchment.

A chloride mass balance was determined for the highly urbanized Highland Creek basin of the Metropolitan Toronto and Region Watershed (Fig. 1). Full details of the balance are given by Howard and Haynes, (1993). The basin is 104 km<sup>2</sup> in area, and it is receiving approximately 17000 Mg of NaCl road de-icing chemicals each year. This represents approximately 200 g of NaCl for every square metre of the catchment. Chloride leaving the basin was determined from stream flow and electrical conductivity measurements recorded at 15-minute intervals over a two-year period. The amount of chloride leaving the basin through stream sediment load was assumed to be negligible. The results are summarized in Table 2. They reveal that only 45% of the salt applied is being removed annually from the catchment by surface water runoff, the remainder entering temporary storage in shallow subsurface waters.

While the total mass of chloride entering the subsurface exceeds the mass of chloride leaving as baseflow to the stream, chloride will accumulate in the ground water, and chloride concentrations in the ground water will increase. Eventually, chloride in the ground water will reach a level at which the mass lost in base flow will match the mass of chloride entering the subsurface. At this stage, steady state will be reached, and no further deterioration of ground-water or stream-water quality will occur. Aquifer recharge in the basin is approximately 162 mm per annum. If present rates of salt application are maintained and 45% of this salt enters the subsurface, chloride concentrations in ground waters discharging as base flow will eventually reach a steady state concentration of >400 mg/L, according to the data. This value represents a threefold increase over present average baseflow concentrations and well exceeds guidelines for drinking-water quality. The impact of sodium will be delayed locally by ion exchange, but similar calculations suggest that steady-state sodium concentrations will reach an equally unacceptable 250 mg/L.

## TRANSPORT MODELS

Although the salt balance calculations are useful in determining the average concentrations of sodium and chloride in base-flow discharge when steady-state

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TABLE 2. SUMMARY OF CHLORIDE BALANCE FOR THE PERIOD NOVEMBER 1, 1988 TO OCTOBER 31, 1991

Season	Total chloride applied (Mg)	Chloride loading in surface runoff		
		Winter months (% of total applied)	Summer months (% of total applied)	Surface runoff (% of total applied)
1988–1989	10 486	>15*	19	>34
1989–1990	11 228	31	14	45
1990–1991	9173	26	-	>26

Note: Data summarized after Howard and Haynes (1993). Dash indicates not determined.

\* Data available for only March and April.

conditions are reached, contaminant transport models are required to investigate spatial and temporal changes in ground-water quality. During the study, three types of model were developed, each designed to meet specific applications.

### "FLOWPATH"

FLOWPATH (Franz and Guiguer, 1990) is a two-dimensional, finite-difference model that can simulate horizontal, steady-state ground-water flow and perform particle tracking in heterogeneous, anisotropic, confined or unconfined and leaky aquifers. The model was applied to a representative 460 km<sup>2</sup> region of the Greater Toronto area. As shown by Figure 1, the area is bounded by a major urban river to the west, an urban catchment divide in the east, and by Lake Ontario and the Oak Ridges moraine to the south and north, respectively. Model data were supplied by 8000 water-well records, 800 of which were used to estimate variations in aquifer transmissivity. Static water levels from all 8000 records were used to generate the potentiometric surface and thereby permit model calibration.

To estimate contaminant travel times in the aquifer, a reverse particle tracking routine was invoked that, in effect, releases particles along the discharge boundary (i.e., terminal streams and Lake Ontario) and measures their rate of progress as they move upgradient along flow lines. By plotting travel times on each of the flow paths, isochrones can be drawn that represent lines of equal travel time to the discharge points.

The value of this approach is demonstrated by Figure 2, which shows isochrones calculated for the southern third of the modeled area. Chemically conservative contaminants released within a few kilometres of the rivers and Lake Ontario will discharge within a 5 yr period. Contaminants released more centrally will take more than 100 yr to leave the system. Assuming that road salt is distributed evenly within the area, an analysis of the cumulative area contained within each isochrone will indicate the time required for steady state to be achieved. For the study area in Figure 1, results are given in Figure 3. The data suggest that average chloride concentrations at discharge points will reach steady-state value within 200 yr of initial salt application.

### Analytical Solutions

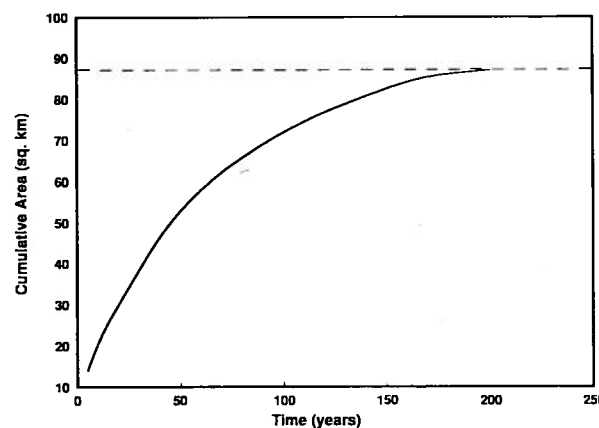
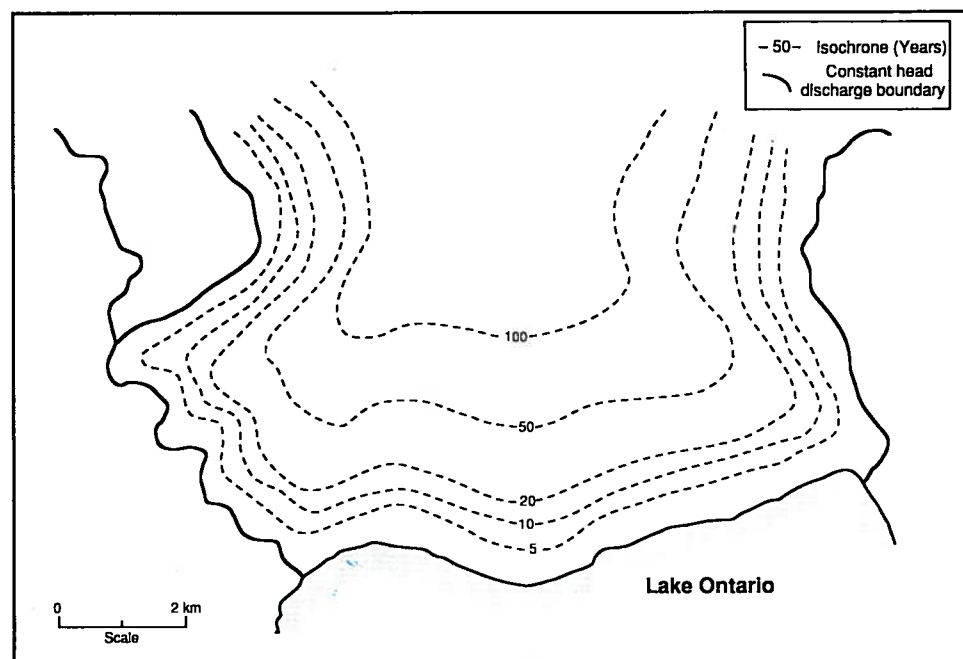
Although FLOWPATH offers a relatively quick and easy-to-use tool for estimating rates of ground-water quality degradation and stream contaminant loadings, it is less suitable for estimating contaminant concentrations within time and space. This type of problem can be approached in many ways, but the simplest and perhaps most useful involves the application of three-dimensional analytical solutions. In most cases, two solutions proved most valuable. The first is designed for single releases of a "slug" and models the transport of finite contaminant sources of dimension X, Y, Z, initial concentration C<sub>0</sub> instantly introduced into a steady-state, uniform flow field (flow in the x-direction). Modified after Taylor and Howard (1988), it takes the form:

$$C(x,y,z,t) = (C_0/8) \cdot \left[ \text{erf}\left[\frac{(x+X/2-vt)/2(a_xvt)^{0.5}}{2(a_xvt)^{0.5}}\right] - \text{erf}\left[\frac{(x-X/2-vt)/2(a_xvt)^{0.5}}{2(a_xvt)^{0.5}}\right] \right] \cdot \left[ \text{erf}\left[\frac{(y+Y/2)/2(a_yx)^{0.5}}{2(a_yx)^{0.5}}\right] - \text{erf}\left[\frac{(y-Y/2)/2(a_yx)^{0.5}}{2(a_yx)^{0.5}}\right] \right] \cdot \left[ \text{erf}\left[\frac{(z+Z/2)/2(a_zx)^{0.5}}{2(a_zx)^{0.5}}\right] - \text{erf}\left[\frac{(z-Z/2)/2(a_zx)^{0.5}}{2(a_zx)^{0.5}}\right] \right], \quad (2)$$

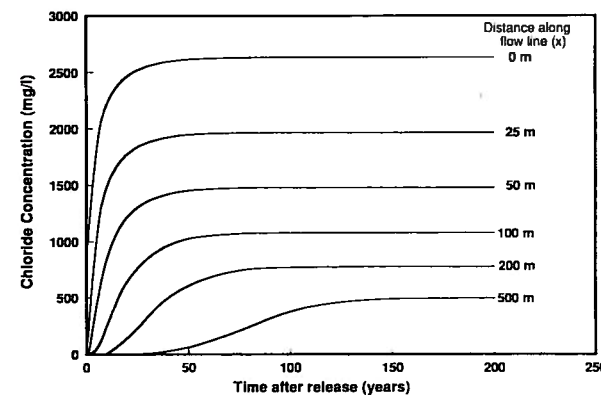
where: x, y, z are distances measured from the center of the source, a<sub>x</sub> is the dispersivity in the x direction, a<sub>y</sub> is the dispersivity in the y direction, a<sub>z</sub> is the dispersivity in the z direction, v is the contaminant velocity, and t is time. The other solution is for a source, concentration C<sub>0</sub> and dimensions Y by Z (in the y and z directions, respectively), introduced continuously into a one-dimensional steady-state flow field (flow in the x direction) (Domenico and Schwartz, 1990). In this solution, the continuous source is considered to approximate the situation where salt applied to a highway of length Y moves vertically downward to the water table and mixes with water moving in the aquifer to a depth of Z. The solution takes the form:

$$C(x,y,z,t) = (C_0/8) \cdot \text{erfc}\left[\frac{(x-vt)/2(a_xvt)^{0.5}}{2(a_xvt)^{0.5}}\right] \cdot \left[ \text{erf}\left[\frac{(y+Y/2)/2(a_yx)^{0.5}}{2(a_yx)^{0.5}}\right] - \text{erf}\left[\frac{(y-Y/2)/2(a_yx)^{0.5}}{2(a_yx)^{0.5}}\right] \right] \cdot \left[ \text{erf}\left[\frac{(z+Z/2)/2(a_zx)^{0.5}}{2(a_zx)^{0.5}}\right] - \text{erf}\left[\frac{(z-Z/2)/2(a_zx)^{0.5}}{2(a_zx)^{0.5}}\right] \right]. \quad (3)$$

**Figure 2.** Contaminant discharge isochrones for the southern third of the FLOWPATH study area. Isochrones are shown for chemically conservative parameters (retardation factor: 1).



**Figure 3.** Cumulative area curve for contaminant discharge isochrones, showing approximate time to steady-state conditions as predicted by FLOWPATH.



**Figure 4.** Variation of steady-state chloride concentration with time as a function of various distances along the flowline.

Whereas the finite source solution (equation 2) is most appropriate for single isolated releases of a chemical (e.g., the use of a snow-salt dump for one season), the continuous-source solution (equation 3) is more effective in situations where salt is applied over an extended period of time. If a series solution is used to calculate the error functions erf and erfc (Walton, 1989), both equations are easily programmed into spreadsheets such as LOTUS 123.

The benefits of the analytical solution spreadsheet approach are illustrated here by an example drawn from the downtown Toronto area. In this example, chloride is applied to a 300 m length of two-lane highway at a rate of 21.5 kg·m<sup>-1</sup>·yr<sup>-1</sup>. Almost half (45%) of the chloride is lost in surface runoff, and the remainder enters the subsurface beneath the road where it mixes with ground water to form a contaminant plume. The initial dimensions, initial concentration, and subsequent behavior of the plume are dictated by local aquifer conditions. In downtown Toronto the aquifer materials can be broadly classified as silty sands with a hydraulic conductivity of 6 x 10<sup>-6</sup> m/s and an effective porosity of 30%. Dispersivities in the x, y, and z directions are estimated to be 20 m, 1 m, and 0.1 m, respectively. The hydraulic gradient is 1%, and this results in an average linear flow velocity of 6.3 m/yr and an aquifer flux of 1.9 m<sup>3</sup>·m<sup>-2</sup>·yr<sup>-1</sup>. If it is assumed that ground water flows perpendicular to the highway, then the initial dimensions of the plume will be the length of the salted section (300 m) by the depth of mixing beneath the highway. The mixing depth (Z) is likely to be somewhere in the range 1 to 5 m. The greater the mixing depth, the lower the concentration at the source. For a mixing depth of 2 m used in the example, initial source concentration is 3120 mg/L. Although errors in the choice of mixing depth can generate errors in plume concentration close to the source, the effects become negligible at distances beyond approximately 20 Z (i.e., >40 m).

The results, shown in Figure 4, show how chloride concentrations at the top of the aquifer (z = 0 m) and in the center of the plume (y = 0 m) vary with time as a function of distance (x) along the ground-water flow line. Highest concentrations (1000-3000 mg/L) are within a few tens of metres of the highway, but thereafter fall rapidly due to dispersive processes. Steady state occurs within a very short time frame (<10 yr). More distant sites do not see the effects of salting for tens of years and are less seriously affected.

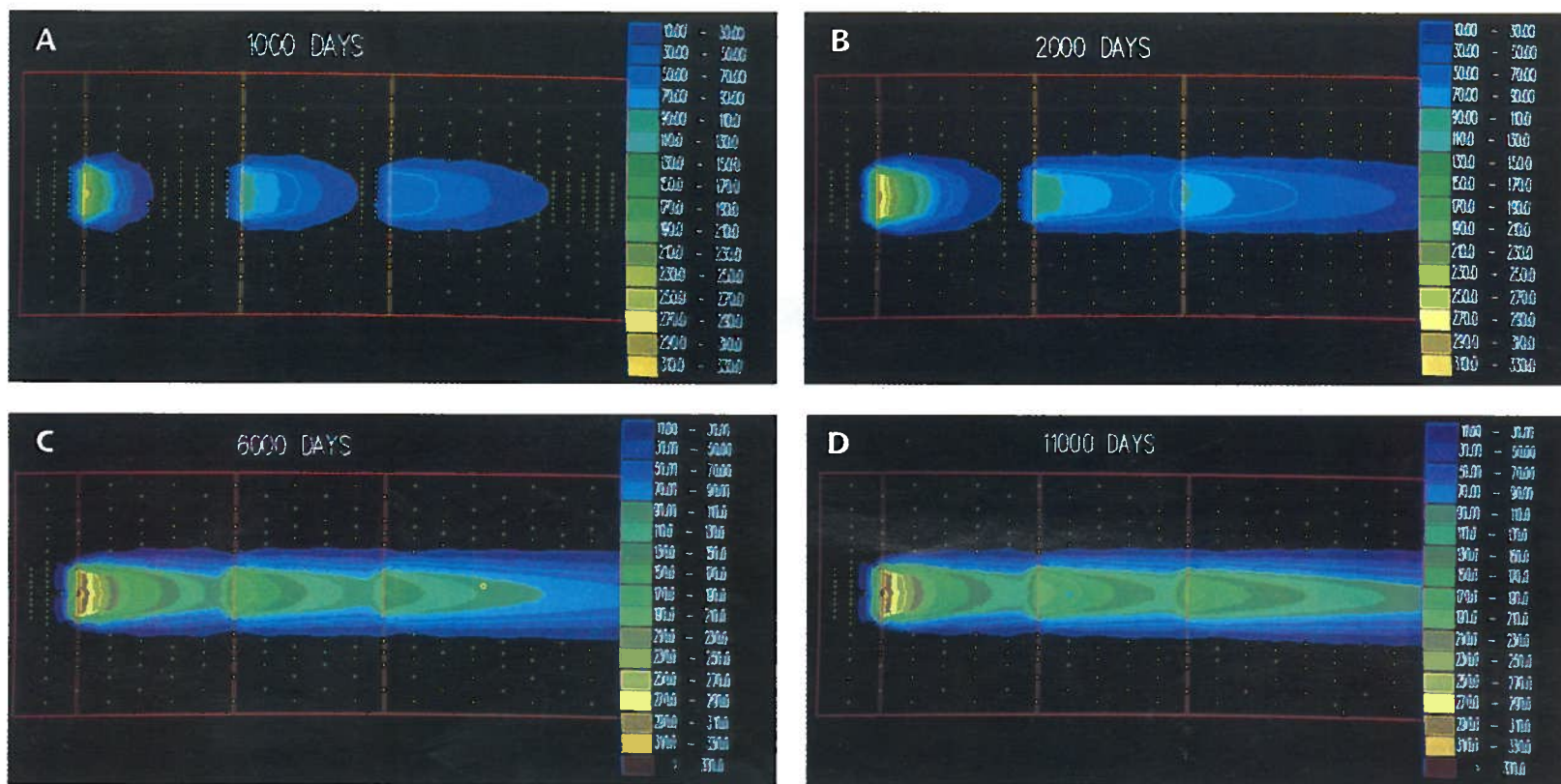
Furthermore, these sites may not reach steady state for 100 yr or more.

The spreadsheet analytical solutions are useful for providing quick answers to relatively simple problems. They are especially valuable for performing sensitivity analyses on the large number of input variables. Simplicity of approach, however, brings limitations, the most important of which include the assumptions of steady-state flow at constant velocity and of aquifer homogeneity. For example, changes in steady-state chloride concentration with distance seen in Figure 4 are almost entirely due to chemical dispersion, or "spreading" in a vertically downward direction. While this is likely to be the major mechanism for dilution at relatively short distances from the highway (typically <500 m) its importance will diminish at greater distances where the underlying aquitard will begin to impose a spreading boundary. At large distances, aquifer recharge can become the most important consideration. Recharge increases aquifer flow velocity and also dilutes the plume with uncontaminated water. To some extent these effects can be incorporated into the spreadsheet by modifying the transport equations. It is often more convenient, however, to approach such situations with finite element models such as AQUA.

### "AQUA"

The importance of recharge as a diluting mechanism for road salt was investigated using AQUA, a two-dimensional finite element model. This model can simulate ground-water flow and mass transport in heterogeneous and anisotropic, confined or unconfined aquifer systems under steady state and transient flow conditions. AQUA was used to simulate ground-water flow conditions in part of a small subcatchment in the Highland Creek basin. The model domain is a 2 km by 1 km rectangular area containing three 10-m-wide roadways. These are spaced at 500 m intervals and are oriented perpendicular to the direction of flow. Highland Creek is represented by a fixed head boundary; the ground-water divide and limiting flow lines are represented by no-flow boundaries. The aquifer is 5 m thick and is recharged everywhere at a rate of 160 mm/yr. The hydraulic conductivity averages 1.2 x 10<sup>-4</sup> m/s, and the effective porosity is approximately 30%.





**Figure 5.** AQUA simulation of chloride plume development, showing rates of migration away from salted roads. Contours range from 10 to 300 mg/L, with a contour interval of 20 mg/L.

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Figure 5 shows plume behavior when salt is applied to 220 m sections of each highway. Concentrations shown are average values over the depth of the aquifer. Highest chloride concentrations are always in the plume nearest the ground-water divide, where Darcy velocities are low and little water is available to dilute the infiltrating salt. At early times plume concentrations are relatively low, but they increase slowly with time as more salt is added to the system. Eventually, steady state is reached at which time salt inputs are balanced by salt output. This occurs after just 30 yr, a period shorter than indicated by FLOWPATH, but reasonable given the relatively small size of the modeled area. At steady state, concentrations of chloride within 200 m of the salted highway are typically two to three times the concentration observed in the discharging base flow.

## CONCLUSIONS

During the past 40 yr, highway departments in snow-belt regions of the world have come to recognize NaCl de-icing chemicals as the most convenient, cost-effective means of maintaining safe winter driving conditions. The environmental damage to vegetation, surface water, and ground water is commonly regarded as acceptable, given the benefits derived. Unfortunately, in "accepting" the observed environmental damage, the commonly held perception is that the system is in equilibrium, and the observed damage is as bad as it is likely to get under the present level of salt application. This is apparently not so. A salt budget determined in the Toronto area suggests that only 45% of the salt applied is being flushed into surface water bodies each year; its environmental damage is readily apparent. The remainder is entering shallow subsurface waters with the result that most will not reemerge for more than 50 yr. If present rates of salt application are maintained, chloride and sodium concentrations in ground waters discharging as stream base flow will eventually reach steady-state concentrations of >400 mg/L and >250 mg/L, respectively. These values represent a threefold increase over present average base-flow concentrations and exceed guidelines for drinking-water quality. The time to steady state will depend on local hydrogeological conditions, including the size of the catchment. Model studies indicate that steady state in the Toronto area may take 200 yr from the time of initial salting of the roads, by which time average concentrations of sodium and chloride in ground water will be similar to predicted base-flow concentrations. Locally, particularly within a few hundred metres of highways, concentrations three to four times the base-flow concentrations can be anticipated.

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