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# Groundwater Contamination Due To Road De-icing Chemicals — Salt Balance Implications

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#### Article abstract

Every year, roads and highways in Met-ropolitan Toronto receive more than 100,000 tonnes (t) of NaCI road de-icingchemicals. While much of this salt isflushed from the region every winterseason by overland flow, a proportion will enter the sub-surface and even-tually discharge to urban streams as baseflow. To determine annual reten-tion rates of de-icing salts in an urbanwatershed, a chloride mass balancehas been applied to the Highland Creekbasin, a typical urban catchment ineastern Metropolitan Toronto. The catchment has an area of 104 km2 and groundwater recharge is estimated to be 162 mm per year. Chloride input to the catchment was determined from unicipal records. These show that the catchment receives approximately 10,000 t of chloride annually, predomi-nantly in the form of NaCI de-icingchemicals which are applied to roads, highways and parking lots during the winter months. Chloride output was es-timated from stream flow and electrical conductivity measurements recorded at 15-minute intervals over a two-year period.

The balance reveals that only 45% of the salt applied to the catchment is being removed annually and that the remainder is entering temporary stor-age in shallow sub-surface waters. If present rates of salt application are maintained, it is predicted that average steady-state chloride concentrations in ground waters discharging as springs in the basin will reach an unacceptable 426  $\pm$  50 mg-L"1 possibly within a 20-year time frame. The value of 426mg-L-1 represents a three-fold increase over present average baseflow con-centrations, and is nearly twice the drinking water quality objective of 250mg»l\_-1 maximum acceptable concen-tration.

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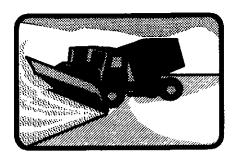


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# Articles



# URBAN GEOLOGY 3. Groundwater Contamination Due To Road De-icing Chemicals — Salt Balance Implications

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#### **ABSTRACT**

Every year, roads and highways in Metropolitan Toronto receive more than 100,000 tonnes (t) of NaCI road de-icing chemicals. While much of this salt is flushed from the region every winter season by overland flow, a proportion will enter the sub-surface and eventually discharge to urban streams as baseflow. To determine annual retention rates of de-icing salts in an urban watershed, a chloride mass balance has been applied to the Highland Creek basin, a typical urban catchment in eastern Metropolitan Toronto. The catchment has an area of 104 km² and groundwater recharge is estimated to

be 162 mm per year. Chloride input to the catchment was determined from municipal records. These show that the catchment receives approximately 10,000 t of chloride annually, predominantly in the form of NaCl de-icing chemicals which are applied to roads, highways and parking lots during the winter months. Chloride output was estimated from stream flow and electrical conductivity measurements recorded at 15-minute intervals over a two-year period.

The balance reveals that only 45% of the salt applied to the catchment is being removed annually and that the remainder is entering temporary storage in shallow sub-surface waters. If present rates of salt application are maintained, it is predicted that average steady-state chloride concentrations in ground waters discharging as springs in the basin will reach an unacceptable  $426 \pm 50 \text{ mg} \cdot \text{L}^{-1}$  possibly within a 20year time frame. The value of 426 mg•L-1 represents a three-fold increase over present average baseflow concentrations, and is nearly twice the drinking water quality objective of 250 mg•L-1 maximum acceptable concentration.

#### INTRODUCTION

During the past 40 years, residents living in the snowbelt regions of Europe, Canada and the United States have come to expect bare-pavement driving conditions throughout the winter. As a result, millions of tonnes of de-icing agents, usually in the form of sodium chloride (NaCl), have been applied to urban roads and highways. The general assumptions have been that the majority of the applied salt is flushed from the basin every season by rain and snowmelt, and environmental impacts are minimal. There is increasing evidence, however, that a significant proportion of the salt may be retained in the basin,

entering the shallow sub-surface and migrating gradually to the watertable (e.g., Diment et al., 1973; Eisen and Anderson, 1980; Pilon and Howard, 1987). In such cases, serious degradation of groundwater quality could be anticipated (Howard and Beck, in press). The scenario shows an ominous resemblance to the situation in the United Kingdom and other European countries (Howard, 1985) where nitrate, innocently applied as fertilizer during post-war years, migrated through the unsaturated zone at a rate of ~1 m per year and eventually caused extensive contamination of major aquifers. In the case of NaCl de-icing chemicals, the most common concern is an increase in salinity to levels which would make the water unsuitable for human consumption and some industrial applications. There is also evidence, however, that sodium, the counter ion to chloride in most road de-icing salts, may have serious health implications. The ion has been strongly linked with the development of hypertension, a condition affecting perhaps 20% of the United States population (Moses, 1980; Craun, 1984; Tuthill and Calabrese, 1979). Elevated sodium intake has also been associated indirectly with hypernatraemia (World Health Organization, 1984). It is generally recommended that sodium concentrations in drinking water should not exceed 20 mg·L-1 for patients with hypertension or congestive heart failure.

Concern for contamination by deicing salts is particularly acute in the Toronto region, where >100,000 t of NaCl are applied to urban roads and highways every year. Within Metropolitan Toronto, major streams regularly contain several hundred mg·L-1 chloride; in winter months, values greater than 1000 mg·L-1 are common. Recent records suggest that values of this order have shown little change in recent years

and, while these levels are unacceptably high, there has been little stream quality evidence to indicate that the situation will become any worse.

It was Paine (1979) who first suggested that road de-icing chemicals may be accumulating in the sub-surface and could one day re-appear to cause serious damage to urban waterways. Paine performed a relatively coarse chloride mass balance on the Don River watershed (Fig. 1) and suggested that as little as 50% of the applied chloride was being removed from the basin annually and that the remainder was being stored in the shallow sub-surface. Follow-up studies by Pilon and Howard (1987), Eyles and Howard (1988), and Taylor et al. (1991) confirmed that concentrations of chloride as high as 14,000 mg·L 1 were accumulating in shallow ground waters beneath Metropolitan Toronto, raising concern that the waters would ultimately enter local streams where serious and uncontrollable contamination would occur.

Recent and current studies at the University of Toronto have been concerned with the impact of urban development on groundwater quality and have focussed especially on the movement and behaviour of shallow ground waters containing elevated concentrations of chloride. An overall goal of the current work is to develop a series of numerical models that will permit the movement of de-icing salts in a catchment to be simulated and thereby allow the impact of alternative salting strategies to be evaluated. The success of these models depends, in turn, on an understanding of the nature of salt behaviour in a typical urban catchment, and, in particular, on an accurate knowledge of the rate at which salt is retained on an annual basis.

The retention rate of de-icing salts in a watershed is most reliably determined using a catchment mass balance approach. In this approach, salt input, represented by the mass of salt applied to the catchment during a specified time frame, is budgeted against salt output in the form of salt loads in the exiting stream. The net difference represents the mass of salt that is stored (retained) within the catchment.

In practice, the rates of salt retention will vary with time. At early times, the amount of salt entering the sub-surface will far exceed the amount leaving in baseflow. As time proceeds, salt con-

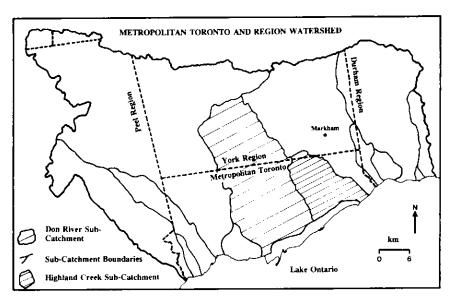


Figure 1 Fourteen sub-catchments of the Metropolitan Toronto and Region Watershed.

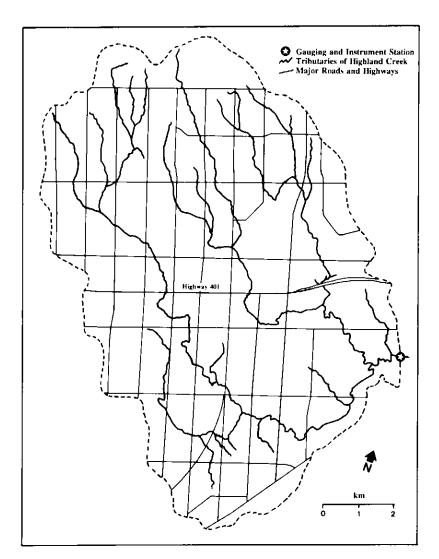


Figure 2 The Highland Creek basin showing distribution of major salted roads and highways. The basin is highly urbanized; minor salted roads (not shown) comprise 75% of the total length of salted roads and highways in the basin.

centrations in baseflow will increase and, on an annual basis, losses will start to approach the amounts entering the sub-surface. Steady state will be reached when the net rate of salt retention equals zero and the inflow of salt matches outflow. While a simple salt balance for a specific drainage system will allow the rate of salt retention to be determined for any one time period, corrections for baseflow contributions to the drainage system must be made if the annual rate of contribution of salt to the sub-surface is to be estimated.

The accuracy of the balance is determined by the quality, frequency and time frame of the data used. Previous studies, conducted in differing types of catchment, have produced figures for the amount of salt (chloride) retained annually, ranging from 19% to 65% (Wulkowicz and Saleem, 1974; Scott, 1980; Paine, 1979). Diment et al., (1973) showed that the amount retained can fluctuate each year, finding that unusually high summer rainfall in the second year of a two-year study resulted in much higher (20%) salt removal than seen in the first year. A criticism of much of the earlier work, however, is that the balances were conducted over a relatively short time (often one year or less) and/or used daily stream flow data. The latter is of particular concern in urban catchments, where stream flow rates and chemical concentrations can vary by three orders of magnitude within a

matter of hours. In the present study, conducted on Highland Creek from March 1989 to April 1991, this short-coming has been surmounted by installation of a data logger to collect the necessary data at 15-minute intervals.

#### STUDY AREA

The chloride mass balance study was performed on Highland Creek basin, one of 14 major sub-catchments in the Metropolitan Toronto and Region watershed (Fig. 1). Annual precipitation in this catchment is approximately 850 mm and Thornthwaite evapotranspiration is estimated to be 600 mm. The catchment has a total area of 104 km<sup>2</sup> and an Environment Canada gauging station is located 5 km upstream of its discharge into Lake Ontario. A review of storm sewer drainage areas and topographic data suggests that the catchment area upstream of the weir has an area of approximately 82 km<sup>2</sup>. This area was used for the mass balance calculations.

The basin is almost entirely urbanized (Fig. 2), with recreational open space along the main Creek valley and some remaining undeveloped land in the extreme northeast. The surface sediments are predominantly silty sand till (Karrow, 1967), but recent flood plain deposits occur extensively along the valley floor. The most important aquifers include the Scarborough Sands and the Lake Iroquois terrace deposits (Ontario Ministry of Natural Resources, 1980).

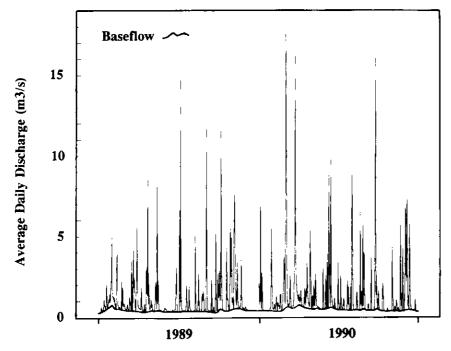


Figure 3 Highland Creek stream hydrograph for the period 1 January 1989 to 30 November 1990.

Locally these are separated by the Sunnybrook diamict. Total aquifer thickness is estimated to be 30 m and the water table depth varies up to 20 m. Groundwater flow velocities are thought to be in the range of 10-100 m per year.

The basin is crossed by Highway 401 (12 lanes wide), and by a grid of two- and four-lane arterial roads about 1.5-2 km apart. These arteries and numerous secondary roads are regularly salted throughout the winter season by five agencies: the Ontario Ministry of Transportation (MTO), Metropolitan Toronto, City of Scarborough, Town of Markham, and the Regional Municipality of York. The basin receives ~17,000 t of NaCl road de-icing chemicals each year. This represents approximately 200 g of NaCl for every square metre of the catchment.

Approximately two years of average daily stream flow data for Highland Creek are shown in Figure 3. Baseflow contributions vary between 0.3 m³•s-¹ and 1.2 m³•s-¹, peaking during the spring, and average 0.42 m³•s-¹ over the year. This represents an average annual recharge to the 82 km² catchment of 162 mm. If all of the applied salt were to enter the sub-surface *via* recharge, average steady-state sodium and chloride concentrations in ground water would approach 500 mg•L-¹ and 800 mg•L-¹, respectively.

#### INSTRUMENTATION

Because no reasonably priced, reliable and rugged chloride sensor was available, electrical conductivity, which is directly related to chloride concentration, was selected as a surrogate for monitoring in the field. Work began in July of 1988 when a YSI conductivity cell was installed at the Environment Canada weir to take advantage of the flow data which were already being collected at 15-minute intervals. Within days, the meter was damaged by a nearby lightning strike and the probe was buried in the stream bed. A second attempt to obtain data was made in March 1989. when an IC Controls temperature-compensated conductivity probe, model CC01, was installed near mid-stream at the weir. This probe is designed specifically for industrial applications, with both the sensor and sensor electronics sealed in PVC. The probe was connected by cable to a conductivity meter which was housed in the Environment Canada monitoring station, and provided a continuous output of electrical voltage as a measure of the conductivity. This output was recorded every 15 minutes by a Lakewood LE7110 data logger, which is capable of storing up to six months of data. When possible, data were retrieved from the data logger monthly using a laptop computer.

The probe sensors were cleaned every 3-4 weeks with a very fine abrasive. Algal growth that accumulates during the summer on the protective mesh around the probe tip was removed manually and appears to have had no effect on the probe function.

#### Calibration

The probe was initially calibrated and tested for drift in the laboratory using NaCl solutions of known conductivity. After installation in the creek, however, a consistent difference was observed between conductivity values calculated from the *in situ* conductivity readings and values measured from stream samples. This discrepancy is largely the result of monitoring in a flowing stream *versus* calibrating in static solutions. A small correction factor is now applied to the field measurements.

To permit conversion of measured electrical conductivity values to chloride concentration, samples of water were collected from the creek on a regular basis and analyzed for both parameters. As shown in Figure 4, the data correlate well. The best line fit is represented by a second order quadratic of the form:

CI concentration (mg•L  $^{1}$ ) = 0 0000025\*E $_{c}$ 2 + 0 31\*E $_{c}$  = 96 (1) where E $_{c}$  is the electrical conductivity in  $\mu$ S/cm at 25°C.

## CHLORIDE BALANCE CALCULATION

The chloride balance study was carried out from December 1988 to April 1991, inclusive, and included three winter seasons' salting. It was performed by estimating the total chloride input to the catchment over a pre-determined period and subtracting the amount of this chloride leaving the watershed during the same period by overland flow. The difference represents the mass of chloride retained, at least temporarily, in sur-

face waters, soils and subsurface waters. In the study, the amount of chloride leaving the basin through stream sediment load was assumed to be negligible. Corrections were made, however, to account for the mass of chloride leaving the basin as baseflow, since very little of this chloride would have originated from the previous salting season.

#### **Chloride Input Data**

Road salt is the major source of chloride entering the basin. It is applied as pure

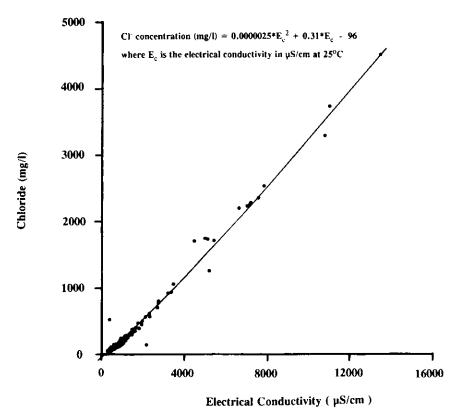


Figure 4 Relationship between chloride and electrical conductivity used for site calibration.

| Table 1           | Annual rates of NaCl application to the Highland Creek catchment. |                                      |                        |                       |                       |  |  |  |
|-------------------|---|--------------------------------------|------------------------|-----------------------|-----------------------|--|--|--|
|                   |   | CHLORIDE                             |                        |                       |                       |  |  |  |
| Salting<br>Season | Applied<br>to Roads/<br>Highways<br>(t)                           | Applied<br>to Parking<br>Lots<br>(t) | Domestic<br>Use<br>(t) | Basin<br>Total<br>(t) | Basin<br>Total<br>(t) |  |  |  |
| 1988-89           | 15.031  | 2104                                 | 150                    | 17,285                | 10,486                |  |  |  |
| 1989-90           | 16,095  | 2253                                 | 161                    | 18,510                | 11,228                |  |  |  |
| 1990-91           | 13,149  | 1841                                 | 131                    | 15,122                | 9,173                 |  |  |  |
| Annual<br>Average | 14,758  | 2066                                 | 147                    | 16,972                | 10,295                |  |  |  |

salt (NaCI) or as a salt/sand mixture. Daily salt application was determined from the yard records of the five agencies applying salt. Where salt/sanding routes straddled the catchment boundary, the total salt applied was apportioned to the catchments on the assumption that rates of application remained consistent along the routes. Total salt application in the study area

during the winters of 1988-89, 1989-90 and 1990-91 is shown in Table 1. The annual distribution of chloride application from 1 November 1989 to 30 April 1991 is shown in Figure 5. It is estimated that these figures are accurate to  $\pm 5\%$ .

Also included in Table 1 are estimates of other sources of chloride input. These include the amount of salt applied to parking lots, for which it was assumed

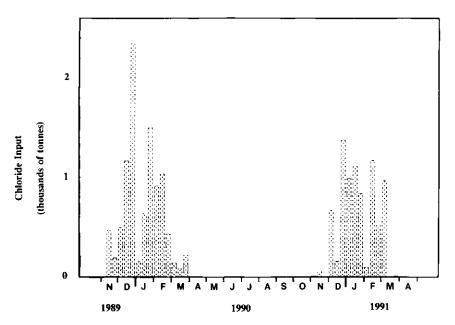
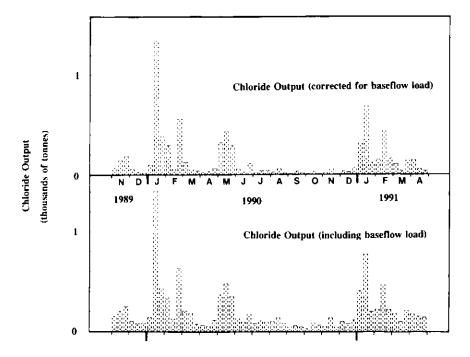


Figure 5 Temporal distribution of chloride input for the period 1 November 1989 to 30 April 1991. Data are plotted for periods ending on the tenth, twentieth and last day of each month.



**Figure 6** Temporal distribution of chloride output in Highland Creek for the period 1 November 1989 to 30 April 1991. Data are plotted for periods ending on the tenth, twentieth and last day of each month.

that rates of application for shopping centre lots were the same as those for major roads, and for other lots, one-half this rate (Scott, 1980). Salt applied to parking lots represented about 14% of the total salt applied. Application by private home-owners was estimated by multiplying the approximate number of single-family residences by an average annual rate of 4 kg/household. This represented <1% of the total salt application.

Other sources of chloride are relatively insignificant. Chloride concentration in precipitation around Metropolitan Toronto during 1986 averaged 0.2 mg•L-1 (Ontario Ministry of the Environment, 1988), which converts to ~0.1% of the total chloride input. A calcium chloride de-icing additive is used occasionally in the area, but contributes <0.1% of the total chloride input. There are no known sanitary-storm sewer interconnections in the basin (Scarborough Works; pers. comm.). Depending on their chemical formulation, fertilizers may contain a significant amount of chloride; however, this potential contribution is not thought to be significant and has not been quantified in this study.

#### **Chloride Output Data**

CI = Cm \* Q

Chloride discharge or "loading" in a stream can be calculated by:

terisk to indicate that some data were lost during the time period: data extra-

polation was required in those cases.

Also shown in Table 2 are estimates of the mass of chloride entering the stream as a result of baseflow. These were determined by multiplying the average baseflow for the time interval of interest by the estimated chloride concentration. Normally, this would be the chloride concentration in the stsream at a time, usually following several days of dry weather, when stream flows are maintained entirely by baseflow. Most of

the chloride contained in the baseflow is unlikely to have originated during the previous winter's salting, and instead represents chloride that has accumulated in the basin over its history of salting. As such, the baseflow contributions must be subtracted from the total chloride load to calculate the amount of chloride retained in the basin as a result of the previous winter's salting. A summary of the results is shown in Table 3.

### RESULTS AND CONCLUDING DISCUSSION

Urbanized catchments of the Metropolitan Toronto and Region watershed have, for several decades, received more than one hundred thousand tonnes of de-icing salts annually. For much of this time, it has been assumed that most of this salt is flushed from the catchments each season by overland flow and that sub-surface impacts are

minimal. However, recent evidence of elevated chloride in ground water beneath the catchments suggests that a significant proportion of the applied salt may be retained in the basin each season and may, therefore, be responsible for the observed degradation in groundwater quality.

The salt balance performed on the Highland Creek basin of Metropolitan Toronto has generated a large volume of

| lonth   | Period         | Input<br>(t)    | Baseflow<br>load<br>(t) | Output <sup>1</sup><br>(t) | Input<br>(t) | Baseflow<br>load<br>(t) | Output'<br>(t) | Input<br>(t) | Baseflow<br>load<br>(t) | Output¹<br>(t) |
|---------|----------------|-----------------|-------------------------|----------------------------|--------------|-------------------------|----------------|--------------|-------------------------|----------------|
|         |                | • • • • • • • • |                         |                            |              |                         |                |              |                         |                |
|         |                |                 | 1988                    |                            |              |                         |                |              |                         |                |
| Dec.    | 1-10           | 228 62          | -                       | -                          |              |                         |                |              |                         |                |
|         | 11-20          | 1802 65         | -                       | -                          |              |                         |                |              |                         |                |
|         | 21-31          | 973.62          | _                       | -                          |              |                         |                |              |                         |                |
|         |                |                 | 1989                    |                            |              | 1990                    |                |              | 1991                    |                |
| Jan.    | 1-10           | 1761 81         | -                       | -                          | 173.83       | 4725                    | 96.5 <b>4*</b> | 1136 75      | 94 05                   | 319 84         |
|         | 11-20          | 52617           | _                       | -                          | 728.48       | 47.25                   | 1359 52*       | 1276 50      | 94 50                   | 684.27         |
|         | 21-31          | 412 93          | -                       | -                          | 1725.53      | 4725                    | 38174*         | 962 56       | 90.00                   | 117 50         |
| Feb.    | 1-10           | 1031 09         | _                       | _                          | 1052.91      | 4725                    | 291 94"        | 111 95       | 81 00                   | 14793          |
|         | 11-20          | 239 59          | _                       | _                          | 1189 35      | 76.32                   | 51 33          | 134716       | 43 20                   | 429.98         |
|         | 21-28          | 1453 80         | _                       | -                          | 494.25       | 75 60                   | 558 13         | 59711        | 61 20                   | 166 43         |
| March   | 1-10           | 735 89          | _                       | _                          | 160 74       | 87.08                   | 123 51         | 1111 99      | 81 90                   | 103.40*        |
| Mar CI) | 11-20          | 1024 05         | 112 50                  | 810 70                     | 95 32        | 135 00                  | 49.88          | 0 67         | 70 20                   | 3709*          |
|         | 21-31          | 164 70          | 121 50                  | 588 53                     | 25177        | 44.55                   | 34 93          | 9 00         | 79 56                   | 134 65*        |
| Apr.    | 1-10           | 130 88          | 108.00                  | 112 21                     | 0 00         | 40.50                   | 24 70          | 0 00         | 40 50                   | 140.76*        |
|         | 11-20          | 0 00            | 99 00                   | 109 54                     | 0.00         | 26 64                   | 28.93          | 0 00         | 108.00                  | 51.73          |
|         | 21-30          | 0 00            | 45.00                   | 29 60                      | 0.00         | 54.00                   | 62 38          | 0 00         | 112 50                  | 36.11          |
|         | 1-10           | 0 00            | 61 20                   | 235.56                     | 0.00         | 51.75                   | 319 30         | _            | -                       | -              |
| May     | 11-20          | 0 00            | 76 50                   | 201.86                     | 0.00         | 56 25                   | 42758          | =            | =                       | _              |
|         | 21-31          | 0 00            | 45 90                   | 18765                      | 0.00         | 63.00                   | 289.23         | =            | =                       | -              |
|         | 1-10           | 0 00            | 45.00                   | 104 50*                    | 0.00         | 79.20                   | 56 15          | _            | -                       | _              |
| June    | 11-20          | 0 00            | 36 00                   | 92 94*                     | 0.00         | 75 26                   | 23.45          | -            | -                       | -              |
|         | 21-30          | 0 00            | 34 20                   | 47 23                      | 0.00         | 64.80                   | 110 19         | -            | -                       | -              |
|         |                |                 |                         | 49.14                      | 0.00         | 69.84                   | 14.00          | _            | -                       | _              |
| July    | 1-10           | 0 00            | 45 36                   | 49.14<br>18.70             | 0.00         | 73 80                   | 36 68          | _            | _                       | _              |
|         | 11-20<br>21-31 | 0 00<br>0 00    | 48 60<br>54 00          | 917*                       | 0.00         | 55.44                   | 38 98          | -            | -                       | =              |
|         |                |                 |                         |                            |              | 79.70                   | 22 13          | _            | _                       | _              |
| Aug.    | 1-10           | 0 00            | 63.00                   | 353 27*                    | 0.00         | 79.70<br>85.32          | 55 15          | _            | _                       | _              |
|         | 11-20          | 0.00            | 54.72                   | 174.85<br>87.81            | 0.00<br>0.00 | 72.00                   | 1196           | _            | _                       | -              |
|         | 21-31          | 0 00            | 51 98                   |                            |              |                         |                |              |                         |                |
| Sept.   | 1-10           | 0 00            | 51.84                   | 60.61                      | 0 00         | 38 93                   | 9 07           | _            | -                       | _              |
|         | 11-20          | 0.0             | 70.20                   | 14.62                      | 0.00         | 32.63                   | 27.76          | _            | _                       | _              |
|         | 21-30          | 0 00            | 36 99                   | 63.30                      | 0.00         | 35.10                   | 11 56          | -            | _                       | =              |
| Oct.    | 1-10           | 0.00            | 4725                    | 66.64                      | 0 00         | 31 86                   | 3 87           | -            | -                       | -              |
|         | 11-20          | 0 00            | 2700                    | 2 01                       | 0 00         | 60 75                   | 30 18          | _            | -                       | -              |
|         | 21-31          | 0 00            | 16.88                   | 1.14                       | 0.00         | 64 08                   | 5.49           | -            | -                       | -              |
| Nov.    | 1-10           | 0 00            | 86.76                   | 67.49                      | 10.89        | 43.88                   | 12.98          |              |                         |                |
|         | 11-20          | 534 28          | 6750                    | 138.83*                    | 70 76        | 88 20                   | 50 47          |              |                         |                |
|         | 21-30          | 217.00          | 67.50                   | 182.03*                    | 0.00         | 44.10                   | 3 51*          |              |                         |                |
| Dec.    | 1-10           | 571 04          | 54 00                   | 52.50                      | 773 43       | 70.56                   | 34.43*         |              |                         |                |
|         | 11.20          | 1340.71         | 60.75                   | 23.50                      | 181.72       | 61.74                   | 22 42*         |              |                         |                |
|         | 21-31          | 2,693.18        | 70 20                   | 14.60*                     | 1582 66      | 52.92                   | 67.85*         |              |                         |                |

Output has been corrected for baseflow load.

- Not determined.

\* Some data infilling required.

Notes:

|                      |   | (t)   | (t)  |   | (as % of salt applied during salt season)  | %   |  |
|----------------------|---|---|--|---|--|---|--|
| er (1 Nov30 April)   | 10,486  | 21372   | 486²   | 16512   | >152   | - 24  |  |
| mer (1 May-31 Oct.)  | NIL   | 2889  | 867  | 2022  | 19   | >34   |  |
| er (1 Nov.–30 April) | 11,228  | 4562  | 1135   | 3427  | 31   | 45  |  |
| mer (1 May-31 Oct.)  | NIL   | 2699  | 1089   | 1609  | 14   | 45  |  |
| er (1 Nov.–30 April) | 9173  | 3651  | 1318   | 2333  | 26   |   |  |
| mer (1 May-31 Oct.)  | NIL   | _   | -  | -   | -  | >26   |  |
|                      | mer (1 May-31 Oct.) er (1 Nov30 April) mer (1 May-31 Oct.) er (1 Nov30 April) mer (1 May-31 Oct.) ut has been corrected f | er (1 Nov30 April) 11,228 mer (1 May-31 Oct.) NIL er (1 Nov30 April) 9173 mer (1 May-31 Oct.) NIL | er (1 Nov.–30 April) 11,228 4562<br>mer (1 May–31 Oct.) NIL 2699<br>er (1 Nov.–30 April) 9173 3651 | er (1 Nov30 April) 11,228 4562 1135 mer (1 May-31 Oct.) NIL 2699 1089 er (1 Nov30 April) 9173 3651 1318 mer (1 May-31 Oct.) NIL | er (1 Nov.–30 April) 11,228 4562 1135 3427 mer (1 May–31 Oct.) NIL 2699 1089 1609 er (1 Nov.–30 April) 9173 3651 1318 2333 mer (1 May–31 Oct.) NIL – – – | er (1 Nov.–30 April) 11,228 4562 1135 3427 31 mer (1 May–31 Oct.) NIL 2699 1089 1609 14 er (1 Nov.–30 April) 9173 3651 1318 2333 26 mer (1 May–31 Oct.) NIL – – – |  |

reliable data. Most of the data gaps are due to the failure of flow logging instruments; these gaps were usually filled by correlation with data from neighbouring catchments. In total, a full chloride balance was completed for 26 months, extending over three salting seasons.

The results (Table 3) are consistent over the period of study. Each year, during the winter period (1 November to 30 April), approximately 10,000 t of chloride was applied to the Highland Creek catchment. Only 45% of this was removed by surface run-off before the following winter, when a new salting season began. Most of the chloride removed was flushed from the catchment during the winter in which it was applied. In the 1989-90 salting season, for example, 3427 t of chloride left the catchment by overland flow before the end of April, representing 31% of the total chloride applied. A further 1609 t (or 14% of the total) were removed by summer rain between 1 April and 30 October. Data are incomplete for the salting seasons 1988-89 and 1990-91, but the available results are comparable to those for 1989-90. For example, in 1990-91, 26% of the total chloride applied left the basin during the winter months; in 1988-89, 19% of the total chloride applied was removed during the summer.

If only 45% of the salt applied to the catchment is being removed annually, then the remainder is being stored, pre-

sumably in underlying ground waters. The rate of accumulation will depend on the rate of groundwater movement in the basin. While the total mass of chloride entering the sub-surface is greater than the mass of chloride leaving as baseflow to the stream, chloride will accumulate in the ground water, and groundwater chloride concentrations will increase. For the period of study, total input of chloride far exceeds output (including baseflow load) and significant accumulation occurs. Eventually, chloride in the ground water will reach a level at which annual baseflow losses will match the amount of chloride entering the sub-surface. At this stage, steady-state will be reached and no further deterioration of groundwater or stream water quality will occur. Numerical modelling will allow the rates of change of ground water and streamwater quality to be predicted with more certainty. Assuming an annual recharge of 162 mm, an aquifer thickness of 30 m, a specific yield of 20%, and groundwater flow velocities of 100 m per year, deployment of analytical transient solutions for the transport of contaminants from continuous line sources (Domenico and Schwartz, 1990) indicates that steady state concentrations could be achieved within 60 years of initial salt application, or approximately 20 years from the present.

When steady state is reached, inflow

and outflow of chloride will be in balance and the mass of chloride stored within the basin will remain unchanged. The stored chloride may not be evenly distributed within the sub-surface and water quality stratification will occur depending on the local groundwater flow regime. If conditions in the catchment remain the same and present rates of salt application are maintained, however, a simple division of the total chloride entering the sub-surface by the annual recharge reveals that average chloride concentrations in ground waters discharging as baseflow in the basin will reach 426 ± 50 mg·L-1. This value represents a three-fold increase over present average baseflow concentrations, and is nearly twice the drinking water quality objective of 250 mg·L-1 maximum acceptable concentration.

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