

# **Deicing Chemicals as Source of Constituents of Highway Runoff**

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# Deicing Chemicals as Source of Constituents of Highway Runoff

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The dissolved major and trace constituents of deicing chemicals as a source of constituents in highway runoff must be quantified for interpretive studies of highway runoff and its effects on surface water and groundwater. Dissolved constituents of the deicing chemicals—sodium chloride, calcium chloride, and premix (a mixture of sodium and calcium chloride)—were determined by analysis of salt solutions created in the laboratory and are presented as mass ratios to chloride. Deicing chemical samples studied are about 98 and 97 percent pure sodium chloride and calcium chloride, respectively; however, each has a distinct major and trace ion constituent signature. The greatest impurity in sodium chloride road salt samples was sulfate, followed by calcium, potassium, bromide, vanadium, magnesium, fluoride, and other constituents with a ratio to chloride of less than 0.0001 by mass. The greatest impurity in the calcium chloride road salt samples was sodium, followed by potassium, sulfate, bromide, silica, fluoride, strontium, magnesium, and other constituents with a ratio to chloride of less than 0.0001 by mass. Major constituents of deicing chemicals in highway runoff may account for a substantial source of annual chemical loads. Comparison of estimated annual loads and first flush concentrations of deicing chemical constituents in highway runoff with those reported in the literature indicate that although deicing chemicals are not a primary source of trace constituents, they are not a trivial source, either. Therefore, deicing chemicals should be considered as a source of many major and trace constituents in highway and urban runoff.

The primary constituents of deicing chemicals and their effect on the water quality of highway runoff and receiving waters is well documented (1–8). Deicing chemicals are a substantial source of constituents in highway runoff, accounting for 67 percent of the chemical constituents washed off the road surface as described in a highway runoff study in North Carolina (9). In Massachusetts, 223 million kg of road salt applied to roads maintained by the state each year accounts for 63 percent of the variation of sodium concentrations measured in streams (8). Although many studies examined the occurrence of deicing chemicals and the effects of sodium, calcium, and chloride on the environment (1–8), the other major and trace constituents of deicing chemicals in highway runoff are not commonly known or are not widely reported (10–12). Also, relatively few data are available on the major and trace constituents of deicing chemicals (11,13–16).

Knowledge of the major and trace constituents of deicing chemicals can facilitate the interpretation of highway runoff data. Loads of each constituent in highway runoff, in surface water bodies, in an aquifer, or from an entire drainage basin may be estimated from salt application data using chloride ratios. Chloride ratios for each constituent can be used to indicate the origin of loads and concentrations in highway runoff between deicing chemicals and other possible sources. Constituent concentrations can be estimated using chloride ratios and chloride analyses, ion-specific chloride probes,

or estimation of chloride concentrations from specific conductance data (7).

Ion ratios are an accepted method to examine water quality analyses (17). Mass ratios to chloride are useful in road salt studies for the following reasons:

- Chloride is considered to be one of the best chemical tracers because it is nonreactive and has low retardation rates in many surface- and groundwater environments (17,18).
- When deicing chemical contamination is detected and deicing chemical-application data (or loss data in the case of salt storage areas) are not available, then the total salt load can be estimated from chloride concentrations in affected waters (6,19,20).
- Partitioning of deicing chemical loads to surface and groundwaters from highway runoff can be inferred from chloride concentrations in receiving waters (7,9,10,12,21).
- Molar or equivalent ratios are easily attained from mass ratios to chloride.
- Chloride ratios can be converted easily to deicing chemical ratios by dimensional analysis.

Chloride ratios can be used to indicate the source of salt contamination in freshwater supplies. Soils, sediments, and bedrock in local areas, oceanic aerosols, continental brines, oil or gas field brines, and effluent from septic tanks, industry, and wastewater-treatment plants all contain many of the major and trace constituents of deicing chemicals and may contaminate local waters with these constituents (6,18). However, each source has a unique chemical signature. As highway runoff migrates through the environment, changes in the chloride ratios of each constituent may indicate chemical reactions that should be considered when interpreting chemical analyses of water samples (12,21).

Several researchers used chloride ratios to determine the source of salt contamination in fresh groundwater supplies. Shanley used salt application records and the ratio of major ions to chloride to determine that salt applications increased solute flux in a basin in central Massachusetts by 120 percent (21). Snow et al. used the ratios of bromide and sulfate to chloride to distinguish between ancient seawater trapped in bedrock fissures, modern seawater intrusion, and road salt contamination (20). Howard and Beck used the ratios of iodide to chloride and of fluoride to chloride to differentiate between deicing chemicals and saline bedrock water (11). Knuth et al. used the ratio of bromide to chloride to determine that improperly discharged formation brines from the drilling of a natural gas well were the source of salt contamination in an unconfined aquifer rather than deicing chemicals or naturally saline groundwater (19).

As highway runoff migrates through the environment, ion exchange and other chemical reactions can alter the ratio of each constituent to chloride. Kunkle identified changes in the relative

concentrations of several cations to chloride in a Vermont stream affected by highway runoff (2). Shanley used chloride ratios and ratios of sodium to silica to indicate ion exchange of sodium for calcium and magnesium in a Massachusetts drainage basin (21). Granato, et al. used chloride ratios to indicate that ion exchange and other effects may increase the mobility of the highway constituents in groundwater and can alter the ionic composition of the water (12). Therefore, the ratios presented may be indicative of the input of ions from the deicing chemicals used, but they must be adjusted to reflect dissolution in local precipitation, mixing with local waters, or geochemical reactions.

## PURPOSE AND SCOPE

The purpose of this paper is to demonstrate that deicing chemicals are a substantial source of dissolved major and trace constituents in highway runoff. In addition, mass loading and concentrations of deicing chemical constituents in relation to other sources of constituents in highway runoff are also discussed briefly. The deicing chemicals examined were sodium chloride road salt (SCRS), calcium chloride road salt (CCRS), and premix. Premix is a mixture by weight of 20 or 40 percent CCRS and 80 or 60 percent SCRS, respectively (J. Marquart, Akzo Salt, unpublished data). Samples of SCRS and premix were obtained from a Massachusetts Highway Department (MHD) road maintenance facility for 1990–1995 soon after deicing chemicals were delivered each year. However, these annual samples are not presumed to define the deicing chemicals used throughout Massachusetts, or in any particular year. The constituents of the deicing chemicals are presented as mass ratios to chloride. Laboratory and field data from this study, as well as examples from the literature, are intended to examine deicing chemicals as a substantial source of dissolved major and trace constituents in highway runoff.

## METHODS

MHD deicing chemical application records for 1990–1995 were used to indicate the mass loading of constituents from deicing chemicals. SCRS samples for these years may be considered as typical of New York rock salts (J. Marquart, Akzo Salt, unpublished data). CCRS is applied as a component of premix that is used to improve the performance of the deicers at low temperatures. The CCRS in premix used by MHD is produced from Michigan brines (J. Gall, Dow Chemical, unpublished data).

Samples of deicing chemicals were collected by compositing 6 to 10 smaller samples taken from different places in the enclosed deicing chemical pile soon after the first deicing chemical delivery of each year. The sampling and experimental program used to determine the constituents of deicing chemicals as constituents of highway runoff was designed to minimize contamination of the deicing chemical samples. The collection, storage, and dilution of deicing chemical samples were done using materials and methods designed to avoid contamination of the samples or solutions during processing prior to analysis.

The collected deicing chemicals were added to deionized water and the solutions analyzed to determine the water-soluble major and trace constituents available for dissolution in highway runoff. Samples of SCRS, CCRS, and premix were dissolved in deionized water to form solutions of about 10, 1, 0.5, and 0.001 percent salt for analy-

sis. The 10 and 0.001 percent solutions were analyzed for major constituents, and the 1 and 0.5 percent solutions were analyzed for major and trace constituents. Aqueous samples were analyzed at the U.S. Geological Survey's (USGS's) National Water Quality Laboratory (NWQL) in Arvada, Colorado, and in the USGS research laboratory in Reston, Virginia, following standard procedures (22). One sample of the dilution water was sent to the NWQL for major and trace ion analysis after processing with the labware to provide quality control. This deionized water sample had negligible concentrations of constituents examined, indicating that neither the dilution water nor the laboratory processing introduced contaminants.

Each constituent of the deicing chemicals examined is presented as a mass ratio of that constituent to chloride in aqueous solution. The chloride mass ratios are the quotient of the concentration in milligrams per liter of each constituent divided by the concentration of chloride in milligrams per liter. Resultant ratios are unitless and may be applied to any units except for those based on moles or equivalents. The use of chloride ratios requires the assumption that the concentration of each constituent is directly proportional to the amount of deicing chemicals and, therefore, the concentration of chloride in solution.

The maximum, minimum, and median ratios of each constituent consistently detected in the deicing chemicals examined are presented graphically. However, the minimum ratio does not reflect ratios for constituents diluted to less than detection limits in the 0.5 or 0.001 percent solutions. Instead, the range and median are presented with the number of detections and trials for each constituent. One sample of SCRS was collected each year during 1990–1995; two samples of premix were collected during 1990–1995. At least two water quality samples were analyzed from each deicing chemical sample. Constituents that were consistently less than detection limits are reported with the minimum chloride ratio of the detection limit, the number of trials without detections, and the total number of trials (Table 1). Barium, cobalt, lithium, and zinc were detected

**TABLE 1 Detection Limits Expressed as Mass Ratio to Chloride for Constituents of Sodium Chloride, Calcium Chloride, and Premix in Deionized Water Solution Not Consistently Detected**

Constituent	Mass ratio of detection limit (mg/L per mg/L Cl)	Number of Tests without detection: total number of tests
- Trace cations -		
Arsenic	$<2.2 \times 10^{-7}$	12:12
Barium*	$<2.2 \times 10^{-6}$	13:15
Beryllium	$<2.2 \times 10^{-6}$	12:12
Cadmium	$<2.2 \times 10^{-7}$	12:12
Chromium <sup>b</sup>	$<6.5 \times 10^{-7}$	8:12
Cobalt*	$<2.2 \times 10^{-7}$	11:12
Lithium*	$<2.2 \times 10^{-6}$	23:26
Manganese*	$<2.2 \times 10^{-6}$	6:8
Molybdenum	$<1.1 \times 10^{-6}$	12:12
Silver	$<2.2 \times 10^{-7}$	12:12
Zinc*	$<2.2 \times 10^{-6}$	10:12
- Trace anions -		
Antimony	$<2.2 \times 10^{-7}$	12:12
Cyanide, Total	$<2.2 \times 10^{-6}$	12:12
Selenium	$<2.2 \times 10^{-7}$	12:12

\*Constituent was detected in lower concentration sample but not in higher concentration sample(s).

<sup>b</sup>Detected in calcium chloride and premix, but not sodium chloride.

in the more dilute solutions but were not detected in the more concentrated solutions; therefore, they are reported as not being consistently detected (Table 1).

## DEICING CHEMICALS

### Sodium Chloride Road Salt

The ratio of many major and trace constituents of sodium chloride varies from year to year (Figure 1). Considerable variation in the quantities of each constituent are expected from salt samples within a natural salt deposit (14,15). Also, the inherent variability of laboratory analysis is compounded by the use of ratios, the quotient of two variable numbers. The variability of chloride determinations is from 3 to 5 percent (22). The variability of analyses for other major ions is from 3 to 12 percent and may be as much as 50 to 100 percent for analyses of trace ions when concentrations are near detection limits (micrograms per liter) (22). However, the median of each constituent reported may be considered as characteristic of these deicing chemicals because the analyses of SCRS, CCRS, and premix were done repetitively for samples from different years. The numbers of total detections and trials for SCRS are shown along the abscissa in Figure 1.

Summation of median values presented in Figure 1 indicates that the SCRS samples are about 98 percent pure sodium chloride. Therefore, these samples meet the standard ASTM D632-94, which specifies that SCRS must be a minimum of 95 percent pure sodium chlo-

ride. The greatest impurity in sodium chloride is sulfate, followed by calcium, potassium, bromide, vanadium, magnesium, fluoride, and other constituents with ratios to chloride less than 0.0001 by mass.

One constituent of SCRS used by the MHD but not detected in any of 12 trials (Table 1) is total cyanide (as ferric ferrocyanide or sodium ferrocyanide). Ferric ferrocyanide and sodium ferrocyanide are commonly cited anticake compounds for road salt (9). However, the strong chemical bonds between the cyanide groups and iron in both compounds (17) create relatively stable complexes and reduce toxicity in solution (23). MHD uses about 100 mg of yellow prussiate of soda (sodium ferrocyanide) per kilogram of deicing chemical (S. Pollock, MHD, unpublished data). A commonly specified concentration for use of sodium ferrocyanide is 100 mg/kg or 100 ppm (B. Bertram, Salt Institute, unpublished data). This quantity of hydrated sodium ferrocyanide should theoretically yield a mass ratio of  $5.3 \times 10^{-5}$ , which is well above the reported detection limit of  $2.2 \times 10^{-6}$  (Table 1). The discrepancy between estimated and measured values may be due to the dissociation of cyanide complexes by photolysis and off-gassing of hydrogen-sulfide gas in the clear, well-stirred laboratory solutions (B. Bertram, Salt Institute, unpublished data).

### Calcium Chloride Road Salt and Premix

Although calcium chloride is used only as a component of premix, it was analyzed separately to identify it as an independent source of constituents (Figure 2). The numbers of total detections and trials for

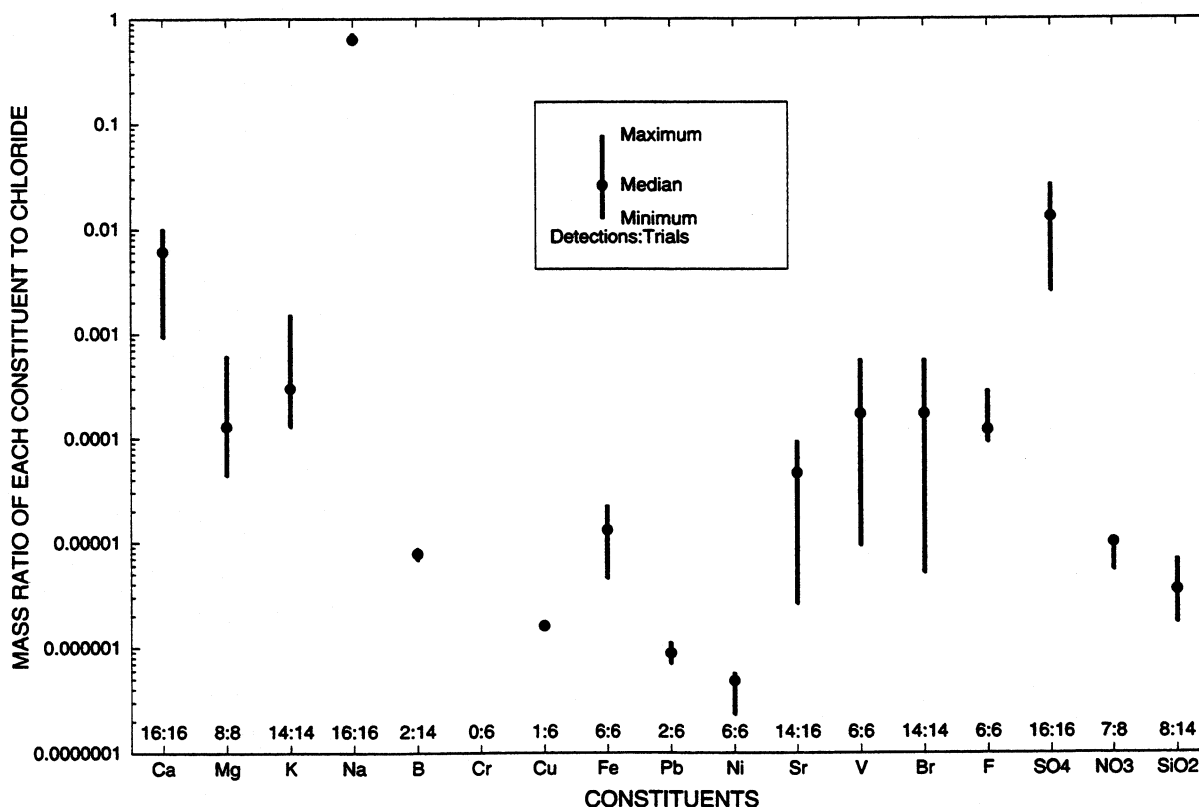


FIGURE 1 Range of and median mass ratios to chloride of major and trace constituents of deicing chemical sodium chloride.

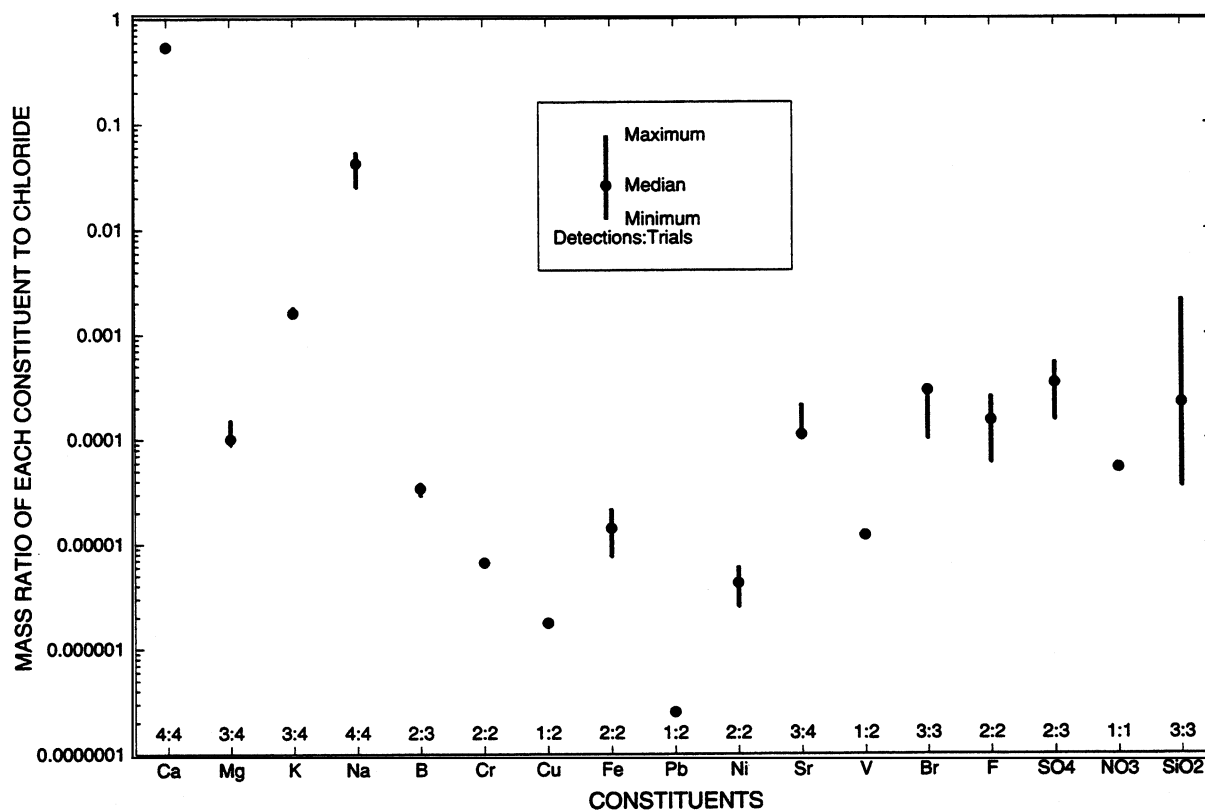


FIGURE 2 Range of and median mass ratios to chloride of major and trace constituents of deicing chemical calcium chloride.

CCRS are shown along the abscissa in Figure 2. CCRS samples contain the same constituents as SCRS with the exception of chromium, which was less than the detection limit in the SCRS samples. Also, the ratios of many of the CCRS constituents were consistently different from the SCRS. Therefore, CCRS is not an independent source of constituents, but it does alter the chemical signature of deicing chemicals applied when it is used in premix. The differences in proportions of minor constituents between SCRS and CCRS may result from geological origin, industrial processing, or both.

The summation of median values presented in Figure 2 indicates that the CCRS samples are about 97 percent pure calcium chloride. Therefore, these samples meet ASTM D98-93, which specifies that CCRS must be at a minimum 90 percent pure calcium chloride. The greatest impurity in the calcium chloride is sodium, followed by potassium, sulfate, bromide, silica, fluoride, strontium, magnesium, and the other constituents with ratios to chloride less than 0.0001 by mass.

Median chloride ratios of the constituents of all the deicing chemicals tested (SCRS, CCRS, and premix) indicate that the composition of the premix samples can be derived by partitioning the constituents of component salts (Figure 3). Ratios for premix were determined by analyzing three separate samples from a mixture of 80 percent SCRS and 20 percent CCRS obtained during the winter of 1990-1991, and three separate samples from a mixture of 60 percent SCRS and 40 percent CCRS obtained during the winter of 1992-1993. The ratio of each constituent of the premix samples generally was between the median ratio for the sodium and calcium chloride salts. Exceptions occur in the minor constituents, probably

because of the greater variability typical for determinations near the detection limits of these constituents. Other exceptions—for example, in magnesium and sulfate ratios—may be an artifact of statistical differences caused by different number of samples for SCRS, CCRS, and premix (which had three independent trials for each mixture), or because the available premix samples do not span the 1990-1995 period.

#### Results of Current Study Compared with Available Literature

A comparison of the constituents of SCRS with values reported for SCRS in the literature (9,10,11,13,15,19,21,24) highlights several points (Figure 4). To date, all the major and trace constituents of SCRS have not been quantified in any specific study. The ratios of the major constituents—sodium, calcium, magnesium, sulfate, and bromide—are relatively consistent between this study and ratios derived from the literature. However, the current study indicates minor and trace constituent ratios that generally are less than ratios indicated by the literature. The differences in ratios between the current study and the available literature may be caused by differences in geologic origin of the deicing chemicals or improvements in chemical sampling and analytical techniques during the period of record.

Available literature does not quantitatively specify the concentrations of major and trace constituents of road salt solutions. Runnels et al. indicate the major and trace constituents of rock salt from Kansas (13). By dissolving rock salt in deionized water and filtering

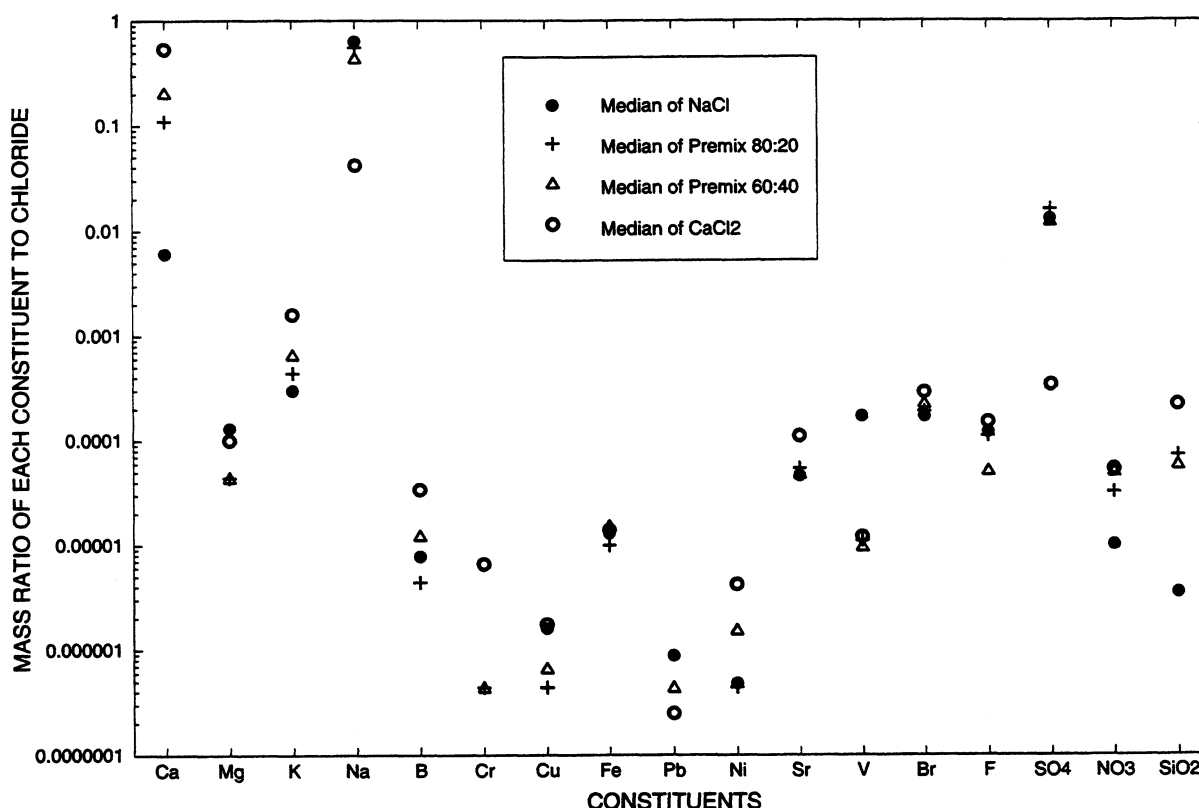


FIGURE 3 Median mass ratios to chloride of major and trace constituents of deicing chemicals sodium chloride, calcium chloride, premix 80:20 (a mixture by mass of 80 and 20 percent sodium and calcium chloride, respectively), and premix 60:40 (a mixture by mass of 60 and 40 percent sodium and calcium chloride, respectively).

out residue, Bloomberg and Ladenburg provide qualitative data on detecting trace elements, both soluble and insoluble, from a wide variety of salt sources (14). Kaufmann quantitatively examines the major constituents of many brines and rock salts but does not include trace constituents (15). Oberts compared the concentrations of a few elements in aqueous solutions containing mixtures of sand and salt, but because the sand was of local origin and was not analyzed separately, results of this study cannot be applied widely (16). Howard and Beck analyzed samples of road deicing chemicals for major and trace constituents (11) but did not find many of the trace constituents detected by Runnels et al. (13), Bloomberg and Ladenburg (14), or the current study. In Howard and Beck's study, dilute solutions (about 30 mg/L chloride, a 0.005 percent solution) were analyzed because of instrument limitations (11). Therefore, it may be hypothesized that the samples used for trace ion analyses were diluted beyond the detection limits for some constituents. However, Howard and Beck detected aluminum, iodide, and barium in their samples. Chloride ratios in SCRS were about  $5.6 \times 10^{-3}$ ,  $6.4 \times 10^{-7}$ , and  $3.7 \times 10^{-4}$  for aluminum, iodide, and barium, respectively, and chloride ratios in CCRS were about  $3.6 \times 10^{-3}$ ,  $2.7 \times 10^{-6}$ , and  $1.9 \times 10^{-4}$  for aluminum, iodide, and barium, respectively (11). Howard and Beck also tested for but did not detect phosphorus.

#### Deicing Chemicals as Constituents of Highway Runoff

A comparison of annual loads of deicing chemical constituents derived from MHD deicing chemical application records in the

study area (7) and annual loads reported in a review of highway runoff literature (25) are given in Table 2. The median ratios of each constituent to chloride in SCRS (which comprises about 95 percent of the deicing chemicals spread in the study area) are used to estimate an annual load for each constituent from the salt application records. Annual mass loading of deicing chemicals in the study area (12) varies by a factor of four because of differences in freezing conditions and snowfall from year to year during 1990–1995. Although deicing chemicals are not a primary source of trace metals, they are not necessarily a trivial source in comparison with other reported sources of highway runoff constituents (25). The relatively low sodium and chloride loads reported in this survey of the literature (25) indicate that representative data for the winter months may not be included. The maximum percentage of reported loads in highway runoff ranged from 2 percent for iron to 40 percent for copper (Table 2). Therefore, deicing chemicals should be considered as a substantial source of many major and trace constituents in highway and urban runoff. However, deicing chemicals are only one of many sources of constituents in highway runoff.

Chloride mass ratios of highway runoff constituents in samples taken during several winter storms during the current study also indicate that deicing chemicals are not a trivial source of many constituents in highway runoff (Figure 5). Samples of highway runoff were collected for analysis of major and trace constituents on March 24, 1993, during a storm when SCRS was applied to the highway. Highway runoff samples analyzed for major constituents

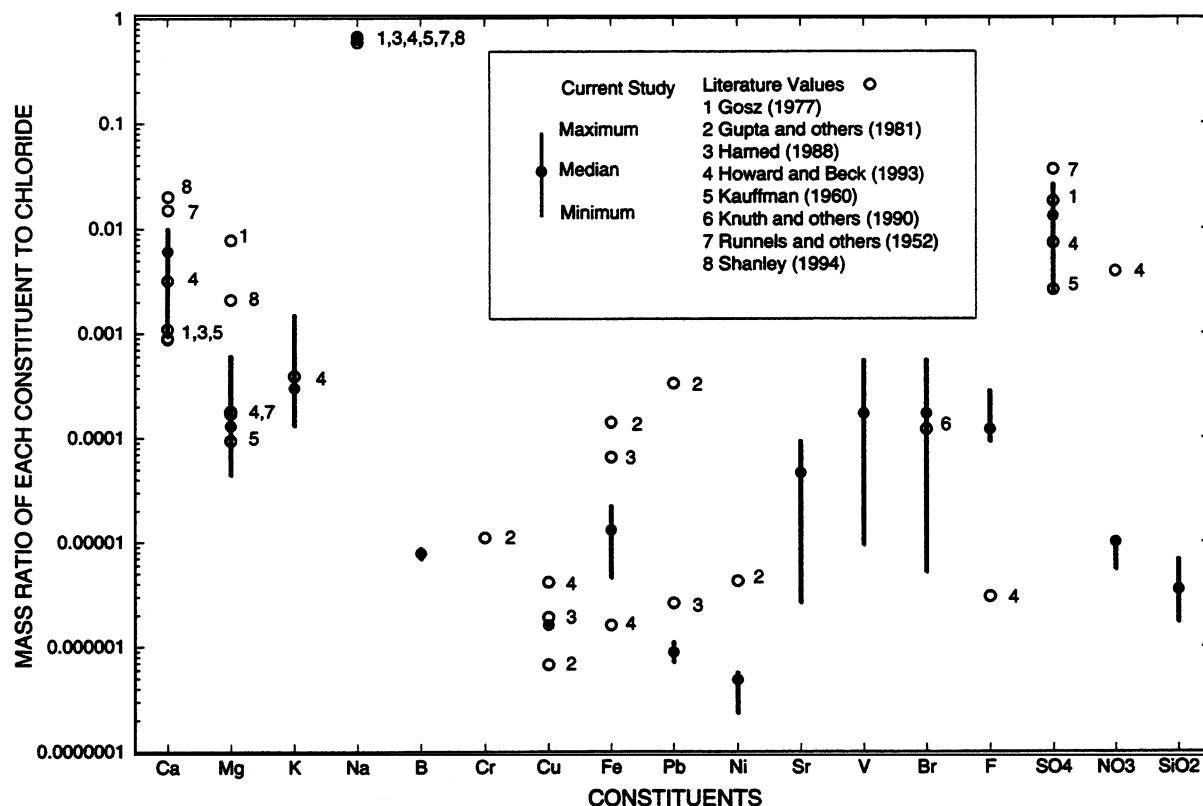


FIGURE 4 Comparison of range of and median mass ratios to chloride of constituents of deicing chemical sodium chloride to values reported in literature.

TABLE 2 Annual Loads of Deicing Chemical Constituents Estimated Using MHD Deicing Chemical Application Records in Study Area (1990–1995) and Median Ratios from SCRS as Compared with Values Reported in Review of Highway Runoff Literature (25)

Constituent of deicing material <sup>a</sup>	The Current Study			Maximum percentage <sup>b</sup> load	Range of loads in literature (kg/ha/yr)
	Minimum load (kg/ha/yr)	Median load	Maximum load		
Total <sup>c</sup>	$3.7 \times 10^3$	$6.9 \times 10^3$	$1.3 \times 10^4$	— <sup>d</sup>	—
Chloride	$2.2 \times 10^3$	$4.1 \times 10^3$	$7.6 \times 10^3$	—	4.63 - 1,344
Calcium	$1.4 \times 10^1$	$2.5 \times 10^1$	$4.6 \times 10^1$	—	—
Magnesium	$2.9 \times 10^1$	$5.4 \times 10^1$	$9.8 \times 10^1$	—	—
Sodium	$1.4 \times 10^3$	$2.7 \times 10^3$	$4.9 \times 10^3$	—	1.95
Potassium	$6.7 \times 10^1$	$1.2 \times 10^2$	$2.3 \times 10^2$	—	—
Sulfate	$2.9 \times 10^1$	$5.4 \times 10^1$	$9.8 \times 10^1$	—	—
Fluoride	$2.7 \times 10^1$	$5.0 \times 10^1$	$9.1 \times 10^1$	—	—
Silica	$7.8 \times 10^3$	$1.5 \times 10^2$	$2.6 \times 10^2$	—	—
Boron	$1.7 \times 10^2$	$3.2 \times 10^2$	$5.9 \times 10^2$	—	—
Chromium <sup>e</sup>	$9.8 \times 10^4$	$1.8 \times 10^3$	$3.3 \times 10^3$	28	0.012 - 0.1
Copper	$3.6 \times 10^3$	$6.6 \times 10^3$	$1.2 \times 10^2$	40	0.03 - 4.7
Iron	$2.9 \times 10^2$	$5.4 \times 10^2$	$9.8 \times 10^2$	2	4.37 - 28.8
Lead	$2.0 \times 10^3$	$3.6 \times 10^3$	$6.7 \times 10^3$	8	0.08 - 21.2
Nickel	$1.1 \times 10^3$	$2.0 \times 10^3$	$3.6 \times 10^3$	5	0.07
Strontium	$1.0 \times 10^1$	$1.9 \times 10^1$	$3.5 \times 10^1$	—	—
Vanadium	$3.8 \times 10^2$	$7.0 \times 10^2$	$1.3 \times 10^1$	—	—
Bromide	$3.8 \times 10^2$	$7.0 \times 10^2$	$1.3 \times 10^1$	—	—
Nitrate	$2.2 \times 10^2$	$4.1 \times 10^2$	$7.6 \times 10^2$	9	0.80 - 8.0

<sup>a</sup>Sodium chloride road salt ratios represent 95 percent of deicing chemicals applied at the test site.

<sup>b</sup>Estimated by quotient of the maximum salt constituent load and the minimum load reported in the literature for each constituent. The maximum is reported because the minimum load is always conceivably zero.

<sup>c</sup>The total of the deicing materials sodium chloride and premix.

<sup>d</sup>Constituent not defined by Barrett and others, (1993).

<sup>e</sup>Calculated from the ratio in premix.

were collected on January 12 and February 23, 1995, during storms when SCRS was applied and on February 28, 1995, during a storm when SCRS and premix were applied to the highway. Sodium, boron, strontium, vanadium, bromide, and sulfate ratios in highway runoff were similar to the ratios in the laboratory dilution. However, calcium, magnesium, potassium, iron, fluoride, nitrate, and silica were enriched with respect to ratios from the laboratory dilution. Although many of these constituents are not associated with vehicular traffic, enrichment of these constituents is to be expected because precipitation, pavement surfaces, and even materials used in the construction of drainage and detention facilities contribute constituents to stormwater runoff (12,21,26). The enriched iron and nitrate are considered common chemical constituents of highway runoff (9). Chromium, nickel, copper, and lead—which also are considered constituents of highway runoff (9,24,25) as well as constituents of deicing chemicals—were not detected in the major and trace constituent analyses (Figure 5). However, the detection limits reported in these highway runoff analyses were higher than the concentrations expected from the chloride ratios of the deicing chemicals. Cadmium and manganese were detected at a constant ratio to chloride in highway runoff samples ( $2.9 \times 10^{-6}$  and  $0.4 \times 10^{-4}$ , respectively), although they were not detected in the laboratory samples of more concentrated salt solutions at much lower ratios to chloride (Table 1). These relations are probably spurious but may result from reactions between the salt and available metals on pavement surfaces (12). In contrast, the ratio of zinc to chloride steadily increased by about

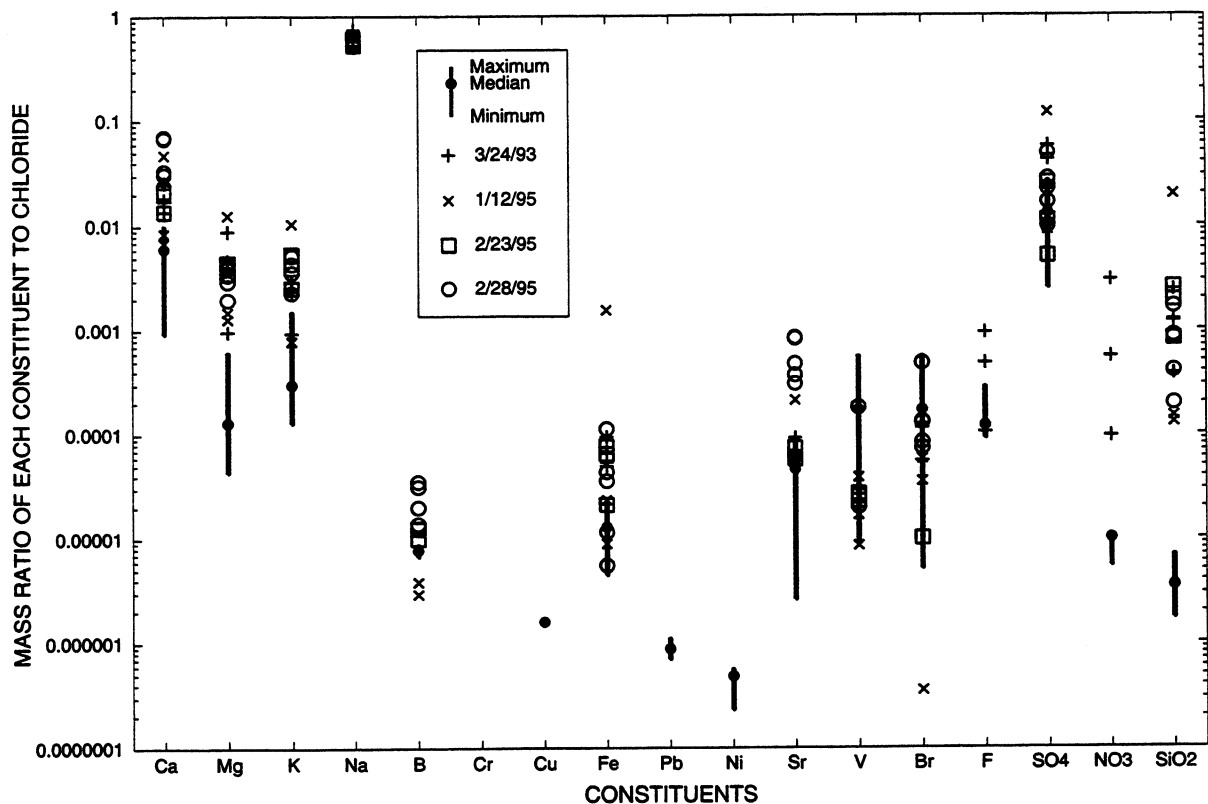


FIGURE 5 Comparison of range of and median mass ratios to chloride of constituents of deicing chemical sodium chloride to ratios of highway runoff constituents in samples taken during current study.

an order of magnitude (from  $0.3 \times 10^{-4}$  to  $2.7 \times 10^{-4}$ ) during the storm as chloride concentrations decreased from 960 to 360 mg/L. Chloride ratios of constituents in highway runoff generally approach laboratory ratios with increasing chloride concentrations (Figure 6). Also, the chloride ratios of calcium, potassium, and strontium in highway runoff show the influence of the CCRS in the premix used during the storm on February 28 (Figure 6). Therefore, investigators may use the chloride ratios presented here to estimate inputs from deicing chemicals based on known chloride concentrations.

Concentrations of the major and trace constituents of deicing chemicals in highway runoff also are substantial in comparison with concentrations reported in the literature (25). Estimates of deicing chemical constituent concentrations based on an analysis of chloride from a highway runoff sample taken from the first flush of a winter storm on January 28, 1994, are presented in Table 3. The constituent concentrations from the deicing chemicals generally are within 10 to 20 percent of the lowest concentrations reported in the literature. Therefore, an analysis of concentrations also indicates that deicing chemicals are not a trivial source of major and trace constituent concentrations in highway runoff.

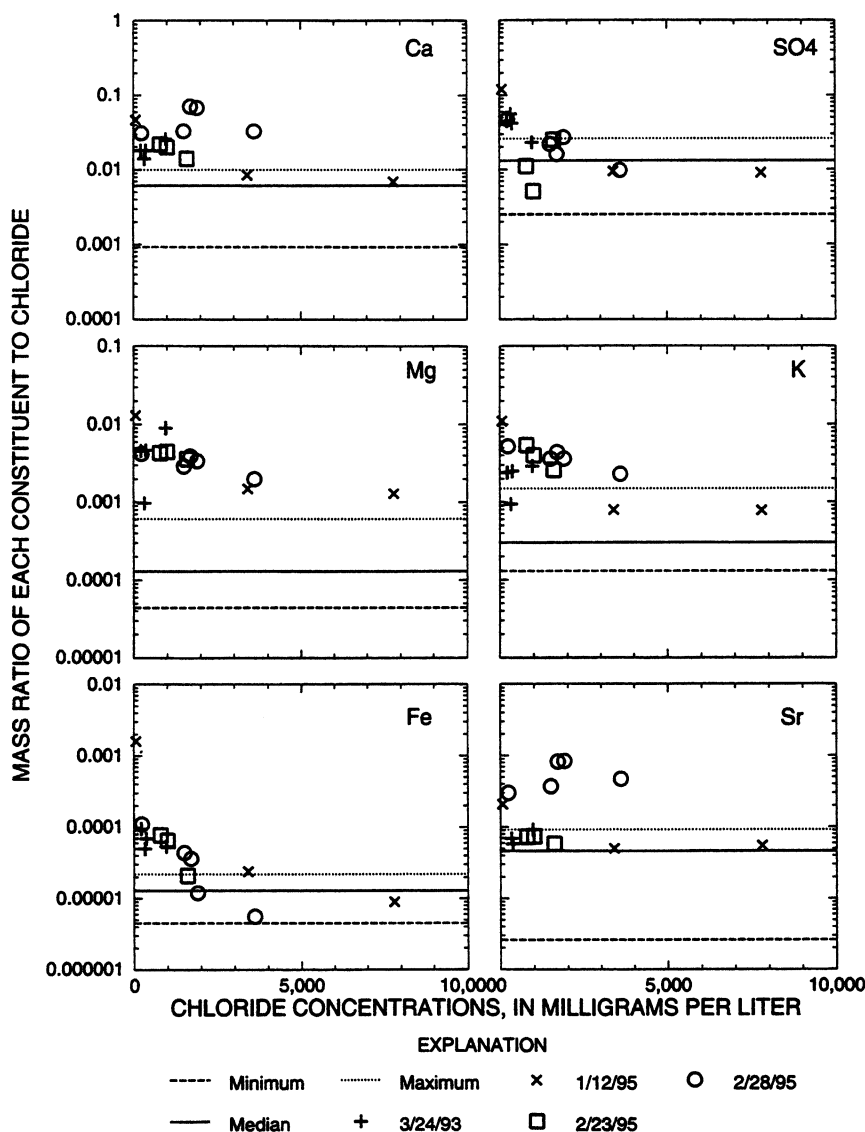
## SUMMARY

Quantification of the dissolved major and trace constituents of deicing chemicals as constituents of highway runoff is needed for inter-

pretive studies of highway runoff and its effects on receiving waters. Although many studies examine the occurrence of deicing chemicals and their effects on the environment, few have examined both major and trace constituents of deicing chemicals in highway runoff. Samples of deicing chemicals examined were obtained from an MHD road maintenance facility for 1990–1995. Dissolved constituents of the deicing chemicals—sodium chloride, calcium chloride, and premix (a mixture of sodium and calcium chloride)—were determined by analyzing samples from laboratory dilutions of deicing chemicals in deionized water. Each constituent of the deicing chemicals examined was presented as a mass ratio of that constituent to chloride in aqueous solution.

The deicing chemicals studied meet ASTM standards for purity but also have a distinct major and trace constituent signature. Summation of median mass ratios indicates that the sodium chloride and calcium chloride samples are about 98 and 97 percent pure, respectively. The greatest impurity in SCRS is sulfate, followed by calcium, potassium, bromide, vanadium, magnesium, fluoride, and other constituents with a ratio to chloride of less than 0.0001 by mass. Generally, CCRS has the same constituents as SCRS, although in different proportions. The greatest impurity in the CCRS is sodium, followed by potassium, sulfate, bromide, silica, fluoride, strontium, magnesium, and other constituents with a ratio to chloride of less than 0.0001 by mass. Although CCRS is only used as a component of premix, it will alter the chemical signature of deicing chemicals applied, and the composition of the premix samples in which it is used can be derived by partitioning the con-





**FIGURE 6** Variation of mass ratios to chloride of constituents of highway runoff samples with chloride concentration.

stituents of component salts. The ratios of the major constituents—sodium, calcium, magnesium, sulfate, and bromide to chloride—are generally consistent between this study and those derived from concentrations reported in the literature. However, estimates of minor and trace constituent concentrations from the current study are generally less than constituent concentrations reported in the literature.

Comparison of the estimated annual loads and first flush concentrations of deicing chemical constituents of highway runoff with those reported in the literature indicates that although deicing chemicals are not a primary source of trace constituents, they are not an unimportant source either. Maximum loads of trace constituents from deicing chemicals ranged from 2 to 40 percent of individual trace constituent loads in highway runoff reported in the literature. Additionally, concentrations of trace constituents from deicing chemicals in the first flush of a typical

winter storm generally are from about 10 to 20 percent of the concentrations in highway runoff reported in the literature. Therefore, deicing chemicals should be considered as a source of both major and trace constituents in studies of highway and urban runoff.

#### ACKNOWLEDGMENTS

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**TABLE 3 Estimation of Each Constituent of Deicing Material Using a Chloride Analysis from Sample Taken from First Flush of Winter Storm (January 28, 1994) Multiplied by Median Mass Ratio of Each Constituent of Sodium Chloride Road Salt**

Constituent of Deicing Material <sup>a</sup>	Estimated Concentration (mg/L)	Literature Range of Concentrations (mg/L)	Maximum Percent <sup>b</sup>
Chloride <sup>c</sup>	$1.7 \times 10^4$	-- <sup>d</sup>	--
Calcium	$1.0 \times 10^2$	--	--
Magnesium	$2.2 \times 10^0$	1.062	208
Sodium	$1.1 \times 10^4$	--	--
Potassium	$5.1 \times 10^0$	--	--
Sulfate	$2.2 \times 10^1$	--	--
Fluoride	$2.0 \times 10^0$	--	--
Silica	$6.0 \times 10^2$	--	--
Boron	$1.3 \times 10^1$	--	--
Chromium <sup>e</sup>	$7.5 \times 10^3$	≤ .04	19
Copper	$2.7 \times 10^2$	0.022 - 7.0	120
Iron	$2.2 \times 10^1$	2.4 - 10.3	9
Lead	$1.5 \times 10^2$	0.073 - 1.78	20
Nickel	$8.2 \times 10^0$	0.053	15
Strontium	$7.8 \times 10^1$	--	--
Vanadium	$2.9 \times 10^1$	--	--
Bromide	$2.9 \times 10^1$	--	--
Nitrate	$1.7 \times 10^1$	0.306 - 1.4	55

<sup>a</sup>Sodium chloride road salt ratios represent 95 percent of deicing chemicals applied at the test site.

<sup>b</sup>Estimated by quotient of the maximum salt constituent load and the minimum load reported in the literature for each constituent. The maximum is reported because the minimum load is always conceivably zero.

<sup>c</sup>Chloride concentration in peak of winter storm first flush as determined in by laboratory analysis of a water sample.

<sup>d</sup>Constituent not defined by Barrett and others, (1993).

<sup>e</sup>Using ratio found in Premix which is below detection limit in sodium chloride analyses.

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