Report No. CDOT-DTD-R-99-10
Final Report

STUDIES OF ENVIRONMENTAL EFFECTS OF MAGNESIUM CHLORIDE DEICER IN COLORADO

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DEPARTMENT OF TRANSPORTATION
RESEARCH

November 1999

COLORADO DEPARTMENT OF TRANSPORTATION
RESEARCH BRANCH

Technical Report Documentation Page

1. Report No. CDOT-DTD-R-99-10	**2. Government Accession No.**	**3. Recipient's Catalog No.**
4. Title and Subtitle STUDIES OF ENVIRONMENTAL EFFECTS OF MAGNESIUM CHLORIDE DEICER IN COLORADO		**5. Report Date** November 1999 **6. Performing Organization Code**
7. Author(s) William M. Lewis, Jr.		**8. Performing Organization Report No.**
9. Performing Organization Name and Address Western Environmental Analysts 2525 Arapahoe, Suite E4-282 Boulder, CO 80302		**10. Work Unit No. (TRAIS)** **11. Contract or Grant No.**
12. Sponsoring Agency Name and Address Colorado Department of Transportation 4201 East Arkansas Avenue Denver, Colorado 80222		**13. Type of Report and Period Covered** Final Report, 3 years **14. Sponsoring Agency Code**

15. Supplementary Notes

Prepared in cooperation with the U.S. Department of Transportation, Federal Highway Administration

16. Abstract

The overall conclusion of the study is that application of magnesium chloride deicer having a chemical composition and application rate similar to those of 1997-98 is highly unlikely to cause or contribute to environmental damage at distances greater than 20 yards from the roadway. Even very close to the roadway, the potential of magnesium chloride deicer to cause environmental damage is probably much smaller than that of other factors related to road use and maintenance, including pollution of highway surfaces by vehicles and use of salt and sand mixtures to promote traction in winter. Magnesium chloride deicer may offer net environmental benefits if its use leads to a reduction in the quantity of salt and sand applied to roadways. The environmental safety of magnesium chloride deicer depends, however, on low concentrations of contaminants and avoidance of rust inhibitors containing phosphorus. Appropriate specifications for vendors and routine testing can insure the continued environmental acceptability of magnesium chloride deicers.

Implementation

Deicers provided by vendors should be monitored independently by CDOT for chemical characteristics. Any significant changes in processing or source material should be disclosed by the vendor. Colorado-based specifications should be developed for vendors. Independent specifications for low elevation could be developed, or the more stringent high elevation specifications can be applied to all purchases.

17. Key Words winter maintenance, deicing, corrosion inhibitors, aquatic life	**18. Distribution Statement** No restriction. This document is available to the public through: National Technical Information Service 5825 Port Royal Road Springfield, Virginia

19. Security Classif. (of this report)	**20. Security Classif. (of this page)**	**21. No. of Pages**	**22. Price**
None	None	101	

Studies of Environmental Effects of Magnesium Chloride Deicer in Colorado

by

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Western Environmental Analysts

Report No. CDOT-DTD-R-99-10
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Prepared by
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Research Branch

November 1999

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Executive Summary

1. The Colorado Department of Transportation plans to increase its use of magnesium chloride liquid deicers. Advantages of deicer solutions on roadways at high elevation include reduction in the use of salt and sand mixtures and improvement of road conditions during storms beyond what is possible by the use of sand and salt mixtures alone.

2. In preparation for increased use of magnesium chloride deicers on roadways at high elevations, the Colorado Department of Transportation (CDOT) initiated environmental investigations during late 1996. These environmental investigations focused on the effects of magnesium chloride deicers on water quality and aquatic ecosystems. The studies included analysis of water quality and aquatic communities as well as biotoxicity testing.

3. The field and laboratory studies of magnesium chloride deicers were preceded by a literature review. The review showed that magnesium and chloride, the main ingredients of magnesium chloride deicers, are unlikely to produce adverse environmental effects except under very unusual circumstances. Chloride may damage vegetation very close to roadways, but is diluted by runoff to such an extent that it is very unlikely to exceed the concentrations that are known to be harmful to aquatic life. Aside from the main ingredients, magnesium chloride deicers can be expected to contain rust inhibitors as well as substances in lower amounts that are included inadvertently. Rust inhibitors and minor constituents of deicers have seldom been studied.

4. The expected dilution of deicers on roadways was estimated as one means of evaluating the expected concentrations of deicer components in runoff as it enters the environment. The median expected dilution of deicer is approximately 1 to 500 prior to its exit

from the roadway, but dilution will vary considerably in relation to rate of application, amount of runoff, and other site-specific factors.

5. Analysis of the deicing mixtures that were in use by CDOT during the winter of 1996-97 showed unexpectedly high concentrations of lead, zinc, and cadmium as well as phosphorus. Ratios of lead, zinc, and cadmium to stream standards exceeded the desired threshold of 500. CDOT tightened its restrictions on vendors for supplies purchased for the winter of 1997-98.

6. Deicers provided by vendors for winter 1997-98 showed lower concentrations of metals and phosphorus than deicer provided by the same vendors during the previous winter. Ratios of contaminants to maximum allowable chronic concentrations in stream water were all below 500, as necessary to assure appropriate dilution prior to entering the environment.

7. Organic materials are expected components of deicers because rust inhibitors may consist of organic compounds. An analysis of the deicing solutions in use during 1996-97 showed that the deicers contained between 280 and 850 mg/L of organic carbon, and that this amount of organic matter would be expected to induce a total oxygen demand between 750 and 2200 mg of oxygen for every liter of deicer applied to the roadway. Deicer supplied for winter 1997-98 contained between 1200 and 2800 mg/L of organic carbon, and would have had oxygen demand higher than that of the previous year (3150-7500 mg for every liter of deicer). Given the extensive dilution of the deicer on and very near the roadway prior to entering the environment, however, this potential oxygen demand appears to present no environmental threat through the depletion of oxygen in streams or other aquatic environments.

8. The biochemical oxygen demand of deicers was measured experimentally. Control sites (i.e., sites not receiving deicers) showed biochemical oxygen demand between 0.04 and 0.11 mg O_2/L/day. No significant increase in BOD could be detected as a result of the addition of

0.3% deicer solution. In addition, no significant change in BOD could be observed as a result of the addition of salt and sand (0.6% by mass).

9. Tadpoles of the boreal toad were subjected to biotoxicity testing under controlled laboratory conditions through exposure to a range of concentrations of 1996-97 deicer. The boreal toad is of particular interest because of its status as an endangered species, and its presence in aquatic environments near roadways that receive deicer. The tadpoles showed no mortality over 96-hour intervals at deicer concentrations of 0.1%, which is close to the expected median concentration of deicer concentrations in runoff as it exits the roadway. The concentration of deicer required to cause 50% mortality (LD50) among tadpoles over a 96-hour period was estimated as 0.32%. Tadpoles were similarly affected by solutions of pure magnesium chloride (LD50=0.65%). Repetition of testing with 1997-98 deicer produced similar results. A sublethal (physiological stress) test was added for 1997-98 deicer; it showed physiological stress at or above 0.1% deicer. The no effect concentration for the sublethal test probably lies in the vicinity of 0.02% deicer.

10. Juvenile rainbow trout were tested with 1996-97 deicer for response to varying concentrations of deicer. The threshold for mortality over 96-hour exposure intervals was approximately 0.5%. The LD50 for rainbow trout was estimated as 1.4% magnesium chloride deicer. Results were similar for 1997-98 deicer.

11. The aquatic invertebrate *Ceriodaphnia* was tested for response to a range of magnesium chloride deicer solutions over an interval of 48 hours. The threshold of mortality for *Ceriodaphnia* was approximately 0.1%. The LD50 for *Ceriodaphnia* was estimated as 0.19% (48 hours). A test of reproductive capability was also performed on *Ceriodaphnia*. The reproductive test indicates the onset of negative physiological effects for *Ceriodaphnia* at about

0.1% deicer. Both mortality and reproductive tests were repeated with 1997-98 deicer; results were similar to those of the previous year.

12. The algal genus *Selenastrum* was tested with 1997-98 deicer for response to magnesium chloride deicer over intervals of 96 hours. The test showed significant suppression of division rate for the algal cells occurring at deicer concentrations slightly in excess of 0.1%. Other indicators of physiological stress appeared at concentrations of approximately 1%.

13. In overview, toxicity tests show that various kinds of aquatic organisms differ in their sensitivity to magnesium chloride deicer. The most sensitive kinds of organisms included in these tests begin to show observable effects at about 0.1% magnesium chloride deicer during exposures ranging from 48 to 168 hours. Because of the presence of melt water, magnesium chloride deicer applied to roadways is diluted to approximately 0.2% prior to leaving the roadway, and an additional amount (to less than 0.1%) within short distances (e.g., 20 yards) of the roadway.

14. Mass transport was estimated from field data for magnesium, chloride, and sodium at 6 field sites (stream study segments) during 1997 and 1998. The amount of magnesium added in the form of magnesium chloride to roadways greatly increased the total annual transport of magnesium. Addition of magnesium chloride raised the concentrations of magnesium in streams by as much as three times above baseline concentrations of 2-3mg/L. Winter concentrations were most strongly affected because stream discharge is low during winter, and thus dilutes the magnesium less than during spring. Even though changes in concentration were substantial, they fell well within the natural range of magnesium concentrations in Colorado waters and raise no specific environmental concerns.

15. For chloride, two different sources are likely to raise concentrations and mass transport above background: magnesium chloride and salt with sand. Background concentrations of chloride are very low (0-2 mg/L); the combination of magnesium chloride and salt with sand raises these background concentrations by 50 to 100 mg/L during winter, when dilution is lowest. Even so, the peak concentrations were below concentrations that could be considered potentially harmful to the most sensitive forms of aquatic life. Annual transport of chloride is accounted for mainly by chloride added to highways in the form of salt with sand. When deicer and salt with sand are applied together, magnesium chloride deicer accounts for 10 - 50% of the total.

16. Sodium is added to highways as salt with sand, but not as a component of magnesium chloride. Use of salt with sand raises the peak concentrations of sodium in stream waters from the range 2-5 mg/L to the range 20-50 mg/L. These concentrations are not considered environmentally damaging, however. The sodium added as salt with sand can be a high percentage of the natural annual transport.

17. Concentrations of other inorganic substances were studied at the 6 field sites through routine monitoring extending from late 1997 to spring 1999. Substances that were monitored included arsenic, cadmium, chromium, copper, lead, mercury, and zinc. In addition, hardness of the water was measured at each site on each monitoring date because regulatory limits for some metals are determined on the basis of hardness. The amounts of substances in the water were undetectable or rarely detectable in most cases. Cadmium, copper, and zinc were detected commonly at some sites. The analysis, therefore, focused on cadmium, copper, and zinc. For sites that are unaffected by mine drainage (main stem of Straight Creek and Laskey Gulch), intersite comparisons show that the application of magnesium chloride deicer has no detectable effect on the concentrations of the substances that were analyzed; concentrations were

consistently far below regulatory limits. The other four sites are affected to varying degrees by mine drainage. Mine drainage causes consistent exceedances of standards on upper Clear Creek and lower North Clear Creek. The amounts of metals transported in watersheds that are either affected or unaffected by mine drainage far exceed the amounts that are added to roadways with magnesium chloride deicer.

18. Deicer contributed less than 5% to transport of phosphorus when no phosphorus-containing rust inhibitors were used.

19. Comparisons were made of algal communities at three locations receiving deicer and three locations not receiving deicer (controls). Analysis of the algal communities indicates no statistically significant difference in the algal communities of control and treatment sites.

20. During spring of 1998, samples were taken of runoff originating from portions of I-70 receiving magnesium chloride deicer. The samples were taken just following a storm during which deicer and salt with sand had been applied, and consisted of a series of transects beginning at the side of the highway and moving along drainage paths leading to the nearest large stream. The purpose of the sampling was to determine the degree and speed of dilution for deicers through chemical analysis of runoff water. The results showed that dilutions were at a minimum 5000 fold and typically 10,000 fold or more at short distances from the roadway (e.g., 20 yds).

21. Water quality was studied in two wetlands, both of which support breeding populations of the boreal toad. One wetland (the north wetland) does not receive highway drainage because it is up slope of the highway, whereas a nearby wetland (south wetland) receives highway drainage from I-70. Studies of the concentrations of major ions, and especially magnesium, indicate that the south wetland received concentrations of deicer not exceeding 0.002% during the toad breeding season (June to early July). Concentrations of metals and

related substances were primarily undetectable except for copper and zinc. Concentrations of copper and zinc were higher in the south wetland, below the highway, than in the north wetland. Mass balance studies showed, however, that the proportion of these elements that can be traced to deicing compounds does not exceed 0.002%. Other highway-derived water quality influences (wear of metallic parts, lubricants, salt and sand applications) may account for concentrations of copper and zinc reaching or exceeding the aquatic life standard, or geologic factors may be involved.

22. The overall conclusion of the study is that application of magnesium chloride deicer having a chemical composition and application rate similar to those of 1997-98 is highly unlikely to cause or contribute to environmental damage at distances greater than 20 yds from the roadway. Even very close to the roadway, the potential of magnesium chloride deicer to cause environmental damage is probably much smaller than that of other factors related to road use and maintenance, including pollution of highway surfaces by vehicles and use of salt and sand mixtures to promote traction in winter. Magnesium chloride deicer may offer net environmental benefits if its use leads to a reduction in the quantity of salt and sand applied to roadways. The environmental safety of magnesium chloride deicer depends, however, on low concentrations of contaminants and avoidance of rust inhibitors containing phosphorus. Appropriate specifications for vendors and routine testing can insure the continued environmental acceptability of magnesium chloride deicers.

Introduction

The State of Colorado, through the Colorado Department of Transportation (CDOT), uses magnesium chloride solutions at numerous locations for highway deicing. CDOT has found that magnesium chloride offers numerous benefits. These include reduction in the need for application salt and sand and improvement of road conditions beyond what would be possible with salt and sand alone. Reduction in the use of salt and sand is valuable environmentally because of the connection between salt and sand and airborne fine particulate material that is regulated for protection of human health. In addition, large volumes of sand can be detrimental to roadside environments, particularly small streams. Deicer also contributes to maintenance of traffic volume, particularly at high elevation, and may increase the safety of travel during storms as well.

Given the benefits of magnesium chloride, CDOT has moved from experimental to routine use of magnesium chloride over the last few years. This type of use for magnesium chloride is by no means unprecedented, given that many local governments as well as governments of other states have in the past used magnesium chloride extensively as a deicer.

Prior to making even further commitments to the use of magnesium chloride, CDOT has anticipated the need for environmental evaluation of magnesium chloride in the context of the Colorado montane environment where extensive amounts of magnesium chloride will be used. A project designed to accomplish this goal was designed in 1996 and implemented toward the end of 1996 and beginning of 1997. The project, which ended in June 1999, had two major components: 1. A review of the literature on environmental effects of magnesium chloride with emphasis on Colorado conditions (Task 1), and 2. Experimental and monitoring work intended to test the potential environmental effects of magnesium chloride deicer in Colorado (Tasks 2-8). The first of these two components was completed during 1997 in the form of a report that reviews the literature on magnesium chloride.[1] The second component of the project, which involved field work at six sites (Figures 1 - 3) and laboratory work, was completed in June 1999. The present report gives the final results of the field and laboratory studies. For purposes of clarity, order of presentation of results below differs from the order of tasks shown in Table 1.

Dilution of Deicer on the Roadway

Dilution of deicer by melting ice and snow following its application to highways at high elevation was determined by (1) estimation of dilution by precipitation, and (2) field sampling at various distances from the highway to which deicer had been applied. The purpose of both of these approaches is to provide context for the evaluation of bioassay tests and chemical tests of deicer composition. Results of the dilution estimates based on precipitation are presented here. Results of the field sampling appear in a separate section of this report (Synoptic Sampling).

The application rate for magnesium chloride on an annual basis varies by location. An approximate rate of application for high elevation is 50,000 L of deicer per mile of interstate highway (I-70: 4 lanes) per year, i.e., about 12,000 L per lane mile per year.[2] This figure will be

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[1]Lewis, W.M. Jr. Magnesium Chloride Deicer: A Literature Review with Emphasis on the State of Colorado. 7 July 1997.

[2]CDOT application records for I70, 1996-97 and 1997-98; see section on mass transport for specific information.

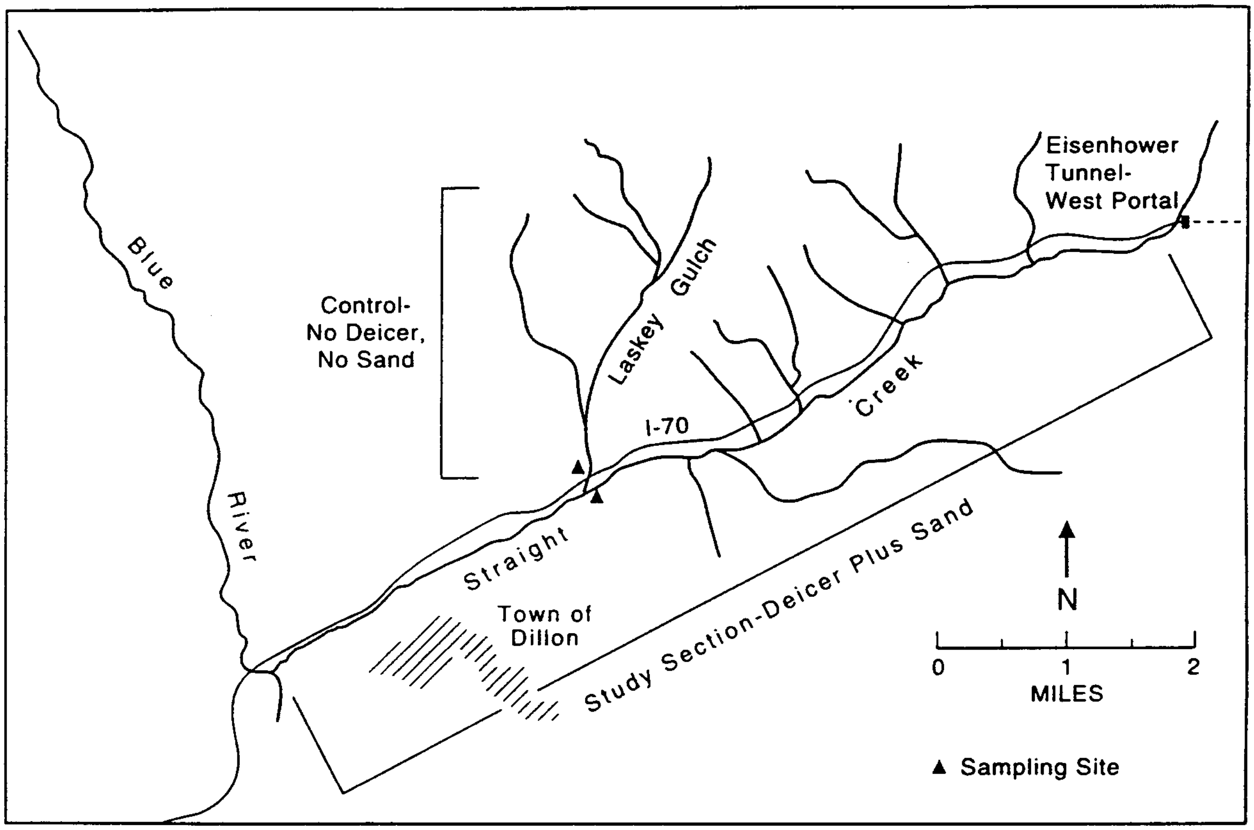

Figure 1. Study segments in the West Portal area.

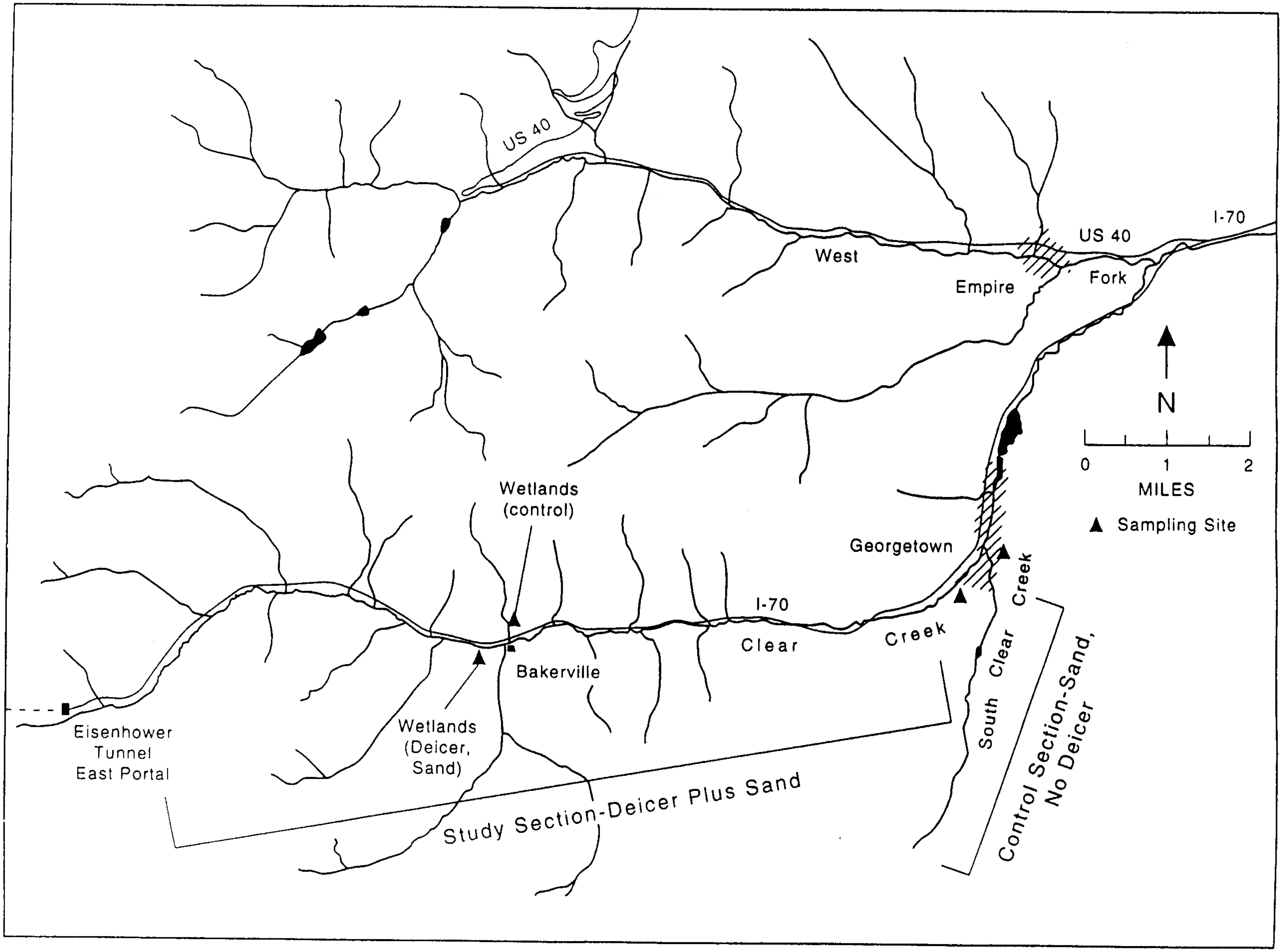

Figure 2. Study segments in the East Portal Area.

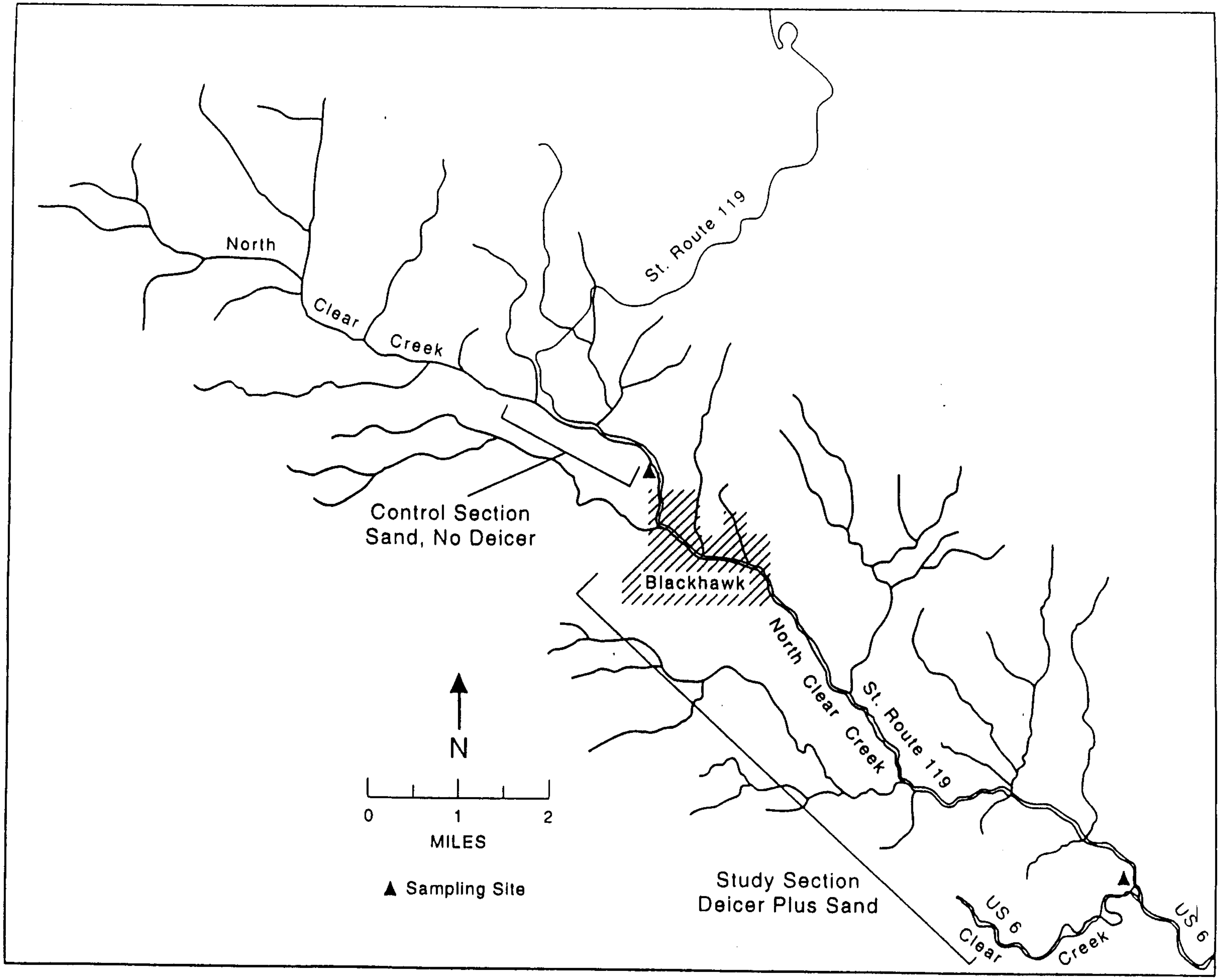

Figure 3. Study segments along North Clear Creek.

Task and Description		
Task 1	A	Literature Review
Task 2	A	Biochemical Oxygen Demand of Deicer
	B	Chemical Analysis of Deicer (organic)
	C	Nutrient Analysis of Deicer
	D	Metal Analysis of Deicer
Task 3	A	Toad Toxicity Test
	B	Trout Toxicity Test
	C	Ceriodaphnia Toxicity Test
	D	Algae Toxicity Test
Task 4		Mass Balance Studies
Task 7		Synoptic Field Studies
Task 8		Community Analysis (algae)

Table 1. Summary of Tasks (Tasks 5 and 6 were canceled).

used in the calculation, with the understanding that the actual application rate in a given situation may vary from this amount (typically lower; seldom higher).

The amount of precipitation and runoff at high elevation in Colorado also varies greatly from year to year and site to site. For present purposes, an example runoff of 300 mm/yr is used.[3] A mile of 4-lane highway has a total constructed area (designated here as roadway, including shoulders and embankments) of about 90,000 m^2 (measured by the author east of Eisenhower Tunnel). The amount of moisture passing from the roadway is about 25,000 m^3 per year, mostly during the season of deicer use. Thus as a rough approximation, the 50,000 L of deicer applied to one mile of 4-lane highway is diluted by about 25,000 m^3 of runoff, i.e., deicer is diluted at approximately 500:1 before it enters the environment. This method of calculation can be adapted to any specific set of conditions, as explained in Appendix A.

The expected dilution on the roadway, although approximate, suggests a first level of screening for the concentrations of substances in the deicer. As a rule of thumb, it is undesirable for any constituent of undiluted deicer to exceed by a factor of 500 or more the allowable concentration of that material in Colorado surface waters, as set by the Colorado Water Quality Control Commission under review by the USEPA. This rule of thumb serves as a means of evaluating concentrations of substances in the deicer. The rule of thumb is probably conservative in that it is based on chronic standards, which are much more stringent than acute standards.

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[3]For example, see Lewis, W.M. et al. 1984. Eutrophication and Land use: Lake Dillon, Colorado. Springer, N.Y. Rain produces little runoff; most runoff originates as snow (see hydrographs in the section of this report on mass transport).

After leaving the roadway, deicer is further diluted by snowmelt. Dilution beyond the roadway was estimated through synoptic studies, which are presented in the last section of this report.

Chemical Composition of Deicers

Inorganic Substances (1996-97)

During the winter of 1996-97, CDOT Region 1 was using deicers from two sources: GMCO and Envirotech (FreezeGard Zero). Task 2 of this project called for analysis of these two kinds of magnesium chloride deicers as a means of determining the amounts of ingredients and trace substances that might be of environmental interest.

Samples of the GMCO and FreezeGard Zero deicers were obtained from CDOT's storage tanks, and were analyzed for a spectrum of substances, including the main ingredients of the mixture (magnesium and chloride) as well as others. The results are summarized in Table 2. Methods are as given in Appendix B.

The intended composition of the deicing material includes: (1) magnesium and chloride ions composing approximately 30% by weight of the deicing mixture, (2) water, which makes up the bulk of the mixture, and (3) a small amount of rust inhibitor that may be organic or inorganic, and is typically treated as proprietary.

As shown by Table 2, the main components of the deicer were as expected: dissolved materials in the mixture were dominated by magnesium and chloride ions. In addition, other substances were present. This is not surprising, given that the parent material for the deicer is

	Standard (chronic)	Typical Stream Concentration	milligrams per liter Deicer Enviro[6]	GMCO	Ratio[5] Enviro	GMCO
Major ions						
Ca	None	20	2260	70	113	3.5
Mg	None	3.5	71,000	65,000	20,380	18,600
Na	None	3.5	1800	1500	515	429
K	None	0.5	820	540	1640	1080
Cl	230	4.0	210,000[4]	190,000[4]	50,000	45,000
Nutrients						
Total P	None[3]	0.015	12	82	800	5500
Other Inorganics (Total Recoverable for Metals)						
Cu	0.0065[1]	---	0.2	0.2	31	31
Pb	0.0015[1]	---	3.4	3.0	2270	2000
Zn	0.069[1]	---	1	39	14	560
As	0.050	---	6.4	5.1	128	100
Cd	0.0007[1]	---	0.6	0.5	860	710
NH_3	2.3[2]	0.010	5.3	3.4	2.3	1.5

[1] Approximate, based on hardness of 50 mg/l
[2] At 15 C, pH 7.5; varies with pH and temperature; expressed as N
[3] Concentration limit exits for Lake Dillon
[4] Computed from molar ratio to magnesium
[5] Ratio of deicer concentration to typical concentration (major ions and nutrients) or to water quality standards (other inorganics; for metals standards are based on the soluble fraction, which may be somewhat less than total recoverable shown in the table).
[6] Envirotech FreezeGard Zero

Table 2. Chemical composition of two sources of $MgCl_2$ deicer used by CDOT Region 1 during winter, 1996-97.

taken from solar ponds, which in turn receive their salts from the Great Salt Lake, a natural source containing the many products of rock weathering. The material is processed to some extent by vendors, mainly for the reduction of sulfate concentrations and addition of rust inhibitor.

Both the GMCO and FreezeGard Zero deicing material contained, in addition to magnesium and chloride, easily measurable amounts of calcium, sodium, and potassium. These ionic substances are not regulated for water quality purposes, unless they are present at such high concentrations that they might influence the total salinity of the water or, in the case of chloride, at concentrations above 230 mg/L (the state standard for protection of aquatic life). The amounts of calcium, sodium, and potassium in the mixture raise no environmental issues related to water quality.

Both deicing mixtures also contained measurable concentrations of a number of heavy metals and some other substances such as arsenic and ammonia. These substances are regulated in surface waters for the protection of aquatic life. A number of them are also regulated for the protection of drinking water supply, although the aquatic life limits are considerably more stringent, and therefore will be the focus of this analysis.

Although the presence of some metals and other contaminants in the sample is anticipated, the concentrations of some substances (specifically cadmium, lead, zinc, and phosphorus) that were found in the 1996-97 samples were surprisingly high, especially with regard to the State of Colorado water quality limits for these substances.

Because the water quality limits for individual substances vary widely, Table 2 includes a listing of the concentration limits for substances that were found in the deicing mixtures. For the metals shown in Table 2, the limits are not fixed, but rather are calculated on the basis of hardness, which varies from site to site and date to date. For purposes of preparing Table 2, a characteristic hardness (50 mg/L) was assumed in the calculations. This is a low hardness, but the hardness of mountain waters is characteristically low, and the result is stringent state standards for metals in montane waters. The table also shows the ratio of concentrations in the undiluted deicers to the concentrations allowed by stream standards. In all cases, the concentration of substances in the undiluted deicer greatly exceeds the stream standards, but this in itself is not cause for concern because of the substantial dilution of deicer on the roadway (approximately 500x, but variable according to circumstances). More meaningful is the last column in the table, which shows the amount of dilution required to bring the concentration of each substance down to the stream standard. When the number in this column is above 500, the substance may leave the roadway at concentrations that exceed the surface water standard (lead, cadmium, and zinc were above 500).

The table also shows the concentration of ammonia, a non-metallic substance that is regulated for the protection of aquatic life, in the deicer. Although the deicing mixture does contain easily measurable amounts of ammonia, the ratio to stream standards is low. Furthermore, ammonia is converted to nitrate or organic nitrogen by natural processes in streams.

The table also contains information on the amounts of phosphorus in the deicers. Unlike heavy metals, phosphorus is not regulated by statewide standards. Instead, it is regulated by site-specific standards. In general, montane waters have low concentrations of phosphorus, and the addition of large amounts of phosphorus has the undesirable effect of causing eutrophication, which results in excessive algal growth and other undesirable outcomes. The deicers did contain substantial amounts of phosphorus (particularly the GMCO deicer). Phosphorus is an effective corrosion inhibitor and may have been added to the GMCO deicer for this purpose.

Overall, analysis of inorganic materials in the 1996-97 deicing materials raised some concerns about potentially excessive amounts of lead, zinc, cadmium, and phosphorus that would be leaving the roadway and entering headwater streams in the montane areas. Subsequent field work involving sampling of the roadside drainage (synoptic sampling) showed that melting of snow from locations close (e.g., 20 yards) to the roadway provides additional dilution of these substances, but still it seems prudent to work toward reduction of concentrations for any substance that would exceed standards after 500-fold dilution on the roadway.

Upon receiving the information in Table 2, CDOT management collected additional samples of the 1996-97 deicer and, although the exact concentrations of various substances varied from one sample to another, confirmed that the concentrations of metals and phosphorus were sufficiently high to raise concerns and to be cause for discussion with vendors.

The source of metals and phosphorus in the 1996-97 deicing materials remains to some extent unexplained. High concentrations of phosphorus in the GMCO material probably reflect the presence of phosphate in corrosion inhibitors, and in this sense were intentional and subject to reversal by substitution of other kinds of inhibitors. Metals could have come from the source ponds, or could have been added or augmented by the processing of the deicer for removal of sulfate. It is also possible that some or all of the trace substances came from CDOT storage tanks rather than vendor sources, although the consistency in presence of contaminants from different tanks casts doubt on this possibility. It is also possible that the material sampled in 1996-97 was atypical in the sense that it was left over after deicing had ceased (Spring 1997).

Inorganic Substances (1997-98)

For the 1997-98 season, CDOT set more stringent conditions for vendors, and preliminary analysis of the deicing material by CDOT Region 1 showed that the deicer had lower concentrations of metals and nutrients than were characteristic of the previous year. Analysis of deicer obtained in the middle of the deicing season (January) is summarized in Table 3. Envirotech deicer was sampled from a CDOT storage tank and also from a delivery truck. The GMCO deicer was sampled from a CDOT storage tank.

As shown by Table 3, the analysis of deicer from the CDOT storage tank and from the delivery truck produced essentially identical results, indicating that the storage tank did not alter the composition of the deicer. As in 1996-97, the analytical results for the Envirotech and GMCO deicers were very similar, although not identical.

In 1996-97, the analysis of metals was for total recoverable amounts. In 1997-98, the analysis was both for total recoverable amounts (abbreviated "tot" in the table) and for the dissolved fraction ("sol"). Regulations for the protection of aquatic life are expressed by the State of Colorado through standards related to dissolved metals rather than total metals, although both may be of interest environmentally.

The 1996-97 analysis can be compared with the 1997-98 analysis (for total recoverable amounts only) of metals that were analyzed in both years. The 1997-98 analysis was for a longer list of substances, but the substances that were added to the list of analyses (Cr, Hg, Ni, Se) were consistently present at concentrations near or below detection limits. For the comparisons that are possible, most show substantial decline in concentration between the two years. Copper showed a slight increase, but this is of little concern because of the ratio of copper to stream standards was among the lowest of the metals to be analyzed. Phosphorus showed a slight increase in the Envirotech deicer, but the increase was probably within the limits of sampling variation. On the other hand, substantial and significant decreases were observed in lead,

		milligrams per liter		
		Deicer		
		Enviro Tank[1]	Enviro Truck[1]	GMCO Tank
Major ions				
Ca		1800	2200	<100
Mg		80,000	80,000	80,000
Na		2900	2700	1900
Cl[2]		230,000	230,000	230,000
Nutrients				
Soluble Reactive P		4.3	2.5	4.4
Total Soluble P		11.7	16.4	7.1
Particulate P		2.7	1.2	0.4
Total P		14.4†	17.6†	7.5*
Other Inorganics				
Cu	sol	0.2	0.1	0.6
	tot	0.7†	0.6†	0.6†
As	sol	2.4	2.2	6.4
	tot	2.2*	2.0*	-
Cd	sol	<0.01	0.01	0.01
	tot	0.11*	0.12*	<0.05*
Cr	sol	<2	<2	<2
	tot	<2	<2	<2
Hg	sol	<0.02	<0.02	<0.02
	tot	<0.02	<0.02	<0.02
Ni	sol	<2	<2	<2
	tot	6	<2	<2
Pb	sol	<1	<1	<1
	tot	<1*	<1*	<1*
Se	sol	0.2	<0.2	0.2
	tot	<0.2	<0.2	<0.2
Zn	sol	<2	<2	<2
	tot	<2	<2	4*

[1] Envirotech FreezeGard Zero
[2] Computed from molar ratio to magnesium
* Lower than in 1996-97
† Higher than in 1996-97

Table 3. Chemical composition of two sources of $MgCl_2$ deicer used by CDOT during winter, 1997-98 (sol = soluble; tot = total recoverable).

cadmium, zinc, and in phosphorus for the GMCO deicer, which had high phosphorus content in 1996-97. These substances were the ones showing the highest ratios to stream standards in 1996-97. For the 1997-98 deicer, ratios of undiluted deicer to stream standards were all well below 500, and thus could be expected to receive the desired 500-fold dilution or more prior to leaving the roadway (plus further dilution close to the roadway).

Chemical Analysis of Salt with Sand and Comparison with Deicer

Salt with sand also was analyzed for major soluble constituents and the soluble and total fractions of inorganic substances. Results are summarized in Table 4. The results are based on water extraction of a measured amount of salt with sand (10 g in 1 L) from CDOT storage piles followed by gravity sedimentation and sub-sampling of the non-settling material (see Appendix B). Results are expressed as μg/g (parts per million by mass), and are not directly comparable to the estimates for magnesium chloride deicer, which are expressed as mg/L (because the deicer is a liquid; see below for method of comparison).

As shown by Table 4, the major ions in the mixture include sodium and chloride, as expected from the presence of salt. Amounts of other major ions were relatively small. Most metals were undetectable, especially in the soluble fraction, but some were present at detectable concentrations. These include copper, cadmium, lead, and zinc. Phosphorus also was detectable in the mixture.

Although many of the values in both Tables 3 and 4 are below detection limits, comparison of the values not below detection limits are possible through use of the application rates for deicer and salt with sand. Deicer is applied at 12,000 L or less per lane mile per year (see section on mass balance). Salt with sand is applied at 500,000 lbs/lane mile/year or less (see

		µg/g dry mass Salt with Sand[2]		
		Redimix 18%	Everist 5%	Mtn. Agg. 5%
Major Ions				
Ca		197	146	101
Mg		138	<5	<5
Na		52,000	18,000	9,000
Cl[1]		79,000	27,000	14,000
Nutrients				
P	Soluble Reactive	0.27	1.01	0.34
P	Total Soluble	0.31	1.20	0.38
P	Particulate	1.60	2.03	2.09
P	Total	1.91	3.23	2.47
Other Inorganics				
Cu	sol	0.15	0.15	0.25
	tot	0.30	2.5	4.3
As	sol	<0.5	<0.5	<0.5
	tot	<0.5	<0.5	<0.5
Cd	sol	<0.00	<0.00	0.01
	tot	0.06	0.06	<0.02
Cr	sol	<1	<1	<1
	tot	<1	<1	<1
Hg	sol	<0.01	<0.01	<0.01
	tot	<0.01	<0.01	<0.01
Ni	sol	<1	<1	<1
	tot	1	<1	<1
Pb	sol	<0.5	<0.5	<0.5
	tot	0.6	<1.7	<4.2
Se	sol	0.15	<0.1	0.1
	tot	<0.1	<0.1	<0.1
Zn	sol	<1	<1	<1
	tot	1.0	5.5	8.6

[1] Computed from molar ratio to sodium.

[2] Nominal percent salt is indicated for each source. Redimix was used on North Clear Creek, Everist on I-70 West Portal, and Mountain Aggregate on I-70 East Portal.

Table 4. Chemical composition of three sources of salt and sand used byCDOT Region 1 during winter, 1997-1998, in and near the study areas.

mass balance section). Table 5 uses these application rates to estimate amounts of various substances applied to a representative length of roadway with a hypothetical treatment scheme involving both deicer and sand with salt at the assumed rates mentioned above.

Organic Matter in the Deicer

Corrosion inhibitors often are organic. Because the inhibitors are proprietary, the vendors may not reveal their composition. Therefore, the purpose of this task was to determine the general chemical nature of the inhibitor, and thus whether it might be of some environmental concern.

After the project started, vendors voluntarily revealed directly to CDOT the composition of their inhibitors for 1997-98, which proved to be small organic molecules commonly found in unprocessed foods. Therefore, the emphasis of this task shifted to quantification of the total amount of organic material in the deicer, and computation of the oxygen-consuming capacity of organic matter in the deicer.

The total amount of organic matter in deicer was determined by use of a carbon analyzer, which converts all organic matter to CO_2. The amount of CO_2 is then used in an estimating the total amount of organic matter.

Table 6 shows the results of the carbon analysis. Both deicers contained substantial amounts of organic matter by comparison with natural waters (200 to 2000x), but the presence of organic matter is not surprising, given that the deicer is a concentrated mixture. For 1996-97, the two sources differed substantially in amount of organic matter. This is probably because one source contained an inorganic rust inhibitor, whereas the other contained an organic rust

	g/km/lane of roadway*/year	
	Deicer	Salt with Sand
Major Ions		
Ca	14,000	21,000
Mg	620,000	<710
Na	23,000	2,600,000
Cl	1,640,000	3,800,000
Nutrients		
P (Total)	112	460
Other Inorganics (Total Recoverable)		
Cu	5	360
As	17	<70
Cd	0.8	8
Cr	16	<140
Hg	0.16	<1.4
Ni	47	<140
Pb	8	<240
Se	1.5	<14
Zn	16	780

*Includes shoulders and embankments.

Table 5. Comparison of deicer (Envirotech FreezeGard Zero, 1997-98) with salt and sand (Everist 5%, 1997-98) in terms of roadway application.

Type of deicer	Amount of organic material (mg/l carbon)	Total potential oxygen demand (mg/l)	Volume of water (liters) providing total oxygen demand for 1 liter of deicer
Deicer for 1996-97			
GMCO	280	750	110
Envirotech*	840	2240	320
Deicer for 1997-98			
GMCO	1180	3150	450
Envirotech*	2810	7500	1070

*FreezeGard Zero

Table 6. Summary of information on organic carbon content of deicer.

inhibitor. For 1997-98, there was a shift up in concentrations, probably because CDOT had requested that inhibitors incorporating phosphorus be replaced with other (organic) inhibitors.

Table 6 also shows the estimated oxygen consumption capacity of the organic matter in the deicer, and the volume of water from which the deicer could consume all of the oxygen in the water at oxygen saturation (about 7 mg/L), without taking into account entry of new oxygen from the atmosphere.

The environmental significance of the organic matter cannot be evaluated solely on the basis of Table 6. It is also important to know how fast the organic material is consumed by microbes, which is the means by which oxygen demand is expressed in the environment (next section).

For 1996-97, GMCO deicer applied at standard rates would have a potential oxygen demand equivalent to 1320 cubic meters of water per lane mile at oxygen saturation (7mg/L);

5400 cubic meters was the comparable figure for GMCO in 1997-98. For FreezeGard Zero in1996-97, the potential oxygen depletion capacity corresponds to 3840 cubic meters per lane mile per year (12,800 cubic meters for FreezeGard Zero 1997-98).

The drainage area per mile of highway required to produce enough runoff to satisfy the oxygen demand for deicer over a one year interval would be 45,000 square meters or less per lane mile. This area extends no more than 20 yards from the roadway (see previous section on dilution). The oxygen demand of the organic matter would be sufficient to exhaust the oxygen content of water on the roadway if the oxygen demand were expressed prior to further dilution of deicer away from the road and at such a high rate as to outstrip physical reoxygenation mechanisms, but such quick expression of oxygen demand is virtually impossible. A 10-fold dilution of runoff from the roadway in transit to streams would be sufficient to reduce oxygen demand to negligible levels and is almost certain to occur before significant oxygen demand could be expressed. Oxygen depletion could occur in ponded areas very near to the highway that might receive and hold deicer diluted only by roadway runoff. Even in this case, the practical effect of the organic matter would depend very much on the rate at which it is degraded. This matter is considered below.

Analysis of the deicer for trace toxic organic substances (e.g., by GC/MS) was beyond the scope of work for this study. Motivation for this type of analysis seems weak on the basis of bioassay data (discussed below), which indicates that biotic effects are explained by major constituents, and not by unknown trace substances.

Biochemical Oxygen Demand

One way in which deicers might impair surface waters is through the transmission of organic matter to surface water in sufficient quantities to raise the biochemical oxygen demand (BOD) of the water. Impairment of this type is most likely under two conditions: 1) addition of substantial amounts of organic matter, and 2) rapid use of the organic matter by microbes. Water temperature would be expected to affect the BOD caused by the addition of organic matter: higher temperatures produce higher BOD if all other factors are equal.

Although the chemical testing of deicers suggests that the amount of organic matter present in them would be insufficient to cause measurable changes in BOD of streams near roads, direct tests of BOD were made. The tests were performed on bottles of water (333 mL) that were closed to the atmosphere after the addition of measured amounts of deicer. The change in oxygen content of the water was measured over 24 hours. The protocol differed from a standard wastewater BOD test in that the objective was to measure oxygen loss under conditions as realistic as possible (low temperature, high O_2 content, natural abundance of microbes).

The BOD test was designed in such a way as to demonstrate not only the potential of deicers to alter oxygen content of stream water taken from the sampling sites, but also the degree of natural variation in BOD from one site to another. For this reason, each deicer was tested with water from a different field site.

Because of a new emphasis in 1997-1998 on the comparison of magnesium chloride deicer with salt and sand mixtures, BOD tests were done also on salt and sand available in winter, 1997-98.

For tests involving deicer, water was transported from the field sites to a laboratory incubator where it could be maintained at a temperature close to the temperature of water at the field site (1-5°C). Water from all sites was tested in duplicate, and each site was represented by two stream water controls to which nothing was added. The test bottles for magnesium chloride deicer received 1 mL of deicing solution, which yielded a concentration of 1/333, or 0.3% deicer. This dilution is about 1.5 times the estimated average concentration of deicer in runoff leaving the roadway. For tests of salt and sand, 2 g were added to each bottle (333 mL). The bottles were shaken periodically during the 24-hour test interval. In addition to the test bottles and site-specific controls, two deionized water controls were included for quality assurance purposes (no oxygen change would be expected in these bottles because of the absence of organisms and biotically active organic substrates).

The results for the BOD tests are shown in Table 7 and Figure 4. The deionized water controls showed no change in oxygen, as expected.

It is useful first to examine the oxygen demand for all of the stream water controls. There were six pairs of these (two replicates from each of six sites). The controls show evidence of site-to-site variation extending from about 0.05 to 0.11 mg O_2 per liter per day. Natural variation of this magnitude is expected. There is no evidence that the control and treatment locations for individual stream segments differ in any consistent way.

The table compares each of the deicing and salt with sand treatments with its appropriate site-specific control. As indicated by the table, there is no evidence for consistent increase in BOD as a result of the addition of either magnesium chloride deicer or salt with sand. In other words, the differences between controls and treatments in the table fall generally within the range

Sample Location/Type	Description	BOD (mg 0_2/L/day)
Deionized Water Control	Control 1	0.000
	Control 2	0.003
	Mean	0.0015
S. Clear Creek Control	Control 1	0.067
	Control 2	0.055
	Mean	0.061
Salt/Sand	Redimix 18% 97-98 1	0.043
	Redimix 18% 97-98 2	0.052
	Mean	0.0475
Clear Creek Control	Control 1	0.043
	Control 2	0.070
	Mean	0.0565
Deicer	GMCO98ST Silverthorne 97-98 1	0.061
	GMCO98ST Silverthorne 97-98 2	0.046
	Mean	0.0535
Deicer	GMCO98 ST Empire 97-98 1	0.083
	GMCO98 ST Empire 97-98 2	0.028
	Mean	0.0555
Laskey Gulch Control	Control 1	0.110
	Control 2	0.113
	Mean	0.1115
Deicer	FreezeGard 96-97 1	0.073
	FreezeGard 96-97 2	0.104
	Mean	0.0885
Straight Creek Control	Control 1	0.061
	Control 2	0.080
	Mean	0.0705
Salt/Sand	Everist 5% 97-98 1	0.034
	Everist 5% 97-98 2	0.101
	Mean	0.0675
N. Clear Crk-Upper Control	Control 1	0.073
	Control 2	0.080
	Mean	0.0765
Deicer	FreezeGard 97-98 (Tank) 1	0.113
	FreezeGard 97-98 (Tank) 2	0.101
	Mean	0.1070
Deicer	FreezeGard 97-98 (Truck) 1	0.043
	FreezeGard 97-98 (Truck) 2	0.040
	Mean	0.0415
N. Clear Crk-Lower Control	Control 1	0.092
	Control 2	0.092
	Mean	0.092
Salt/Sand	Mt Aggregate 5% 97-98 1	0.092
	Mt Aggregate 5% 97-98 2	0.095
	Mean	0.0935

Table 7. Results of BOD tests.

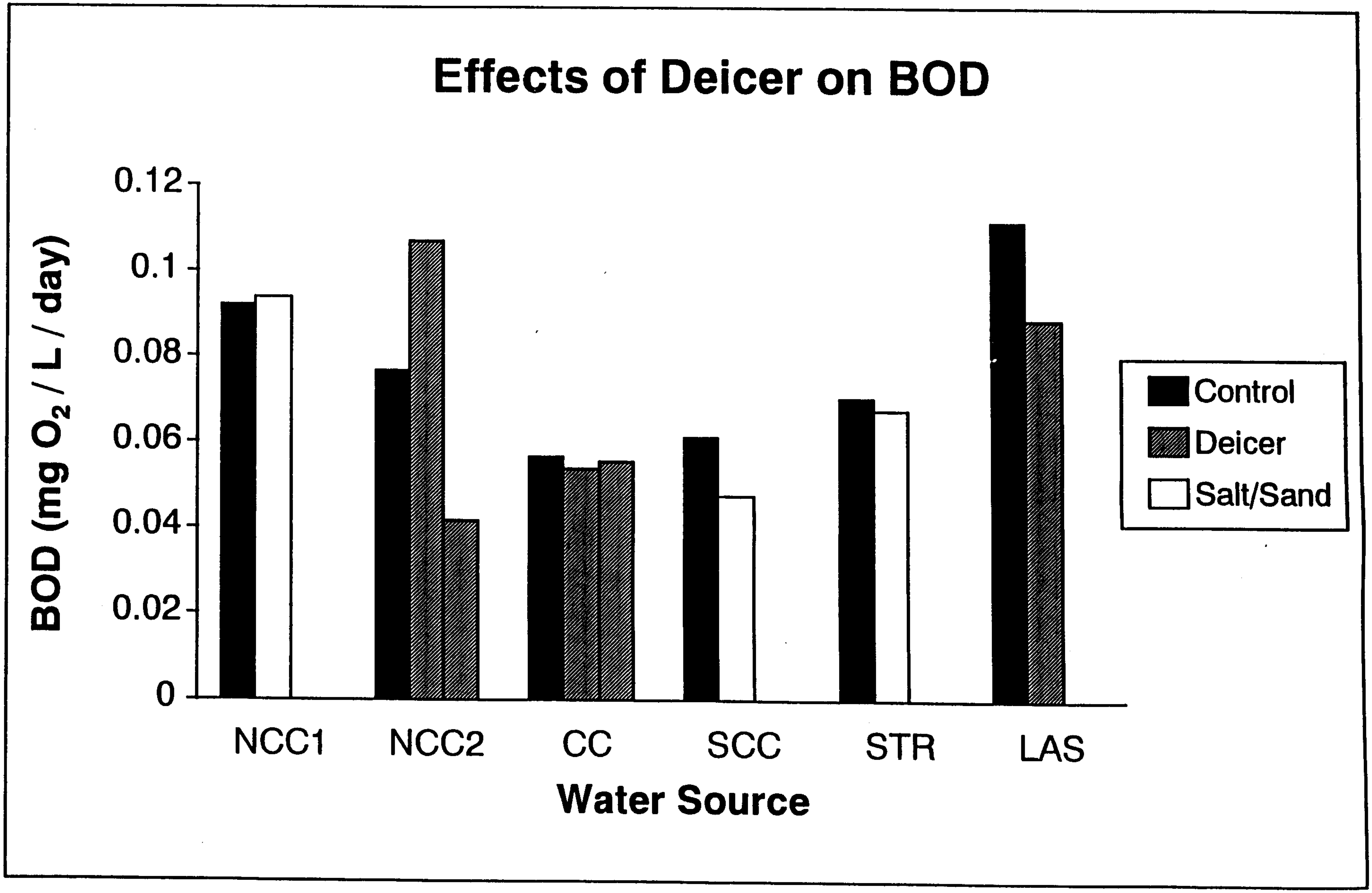

Figure 4. Results of BOD tests.

of controls, and therefore cannot be viewed as significant differences. One possible exception is the FreezeGard Zero sample taken directly from the delivery truck. This sample generated notably lower BOD than a sample of the same material taken from the storage tank. The lower BOD suggests a mild toxicity effect involving the suppression of respiration by microbes in the bottles to which deicer from the truck was added. As shown by biotoxicity testing (given below), biotoxicity effects could occur at the test concentration, which is about equal to concentrations expected just as the deicer leaves the roadway. It is not clear why the effect would occur in magnesium chloride taken directly from the truck but not in the same material taken from the storage tank.

Overall, there is no evidence for any significant increase in BOD of stream water. Very small increases could not be detected without more extensive replication. Such small changes in BOD would, however, have no significance with respect to the biological effects of stream oxygen concentrations.

Biotoxicity Testing

One means of estimating the environmental effects of chemical mixtures is to determine their toxicity by standardized testing under controlled laboratory conditions. Testing protocols for this type of work typically involve exposure of test organisms to a progressive series of concentrations. If mortality occurs and increases toward higher concentrations, it is possible to calculate a standard index value for toxicity, the LC50 (lethal concentration required to produce 50% mortality). In fact, procedures of this type are the main basis for numeric standards protective of aquatic life in Colorado, as determined by the Water Quality Control Commission of Colorado and the USEPA Region VIII.

Toxicity testing for 1996-97 deicer was conducted on four kinds of organisms: boreal toad (*Bufo boreas*), rainbow trout (*Oncorhynchus mykiss*), water flea (*Ceriodaphnia*), and unicellular algae (*Selenastrum*). Some background on each of these organisms is given in connection with the results described below. This range of organisms represents the main groups potentially affected by deicer in aquatic environments (amphibians, fishes, invertebrates, and algae). While individual species of organisms do show variation in chemical sensitivity, the inclusion of four very different kinds of organisms provides a broad view of the level of toxicity potential for magnesium chloride deicer.

Although protocols vary from one group of organisms to another, all organisms were tested under controlled growing conditions at a range of concentrations of deicer. The concentrations were chosen on the basis of some initial scope-finding work.

A special feature was added to the bioassay tests on tadpoles. For these organisms, tests on deicing material were run parallel with equivalent tests of a solution of magnesium chloride from regent-grade (pure) sources. The pure magnesium chloride solution differs from the deicer in its lack of corrosion inhibitor and contaminants. This allowed a comparison of magnesium chloride per se with deicer, which contains not only magnesium chloride but also small amounts of other materials that might affect the toxicity of the mixture.

As is standard for toxicity testing, all tests involved the use of controls, i.e., a group of organisms maintained under identical conditions as the test organisms but not exposed to deicer. Successful toxicity testing requires proof that the organisms can be maintained in healthy condition within the laboratory for the test interval, and this proof is achieved by use of control organisms that are not exposed to substances being tested.

Tests on the toads, fish, and invertebrate species were conducted under the supervision of Dr. Pat Davies and Mr. Stephen Brinkman of the Colorado Division of Wildlife. Tests of algae were conducted under the supervision of Dr. Richard Dufford, consulting phycologist.

Boreal Toad Tadpoles: Tests with 1996-97 Deicer

The boreal toad is native to montane regions of Colorado and in the past has been quite abundant throughout much of the Southern Rockies. Like many amphibians, the boreal toad has been declining steadily in abundance for over a decade.

At present, the boreal toad is listed as an endangered species because of its low abundance and restricted distribution.[4]

The boreal toad was chosen as a test organism because the application of deicing materials occurs in watersheds where the boreal toad is now present as reproducing populations. Thus the toad not only represents amphibians in general, but also the special concern for this particular species. Because the boreal toad is not a standard bioassay test organism, the test

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[4]The boreal toad population of the Southern Rockies is a candidate for Federal listing under the Endangered Species Act. Because of the backlog of species of similar status, U.S. Fish and Wildlife Service has not yet had the opportunity to determine whether the population should be categorized as threatened, endangered, or neither by the Federal government. Species that are candidates for listing under the Federal statute receive special protection and consideration by Federal agencies until their status has been finalized. The population has a priority 3 with U.S. Fish and Wildlife Service on a scale of 1-10, suggesting that the population will eventually be categorized as federally threatened or endangered. In the meantime, the state of Colorado has classified the southern population of the boreal toad within Colorado as endangered. Species listed by the State receive special protection and study under direction of the Colorado Division of Wildlife.

protocol for it is not standardized. The bioassay for the boreal toad in this study does resemble very closely the standard protocols that are used for other test organisms, however (see below).

The tadpole stage of the boreal toad was used for testing because this stage has an extended dependence on acceptable water quality for growth and development to the mature toad, which is primarily terrestrial.

Ten boreal toad tadpoles were used for each treatment and for the controls. Test concentrations and controls were represented by two replicates. The control consisted of source water only (dechlorinated tapwater), and the treatments consisted of 5%, 1% and 0.1% dilutions of deicing compound (FreezeGard Zero 1996-97) and 10%, 2% and 0.2% dilutions of a pure magnesium chloride solution. The tadpoles were tested during the middle stage of development. The tests were conducted in 250-mL beakers containing 100ml each of water or test solution. The beakers were aerated gently and were kept at 12 degrees centigrade with a 12/12 photoperiod. Mortality was recorded daily. Living tadpoles were transferred to fresh solutions every 24 hours over the test interval of 96 hours.

Table 8 and Figure 5 summarize the test results. The table gives not only the mortality in terms of numbers of individuals and percentages, but also reports the hardness of each test solution. The hardness of test solutions containing magnesium chloride deicer is higher than the hardness of the control because magnesium is a component of hardness. Hardness may be relevant to the interpretation of test results because increased hardness reduces the toxicity of metal contaminants in water.

As shown by Table 8, there was no mortality among the control organisms over the entire 96-hour test interval. This indicates that the test conditions were satisfactory for the maintenance

		Deicer			Pure Magnesium Chloride*		
	Control	0.1%	1.0%	5.0%	0.2%	2.0%	10.0%
Hardness (mg/L $CaCO_3$)	56	500	4110	21,060	446	3572	16,690
24 hr. Mortality (%)	0	0	0	100	0	0	100
48 hr. Mortality (%)	0	0	10	100	0	0	100
96 hr. Mortality (%)	0	0	100	100	0	100	100

*Shown here is percent dilution of a pure $MgCl_2$ solution of the same ionic strength as the deicer solution (28% by mass).

Table 8. Hardness and mean mortality of boreal toad tadpoles exposed to various dilutions of pure magnesium chloride solution and deicing compound (FreezeGard Zero, 1996-97).

of the living organisms. In addition, there was no mortality among organisms treated with 0.1% deicer. Mortality occurred among tadpoles exposed to 1% deicer, but only after 48 hours or more. The 5% solution produced quick and consistent 100% mortality.

The pure magnesium chloride solution used for comparison shows in Table 8 as similar in toxicity to the deicing material or perhaps slightly less toxic. In other words, the results suggest that the additive toxicity of contaminants and rust inhibitors in the deicer is small for boreal toads.

Boreal Toad Tadpoles: Tests with 1997-98 Deicer

The boreal toad bioassay of 1997 was repeated in 1998 with 1997-98 deicer. Conditions of the bioassay were the same as for 1997 except for a few adjustments. There were three

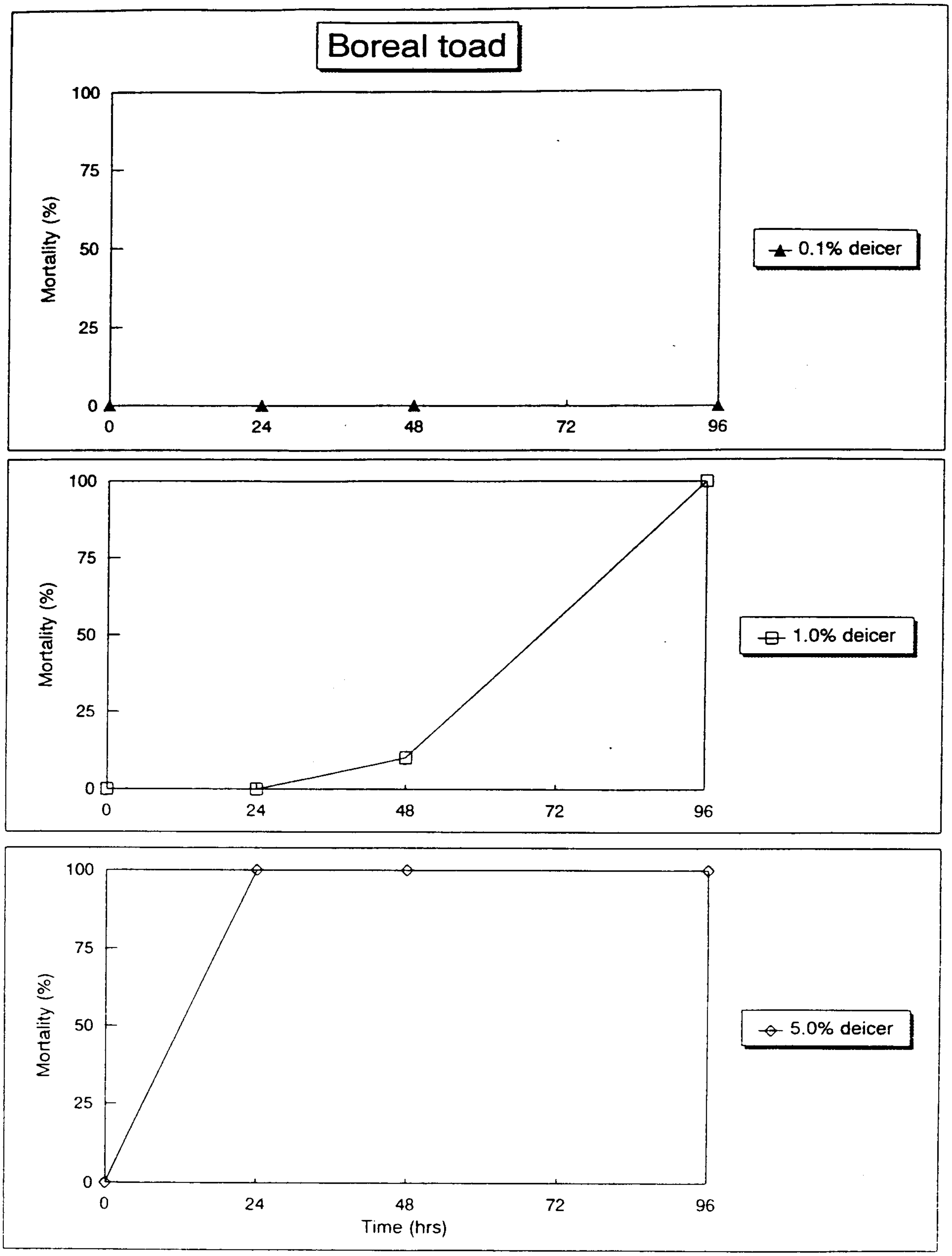

Figure 5a. Biotoxicity tests on the boreal toad tadpole.

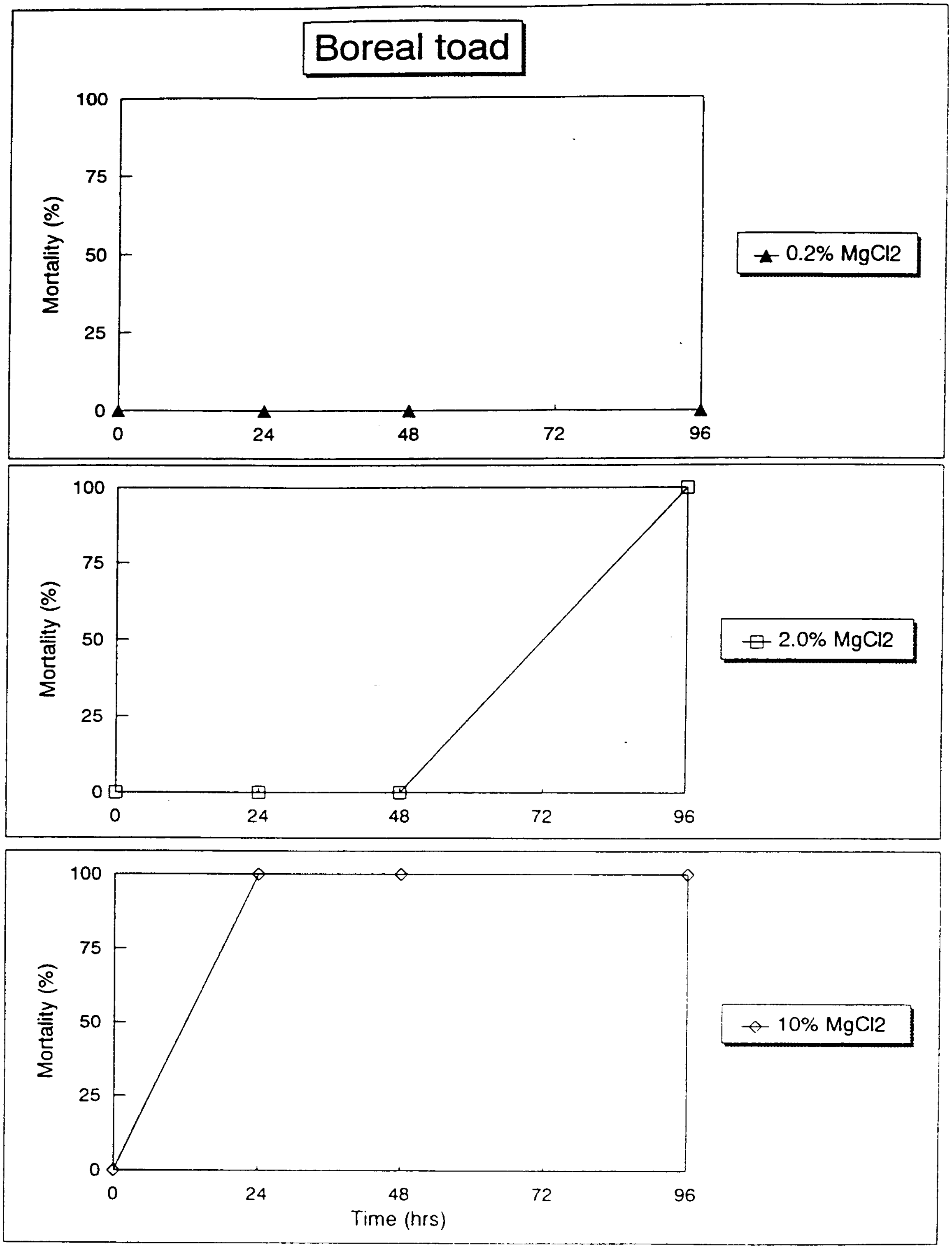

Figure 5b. Biotoxicity tests on the boreal toad tadpole.

replicates in 1998 rather than two, as in 1997. In addition, the range of concentrations differed slightly between the two years (0.1, 1.0, 5.0% in 1997; 0.1,0.5, 1.0, and 2.0% in 1998).

The method of measuring biotoxicity was somewhat different in 1998 than in 1997. In 1997, mortality was measured at intervals of 24, 48, and 96 hours. In 1998, mortality was measured after a much longer interval (168 hours), and the tadpoles were examined individually for diagnosis of developmental stage (Gosner stage) at the end of 168 hours. The value of the Gosner diagnosis is that it provides a sublethal indicator of stress, given that stress is likely to retard development.

Results of the 1998 bioassay are summarized in Table 9. There was no mortality among tadpoles at any concentration of deicer up to the maximum (2%) within 168 hours (7 days). The results were generally similar to those of 1997 (mortality at 2% deicer in 1997 may be explained by slight variations in holding conditions or developmental stage).

In 1998, the study of Gosner development stage showed significant suppression of development at all doses of deicer down to the lowest that was used in the bioassay (0.1%). This result indicates progressive physiological stress sufficient to retard development at concentrations at or above 0.1%. Also, since the degree of developmental retardation appears to be related to concentration, the data imply that concentrations of deicer below 0.1% would also cause some measurable depression of development. If the relationship between concentration and developmental stages is represented by a power function, the no-effect concentration corresponds to about 0.02% deicer. This treatment of the data has a rather weak foundation because of the small number of concentrations and the lack of any information on concentrations below 0.1%.

	Control	Deicer 0.1%	0.5%	1.0%	2.0%
Hardness (mg/L Ca CO_3)	62	2006	4902	15,220	29,600
168 hr. Mortality (%)	0	0	0	0	0
Gosner Development Stage (std. deviation)**	16.3 (0.4)	14.7 (0.6)*	13.6 (0.5)*	13.3 (0.4)*	12.3 (0.9)*

* Significantly lower than control ($p<0.05$).
** Stage at the start of the test was approximately 11.

Table 9. Hardness, mean mortality, and developmental stages of boreal toad tadpoles exposed to deicing compound (FreezeGard Zero, 1997-98) used by the Colorado Department of Transportation.

Rainbow Trout: Tests of the 1996-97 Deicer

The rainbow trout was selected for testing because it is generally representative of the multiple salmonid species that may be found at high elevation Colorado. Although introduced, rainbow trout is the main basis for Colorado fisheries supported by stocking and shows natural reproduction in Colorado waters. Rainbow trout is the most widely used bioassay organism among the cold water fishes.

Hatchery reared rainbow trout with a mean length of 41 mm (0.68 grams) were tested in 2.5-liter glass chambers. Initial range finding studies indicated that test solutions should fall between 5% and 0.5% deicer. Treatments were as follows: 5%, 2.5%, 1%, 0.5%. In addition, a control was maintained. The tests were conducted under environmental conditions and for durations as indicated above for the boreal toad, except that each treatment as well as the control was replicated 3 times instead of 2 times.

As shown in Table 10 and Figure 6, survival of the controls was 100%, which indicates that maintenance conditions for the fish were satisfactory for the test. Mortality of fish began at the lowest concentration of deicer (0.5%). This concentration resulted in low mortality over 96 hours. At 1% deicer, mortality was higher, but did not occur in the first 24 hours. At 2.5%, mortality was complete by 48 hours, and at 5% mortality was complete after 24 hours.

The test results indicate that rainbow trout fall within the same general range of sensitivity as the boreal toad, but that the boreal toad is slightly more sensitive.

Rainbow Trout: Tests of 1997-98 Deicer

Biotoxicity tests for rainbow trout were identical to those for 1997, except that mortality readings were taken after 72 hours as well as 24, 48, and 96 hours. The fish had an average length of 31 mm and an average mass of 0.26 g.

Table 11 summarizes the results of the bioassay. The results were essentially identical to those of 1998. At the shortest exposures (24 hours), mortality did not begin to appear until concentrations reach 2.5%. At the longest exposures (96 hours), small numbers of fish died at concentrations of 0.5%.

Ceriodaphnia: Tests of 1996-97 Deicer

Ceriodaphnia belongs to a group of organisms that occur commonly in many kinds of aquatic environments of Colorado. In addition, this organism thrives under culture conditions. *Ceriodaphnia* is the main invertebrate test organism used in federally and state mandated whole effluent (WET) testing. In fact the organism has been so widely used in testing that protocols

	Control	0.5%	1.0%	2.5%	5.0%
Hardness (mg CaCO3/L)	61	2240	4542	11650	-
Conductivity (μS/cm)	117	3520	6620	15520	-
24 hr. Mortality (%)	0.0	0.0	0.0	63[3]	100
48 hr. Mortality (%)	0.0	0.0	0.0	100	100
96 hr. Mortality (%)	0.0	4[1]	29[2]	100	100

[1]s.d.=7
[2]s.d.=26
[3]s.d.=33

Table 10. Hardness, conductivity, and mean percent mortality of rainbow trout exposed to dilutions of deicer (FreezeGard Zero, 1996-97) for 24, 48, and 96 hours.

	Control	0.5%	1.0%	2.5%	5.0%
24 hr. Mortality (%)	0	0	0	5[1]	85[3]
48 hr. Mortality (%)	0	0	0	5[2]	95[4]
72 hr. Mortality (%)	0	0	17[2]	100	100
96 hr. Mortality (%)	0	7[1]	50[3]	100	100

[1]s.d.=12
[2]s.d.=3
[3]s.d.=0
[4]s.d.=30

Table 11. Mean percent mortality of rainbow trout exposed to dilutions of deicer (FreezeGard Zero 1997-98) for 24, 48, 72, and 96 hours.

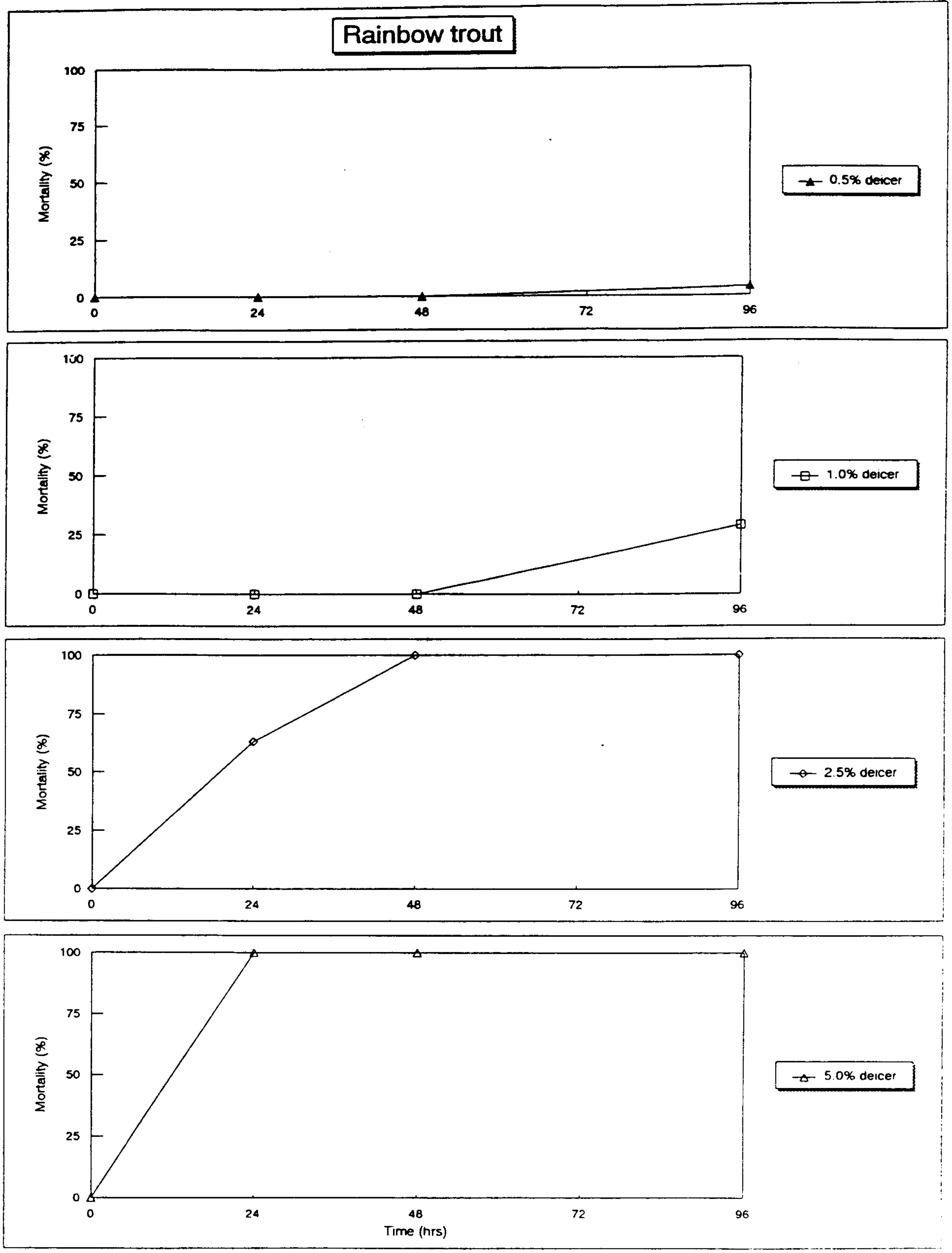

Figure 6. Biotoxicity tests on rainbow trout.

have been developed by the EPA for standardized testing. These protocols were followed in the deicer test (EPA 600/4-90/027F).

Range finding tests showed that *Ceriodaphnia* was likely to be more sensitive than rainbow trout or boreal toad tadpoles. For this reason, the test solutions were set as follows: 0.031%, 0.062%, 0.125%, 0.25% and 0.5%. Following the EPA protocol, the tests were run for only 48 hours rather than 96 hours, as for the vertebrate species. Dilution and control water were collected directly from the Cache la Poudre river above the Division of Wildlife Poudre River Rearing Unit rather from the tap water dechlorinator because of the high sensitivity of *Ceriodaphnia*. Four replicates were used, and there were 5 organisms per replicate.

Table 12 and Figure 7 show the results of the *Ceriodaphnia* toxicity test. As indicated in the table, mortality began to occur at concentrations as low as 0.125% deicer. At 0.25%, mortality was almost complete, and complete mortality occurred at concentrations of 0.5% within 24 hours.

The tests indicate that *Ceriodaphnia* is considerably more sensitive to deicer than either fish or tadpoles. Given the general nature of literature on *Ceriodaphnia* and vertebrate organism such as tadpoles and fishes, the greater sensitivity of *Ceriodaphnia* is not surprising, and may be reflective of relatively high sensitivity in a variety of aquatic invertebrates.

Because *Ceriodaphnia* reproduces more or less constantly during laboratory culture, a second and more subtle type of toxicity test was possible with *Ceriodaphnia*. *Ceriodaphnia* produces and holds embryonic offspring (neonates) in a brood pouch on the back of the female organism (populations are parthenogenetic and typically consist exclusively of females). The rate at which females produce neonates is a reflection of the health of the female. For this

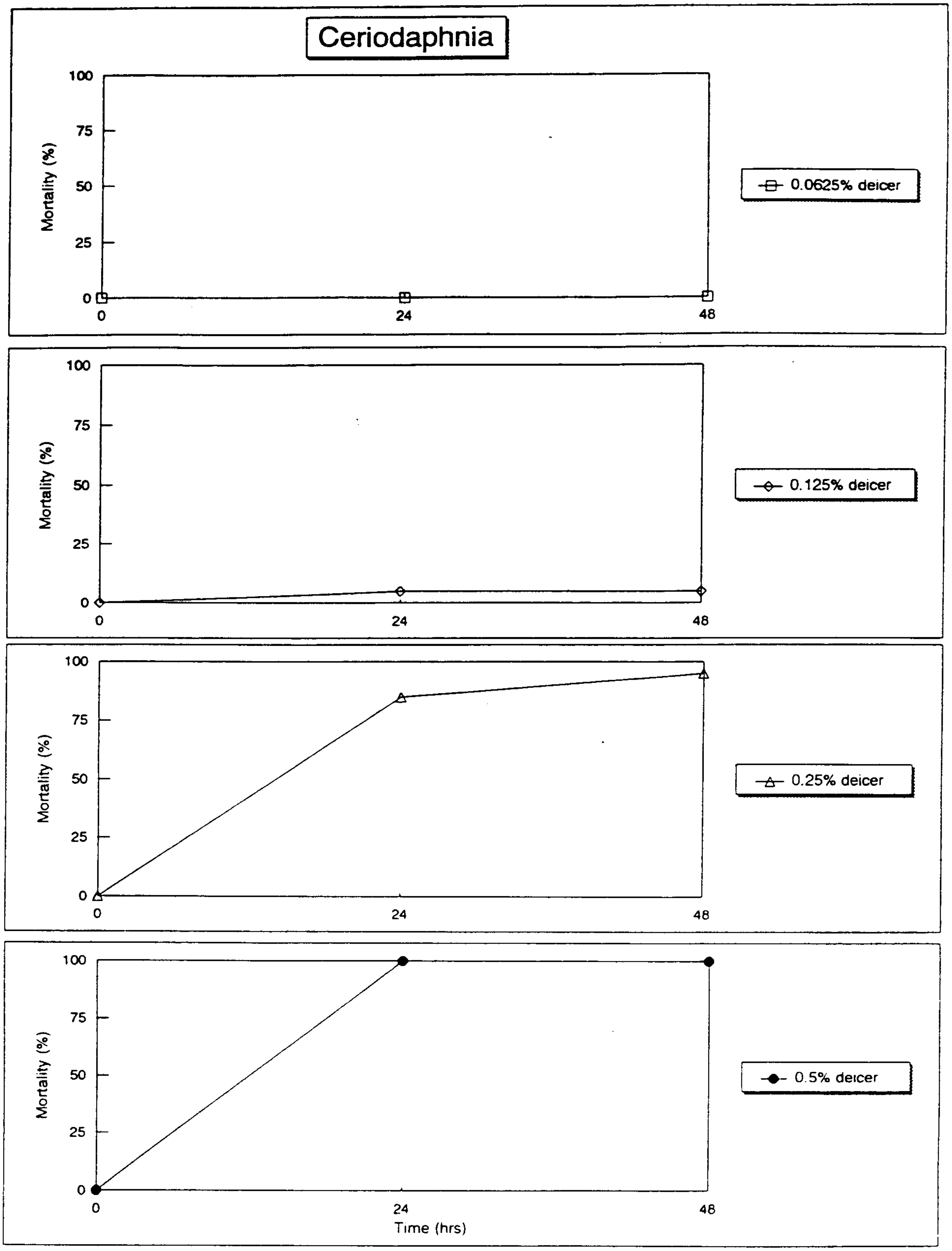

Figure 7. Biotoxicity tests on Ceriodaphnia.

	Control	0.03125%	0.0625%	0.125%	0.25%	0.5%
24 hr. Mortality (%)	0	0	0	5[1]	85[3]	100
48 hr. Mortality (%)	0	0	0	5[2]	95[4]	100

[1]s.d.=10
[2]s.d.=10
[3]s.d.=19
[4]s.d.=10

Table 12. Mean mortality of *Ceriodaphnia* exposed to dilutions of deicing compound (FreezeGard Zero 1996-97) for 24 and 48 hours during the toxicity test.

reason, slight physiological impairment of the female, even if insufficient to cause actual mortality, will appear as suppression of the production of neonates.

A neonate test was conducted with 7 replicates at low concentrations as follows: 0.0125%, 0.025%, 0.05%, 0.10%, 0.20%. Results are shown in Table 13 and Figure 8. The test was conducted by recognized EPA methodology (EPA 600/4-89/001). Although the number of neonates shows some irregularities in the low range of concentrations, the number of neonates per female shows statistical deviation from the control at deicer concentrations of 0.1% and higher.

Ceriodaphnia: *Tests with 1997-98 Deicer*

The *Ceriodaphnia* bioassay was repeated during June of 1998 with FreezeGard Zero deicer obtained from a vendor delivery truck on January 8, 1998. The method of testing was identical to that used during 1997, except that slightly different ranges of concentrations were used, and mortality was obtained after 48 hours rather than both 24 hours and 48 hours, as in 1997. The results are summarized in Table 14.

	Control	0.0125%	0.025%	0.050%	0.10%	0.20%
Neonates per Female	23.6(4.3)	20.1(6.1)	17.3(5.4)*	21.9(4.2)	8.6(4.0)*	0.3(0.8)*

* Significantly different from control ($p<0.05$)

Table 13. Mean number of *Ceriodaphnia* neonates per female exposed to dilutions of deicing compound (FreezeGard Zero, 1996-97). Standard deviations in parentheses.

	Control	0.05%	0.10%	0.125%	0.20%	0.25%
48 hr. Mortality (%)	5[1]	0	5[2]	5[3]	60[4]	100

[1]s.d.=10
[2]s.d.=10
[3]s.d.=10
[4]s.d.=37

Table 14. Mean mortality of *Ceriodaphnia* exposed to dilutions of deicing compound (FreezeGard Zero 1997-98) for 48 hours.

As shown in Table 14, the highest concentration of deicer (0.25%) resulted in 100% mortality within 48 hours. The LC50, as estimated by probit analysis, was 0.175% (95% confidence limits: 0.159 - 0.193). This LC50 is very similar to the one obtained in 1997 (0.177%). The no-effect level for the test fell near 0.1% deicer, as in 1997.

For the non-lethal test, which involved the counting of neonates per female in the presence of various concentrations of deicer, the threshold for statistically significant effects fell between 0.025% and 0.05% (Table 15). The results were very similar to the results for 1997.

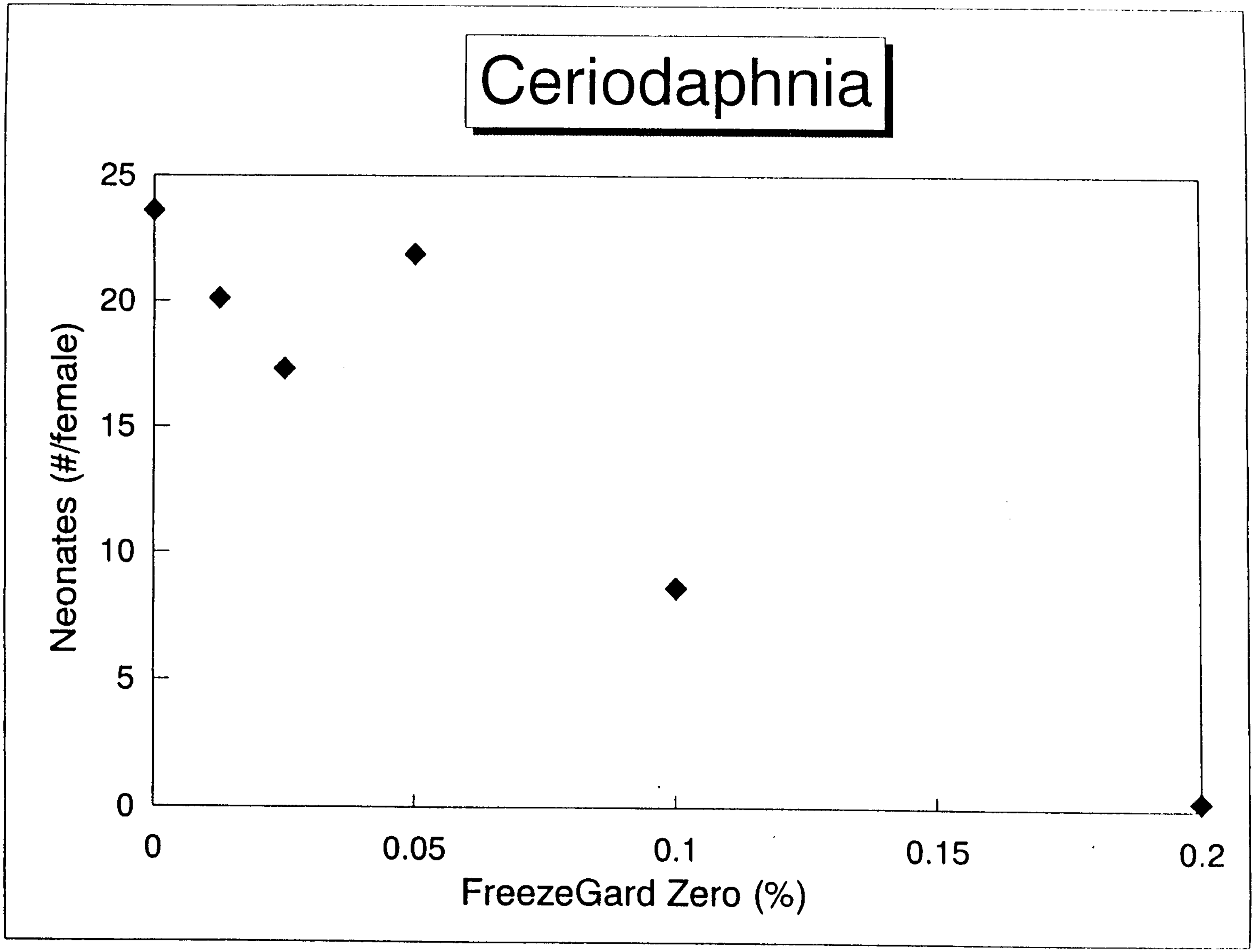

Figure 8. **Biotoxicity tests on *Ceriodaphnia* (neonates).**

	Control	0.0125%	0.025%	0.050%	0.10%	0.20%
Neonates per Female	33.1(5.5)	32.7(5.4)	31.2(5.2)	20.2(8.5)*	4.9(5.1)*	0.0(0)*

* Significantly different from control ($p<0.05$)

Table 15. Mean number of *Ceriodaphnia* neonates per female exposed to dilutions of deicing compound (FreezeGard Zero, 1997-98). Standard deviations are shown in parentheses.

Selenastrum

In streams receiving roadside runoff, unicellular algae will be represented by a complex community consisting of 50 or more species. Although species vary in their sensitivity, species of the genus *Selenastrum* are often used as a general representative of algal response to toxic agents.

The protocol for the *Selenastrum* bioassay is based on EPA guidelines for algal bioassay (EPA 600-4-91-002; July 1994). Individual flasks (125-mL) were seeded with equal numbers of cells from an algal culture (Texas Culture Collection). The flasks contained water and growth medium sufficient to insure that the cells could take up sufficient nutrients to grow at their physiological maximum (at 26°C) over the course of the incubation. The flasks were maintained under continuous light at sufficient intensities to insure rapid growth. The growth interval extended over 96 hours, and included periodic agitation of the samples.

Growth of *Selenastrum* is referenced to a set of control flasks containing water and growth medium but lacking deicer. Concentrations of deicer in treatment flasks were 0.156%, 0.312%, 0.625%, 1.25%, and 2.5%.

Cells from each flask were counted quantitatively at the end of the 96-hr growth interval and converted to cells per milliliter. In addition, the appearance of the cells was recorded for each flask.

Results of the algal bioassay are summarized in Table 16 and Figure 9. The last column of numbers in the table shows the percent growth over the 96-hour interval. As shown by the table, the abundance of cells increased 50-fold over the 96-hour interval in the control flasks. The increase was almost as great at deicer concentrations of 0.156%. At greater concentrations of deicer, there was a notable depression of the amount of growth. At concentrations of deicer equal to 2.5%, growth essentially ceased. Cells showed reduced rates of division at 0.15 - 0.30%deicer and began to show other signs of physiological stress at concentrations of deicer between 0.3 and 0.6%.

Overview of Bioassay Results

The bioassay results are summarized in Table 17 and Figure 10. Results for tadpoles, trout, and *Ceriodaphnia* are expressed in terms of LC50, i.e., the threshold concentration required to result in 50% mortality in the test population after the specified duration of exposure. The data are expressed in slightly different form for *Selenastrum*: the percent given for *Selenastrum* is the concentration required to reduce the growth rate of the population by 50%.

Threshold concentrations shown in Table 17 vary from one type of organism to another. *Ceriodaphnia* appears to be the most sensitive and trout the least sensitive. Taking all of the results together, it appears that the threshold for observable biological effects over exposures of

Deicer Concentration (%)	Start (0 hr)	Stop (96 hr)	S. D.	% Growth	Comments
Control	11,929	600,717	11,959	4936	small green dividing cell
0.156	11,630	535,340	37,319	4503	small green dividing cells
0.312	11,800	387,887	73,172	3187	small green dividing cells
0.625	11,645	274,656	55,312	2259	small green cells
1.25	11,602	73,059	43,843	525	large green cells
2.5	11,566	26,824	3007	132	large yellow senescent cells

Table 16. Results of algal (*Selenastrum*) bioassay with deicer (FreezeGard Zero, 1996-97). Numbers are cells per mL.

	Boreal Toad Tadpoles		Rainbow Trout	*Ceriodaphnia*	*Selenastrum*
	Pure $MgCl_2$*, %	Deicer %	Deicer, %	Deicer, %	Deicer, %
24 HR. LC50(%)	4.4	2.2	2.5	0.26	-
48 HR. LC50(%)	4.4	1.8	1.8	0.19	-
96 HR. LC50(%)	0.65	0.32	1.4	-	0.55**

* Percent dilution in the table is for an $MgCl_2$ solution of the same ionic strength as the deicer.
** Concentration at which growth rate is reduced 50%.

Table 17. Summary of biotoxicity data (1997 and 1998 combined).

short to medium duration would fall between 0.02 and 0.1% deicer. This impression is confirmed by the sensitive *Ceriodaphnia* neonate tests, which show evidence of sublethal effects at a concentration range between 0.05 and 0.10%. The boreal toad test involving pure

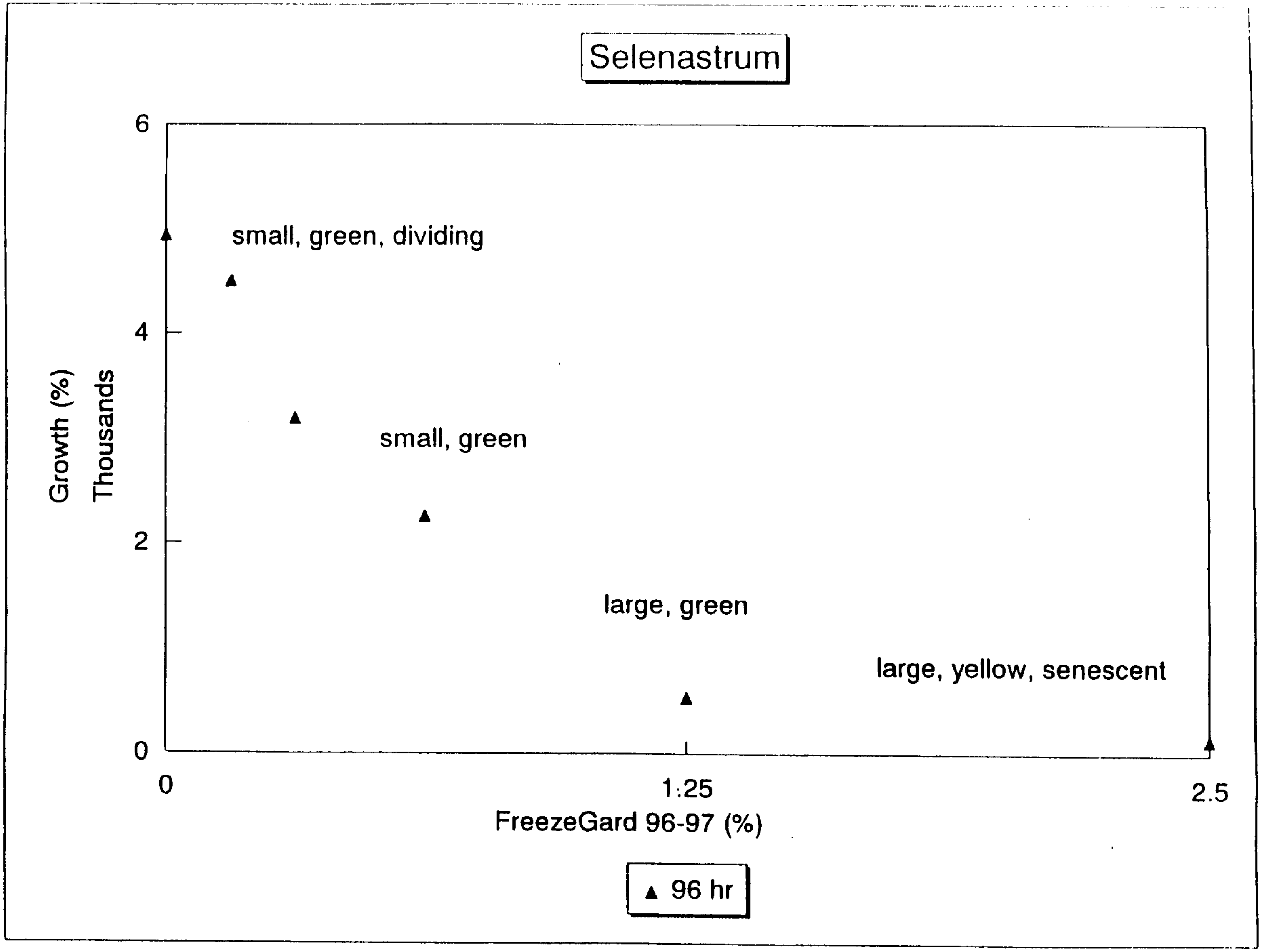

Figure 9. _Selenastrum_ biotoxicity test.

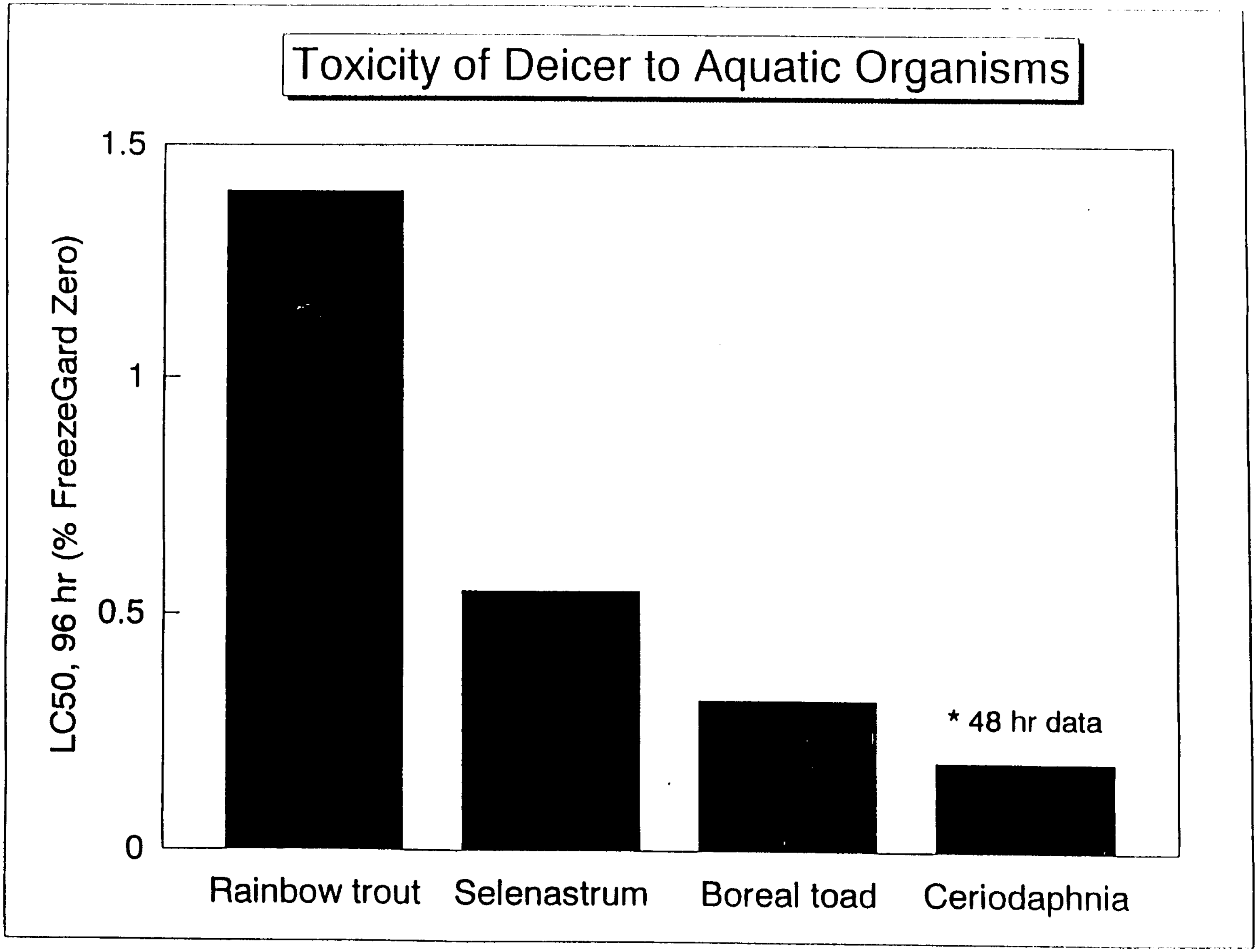

Figure 10. Summary of biotoxicity tests.

magnesium chloride indicates that toxicity is mainly explained by magnesium and chloride ions, and not by contaminants or rust inhibitors, although the contaminants and inhibitors may have a small additive effect on toxicity.

Mass Balance Studies

The purpose of the mass-balance studies is to relate the application of deicer to concentrations of deicer components in surface waters receiving drainage from highways. Although this portion of the study could have been approached strictly from the viewpoint of concentrations, a more fundamental understanding is achieved by mass-balance analysis, which relates the mass of substance applied to the highway to the mass transport of the same substance by adjacent streams.

Study Segments

The mass balance studies were carried out in three pairs of study segments, as shown in Table 18. For each of the three pairs, one study segment served as a control, i.e., it received no application of deicer. One of the control segments did receive salt with sand, however. Paired with each control segment is a study segment that serves as the treatment, i.e., it received routine application of deicer at known rates. Contrary to planning, the control segment above Blackhawk did receive some deicer.

Study Section Designation	Highway Lanes	$MgCl_2$ Deicer Gallons/Mile		Salt with Sand Tons/Mile	
		1997[4]	1998	1997	1998
West Portal Area					
Laskey Gulch (LAS, control)	0	0	0	0	0
Straight Creek[1] (STR, treatment)	4	12,000	11,000	1000	1200
East Portal Area					
South Clear Creek (SCC, control)	2	0		–	
Clear Creek, Tunnel to Georgetown (CC, treatment)[2,3]	4	12,000	15,000	1000	400
North Clear Creek					
Above Blackhawk (NCC2, control)[2]	2	540	660	160	120
Below Blackhawk (NCC1, treatment)[3]	2	625	1700	240	120

[1]GMCO
[2]Inadvertently received some treatment.
[3] Envirotech FreezeGard Zero
[4]Here and elsewhere in the mass-balance analysis, 1997 indicates 1 November 1996 to 31 October 1997; 1998 indicates 1 November 1997 to 31 October 1998.

Table 18. Amounts of deicer and salt with sand added to study areas (amount per mile of roadway, as recorded by CDOT).

One pair of study segments was located at moderate elevation (near Blackhawk), and the other two were located at high elevation (near the Eisenhower Tunnel), as shown by Table 18 and Figures 1 through 3.

For the mass-balance analysis, the actual application rates for deicing materials, and also the application rates for salt and sand, are essential. A summary of the application rates is shown in Table 18.

Time Intervals

Because the information on mass balance spans two years, it is possible to make two annual mass balances for each station. Use of calendar years is not desirable for this purpose because both deicer and salt with sand are applied across the transition between calendar years. Separation of the data by water years (i.e., beginning October 1) would be suitable, but the data collection did not begin until November of 1996. Therefore, the time span 1 November - 31 October is used as the annual interval for mass balance. This interval captures the applications for a given snow season (minus perhaps some limited applications late in October), plus the following runoff season when the materials applied to the roadways during winter are most likely to be mobilized.

Discharge

The hydrograph for each one of the study segments is relevant to the interpretation of concentrations and is a component in the computation of mass balance for all substances. The hydrographs for all six study segments in 1997 are shown in Figure 11. As expected, all hydrographs are dominated by spring runoff, and all study segments show low flow between fall and early spring.

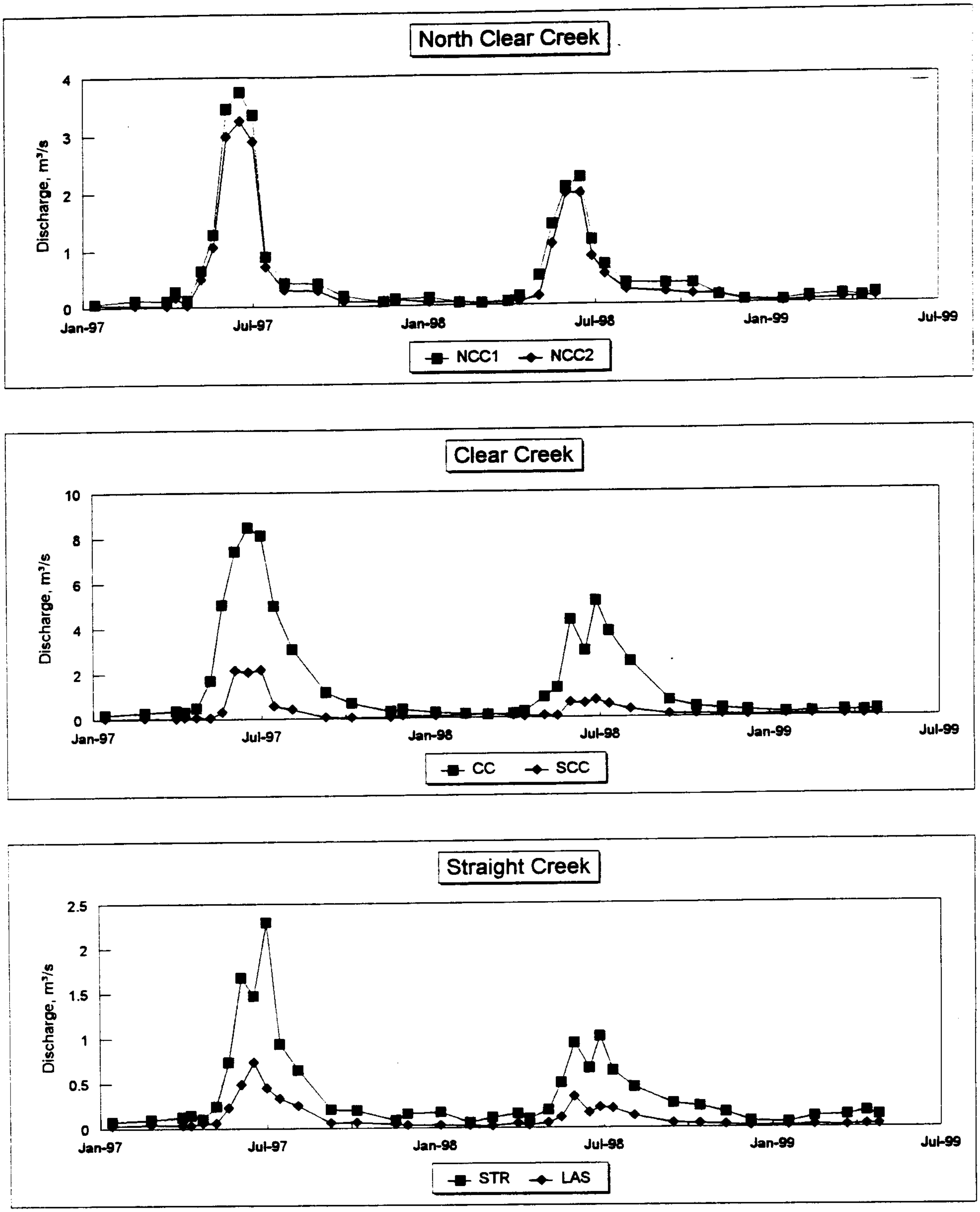

Figure 11. Discharge at study sites.

Magnesium

The concentrations of magnesium (Mg++) for all six study locations are shown in Figure 12 (see Table 19 for station codes used in Figure 12). Figure 13 shows the mass transport for the six stations, and Table 19 gives the annual total mass transport and the amount of magnesium added in the form of magnesium chloride during both years of sampling.

The control stations vary in magnesium concentration for any given time of the year, as expected given the variations in sizes of the streams and in their locations, but it is clear that magnesium chloride in deicer increases the concentrations of magnesium. Flows in the winter are small, and account for only a minor portion of total annual transport, which is dominated by the season of high discharge (spring runoff). During the winter, the discharge is sufficiently small that the magnesium added to the roadway has a large influence on the concentrations (2x or more). During the spring, the influence is smaller because the amounts of water moving past the stations are very large. There is no obvious reason for concern over elevated concentrations of magnesium, however, because magnesium in such small quantities as these is not known to have any negative effects on organisms or biological processes.

Table 19 shows that the total amount of magnesium transport on an annual basis for either a control site or a site receiving deicer is large. Individual stations vary in total transport mostly in relation to the total annual flow; stations with smaller total annual discharge transport smaller amounts of magnesium. The amount of magnesium added to the roadway expressed as a percentage of the total annual transport of magnesium also varies greatly. The amount of magnesium added is sufficient to augment total annual magnesium transport significantly for some locations (Straight Creek, upper Clear Creek), but not others (North Clear Creek). For

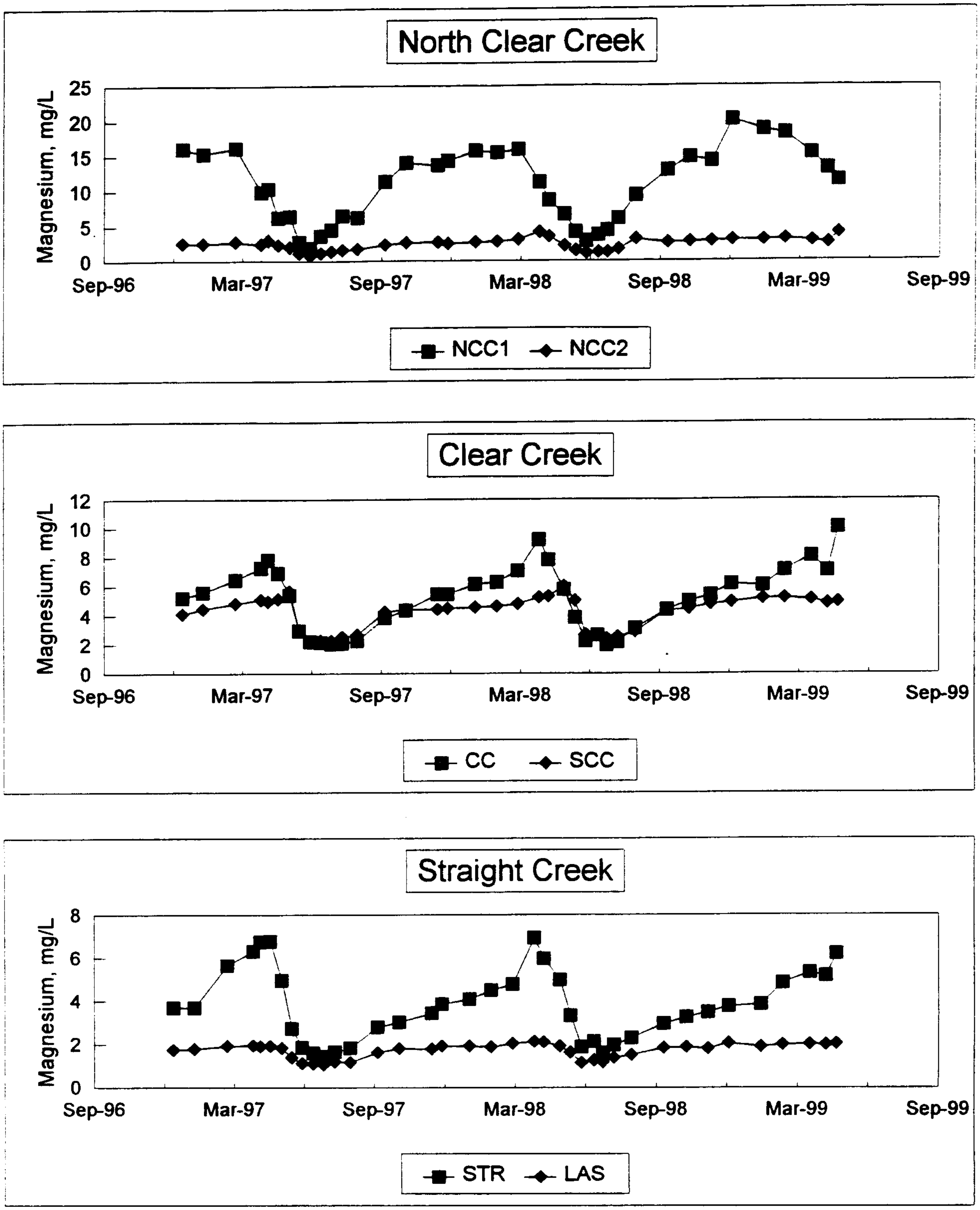

Figure 12. Magnesium concentrations.

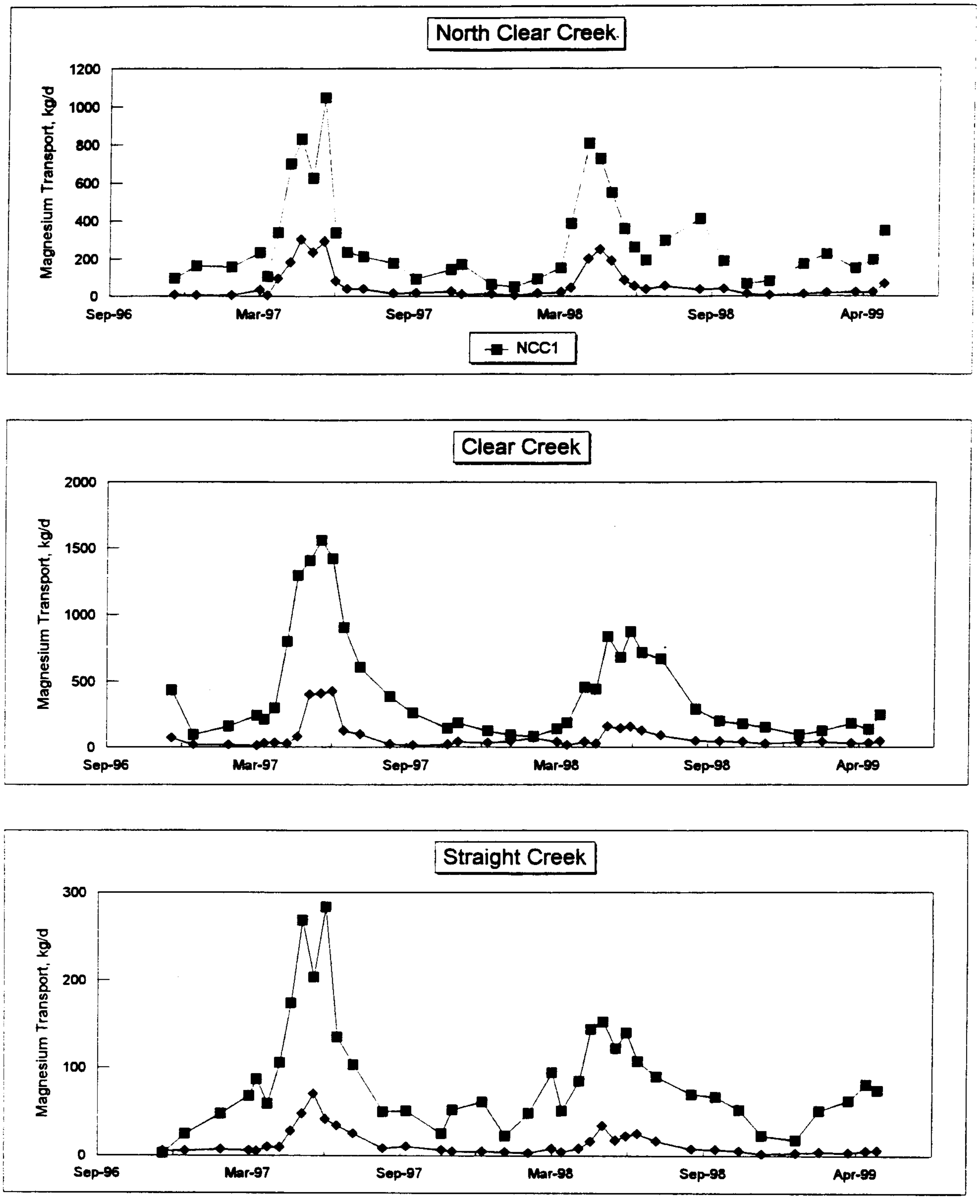

Figure 13. Magnesium transport.

	Discharge[1]		Transport[2]		Weighted Concentration[3]		Peak Concentration[3]		Amount Added[2]		Added as % Transport	
Stations	1997	1998	1997	1998	1997	1998	1997	1998	1997	1998	1997	1998
West Portal Area												
Laskey (Control)	4500	2600	5800	3900	1.3	1.5	1.9	2.1	0	0	0	0
Straight Creek (Deicer, Salt/Sand)	13,000	9,600	29,200	27,300	2.2	2.8	6.8	6.9	27,300	29,400	94	108
East Portal Area												
South CC (Control)	12,000	6800	32,000	23,100	2.7	3.4	5.7	6.0	0	0	0	0
Upper CC (Deicer, Salt/Sand)	65,400	38,000	192,000	122,000	2.9	3.2	7.9	9.2	49,000	67,600	26	56
North Clear Creek												
Upper (Control)	15,900	11,200	21,600	20,400	1.4	1.8	2.9	4.1	440	610	2.0	3.0
Lower (Deicer, Salt/Sand)	20,000	14,700	96,800	97,900	4.8	6.7	16.2	15.9	1300	4100	1.4	4.1

[1]Thousands of m^3 per year.
[2]kg per year of Mg added as deicer.
[3]mg/L, discharge weighted.

Table 19. Magnesium: mass transport and concentrations.

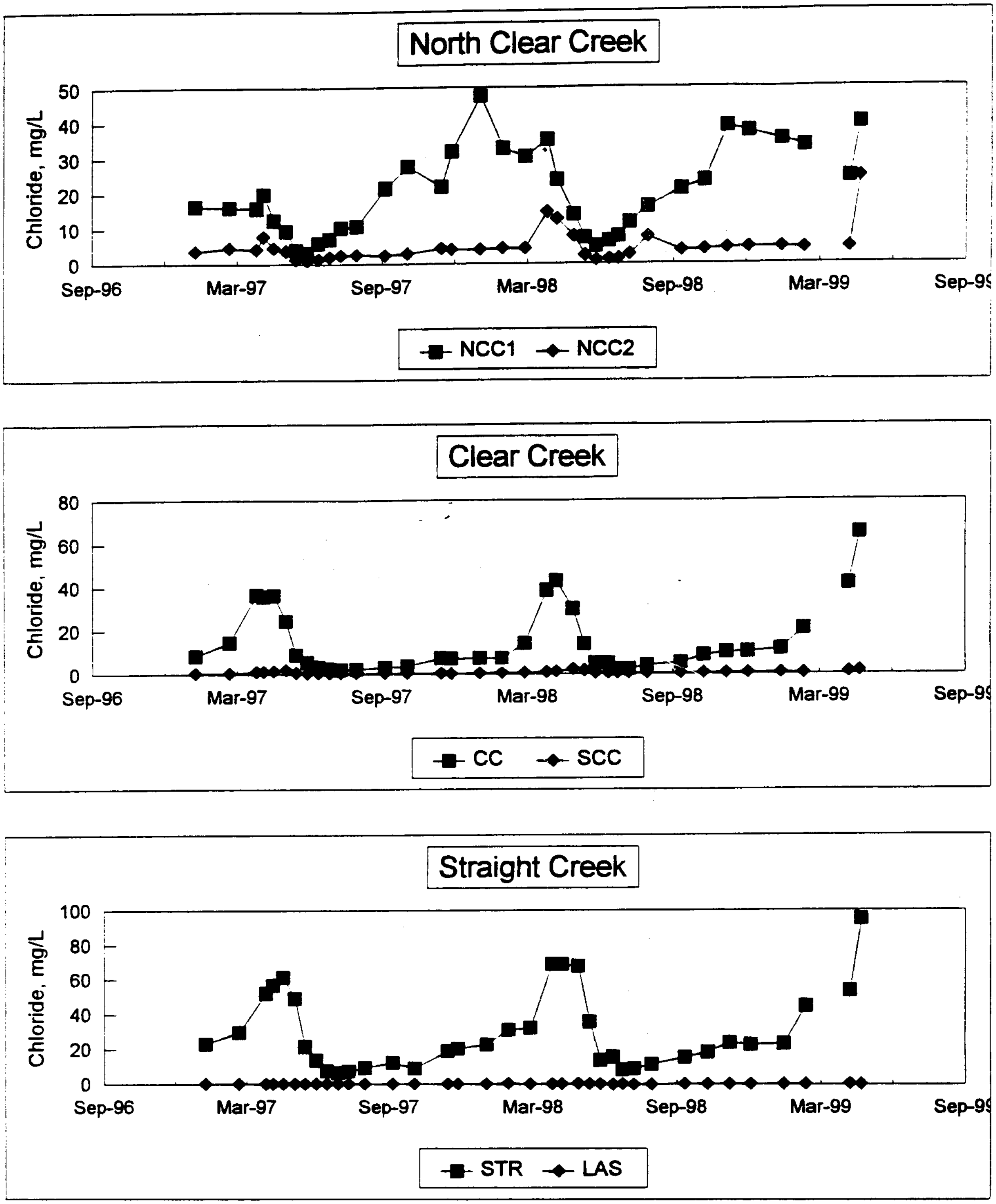

Figure 14. Chloride concentrations

Straight Creek, magnesium addition to roadways is approximately equal to total annual transport. This suggests that some of the magnesium added to the roads is stored in soils, i.e., natural sources plus roadway application exceed total transport, but other factors may need to be considered as well (see discussion on chloride).

Lower North Clear Creek shows a low percentage contribution of deicer to magnesium transport, but has exceptionally high concentrations of magnesium. Mine drainage rather than deicer is probably the source of high magnesium concentrations.

Chloride

The situation for chloride (Cl^{-}) is somewhat different from that of magnesium. There are two anthropogenic sources of chloride: magnesium chloride and salt with sand. In addition, the background (natural) concentrations of chloride in montane stream waters are much lower than those of magnesium.

Figures 14 and 15 show the concentration and transport of chloride at all six stations (see Table 20 for station codes), and Table 20 provides a summary of the mass transport on an annual basis. Both concentration and transport are strongly affected by addition of magnesium and sodium chloride (NaCl), as shown by comparison of Laskey Gulch or South Clear Creek, where neither of these was added, with the other stations, all of which received some combination of deicer and salt with sand (the South Clear Creek station does receive a small, unmeasured amount of salt with sand.

As indicated by Table 20, the amount of chloride added to the roadways typically exceeds the background mass transport, which corresponds to weighted mean concentrations below 1

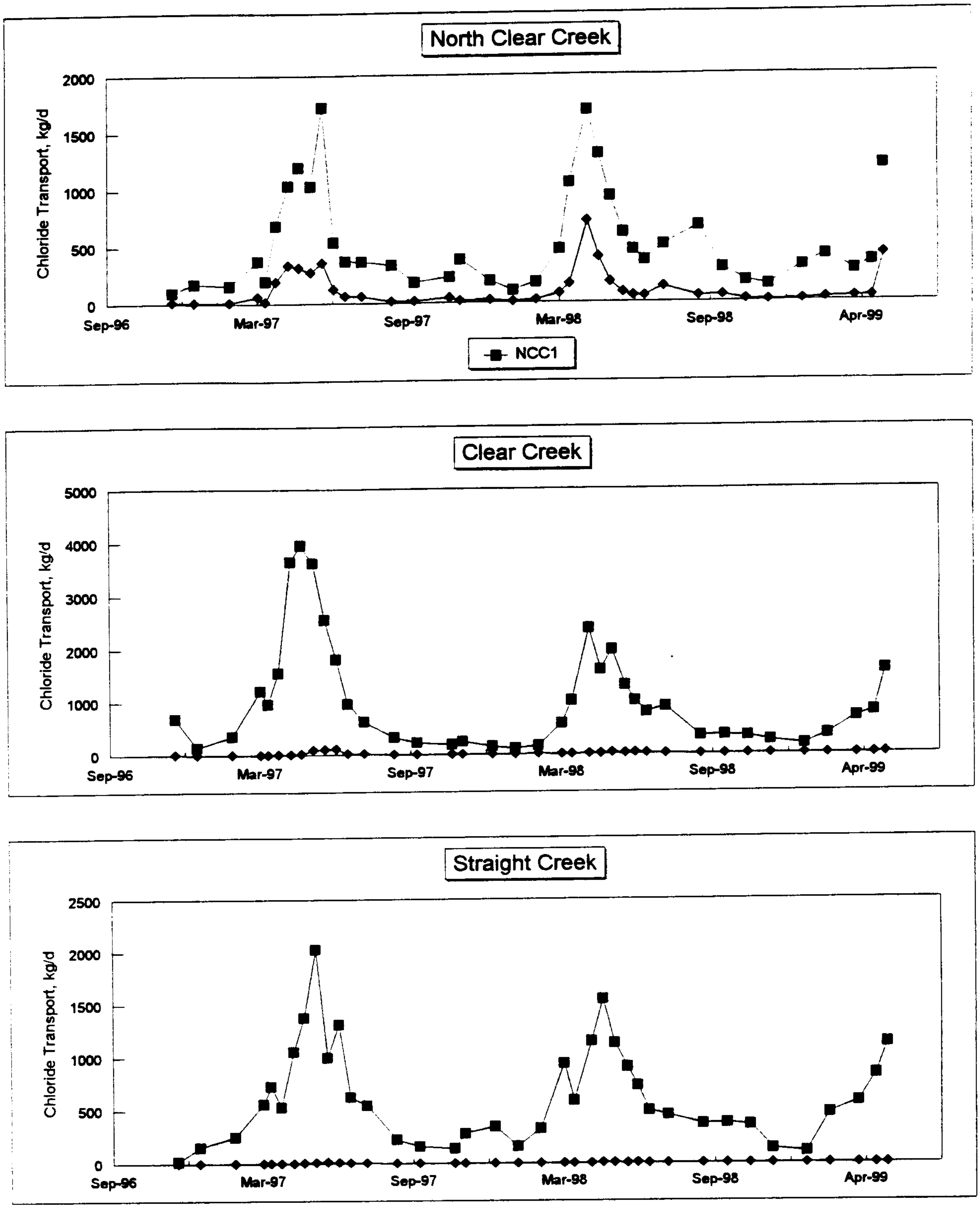

Figure 15. Chloride transport.

	Transport[1]		Weighted Concentration[2]		Peak Concentration[2]		Added[1] as $MgCl_2$		Added[1] as NaCl		Added[1] Total		Added[1] as % Transport	
Stations	1997	1998	1997	1998	1997	1998	1997	1998	1997	1998	1997	1998	1997	1998
West Portal Area														
Laskey (Control)	980	520	0.2	0.2	0.3	0.5	0	0	0	0	0	0	0	0
Straight Creek (Deicer, Salt/Sand)	177,000	193,000	13.6	20.0	61.5	69.1	79,900	84,600	258,000	167,000	338,000	251,000	191	130
East Portal Area														
South CC (Control)[3]	7000	4000	0.6	0.6	2.1	2.3	0	0	0	0	0	0	0	0
Upper CC (Deicer, Salt/Sand)	389,000	244,000	6.0	6.4	36.9	43.2	145,000	194,000	413,000	298,000	558,000	493,000	143	202
North Clear Creek														
Upper (Control)	30,000	40,000	1.9	3.6	7.8	14.7	1310	1740	48,000	35,000	50,000	37,000	168	93
Lower (Deicer, Salt/Sand)	150,000	189,000	7.4	12.8	27.5	47.5	3860	11,600	186,000	92,000	190,000	103,000	128	55

[1]kg per year; discharge at each station is shown in Table 19.
[2]mg/L.
[3]South Clear Creek receives small amounts of salt and sand (unmeasured).

Table 20. Chloride: mass transport and concentrations.

mg/L. Even though the perturbation of chloride transport by the addition of salt with sand plus deicer is very high, concentrations do not reach or approach the thresholds that are known to cause harm to aquatic organisms. Table 20 shows that sodium chloride from salt and sand is the largest source of chloride when both salt and sand and magnesium chloride are used together. Magnesium chloride accounts for a quarter (range, 10 - 50%) of the total mass transport of chloride if salt with sand is also being used and may in fact result in a reduction in the total mass transport of chloride if the use of the deicer allows reduction in the total tonnage of salt with sand mixture that is added to the roadway.

The mass transport analysis shows that addition of chloride in the form of salt with sand plus deicer typically exceeded the total observed transport of chloride. This observation could be interpreted as indicating the storage of some of the chloride in the watersheds. While some storage may occur, chloride is highly mobile wherever water movement occurs. Therefore, it is necessary to consider other possibilities before concluding that there is a net storage of chloride. As shown in Table 3, the nominal sodium chloride content and the actual sodium chloride content in a sample of salt with sand can differ by as much as 50%. There may be a tendency to overestimate sodium chloride content of sand because sodium chloride, when weighed for addition to sand, would contain moisture that contributes to the nominal weight of sodium chloride. Furthermore, this effect could vary considerably according to the conditions of salt storage. A good remedy for this problem in mass balance analysis would be use of measured concentrations of sodium chloride rather than nominal weight percentages for sodium chloride, but the large heterogeneity within batches and variations from one batch to the other would require much more extensive sampling that was possible for this study. Therefore, use of the nominal salt content (5% for I-70, 18% for North Clear Creek) is necessary but probably entails an overestimate of the salt contribution from salt with sand. Thus the tendency of total annual transport to be less than total annual additions of chloride may be, at least in part, explained by inaccuracies in the estimates of the amount of chloride applied to the roadway.

Sodium

Concentrations and mass transport for sodium (Na+) are shown in Figures 16 and 17 and are tabulated in Table 21 (1997 and 1998). The addition of sodium with deicer is so small as to be irrelevant; salt with sand is the main factor affecting transport of sodium. Addition of sodium in salt with sand augments sodium transport, and causes considerable increase in sodium concentrations in the roadway drainage during winter. Even so, concentrations do not approach those that are known to be harmful to aquatic life. Addition of sodium can exceed sodium transport; potential explanations are the same as for chloride.

Overview of Mass Transport for Major Ions

For chloride, salt with sand is the dominant control on concentrations and mass transport near roadways that are simultaneously receiving deicer and salt with sand. The augmentation of total transport and concentrations is very high, but does not approach concentration limits that are known to be harmful to aquatic organisms. Augmentation of transport and concentrations also occurs for magnesium where deicer is added, but is less extreme than for chloride. Sodium, which is affected by salt/sand additions rather than deicer, shows augmentations intermediate

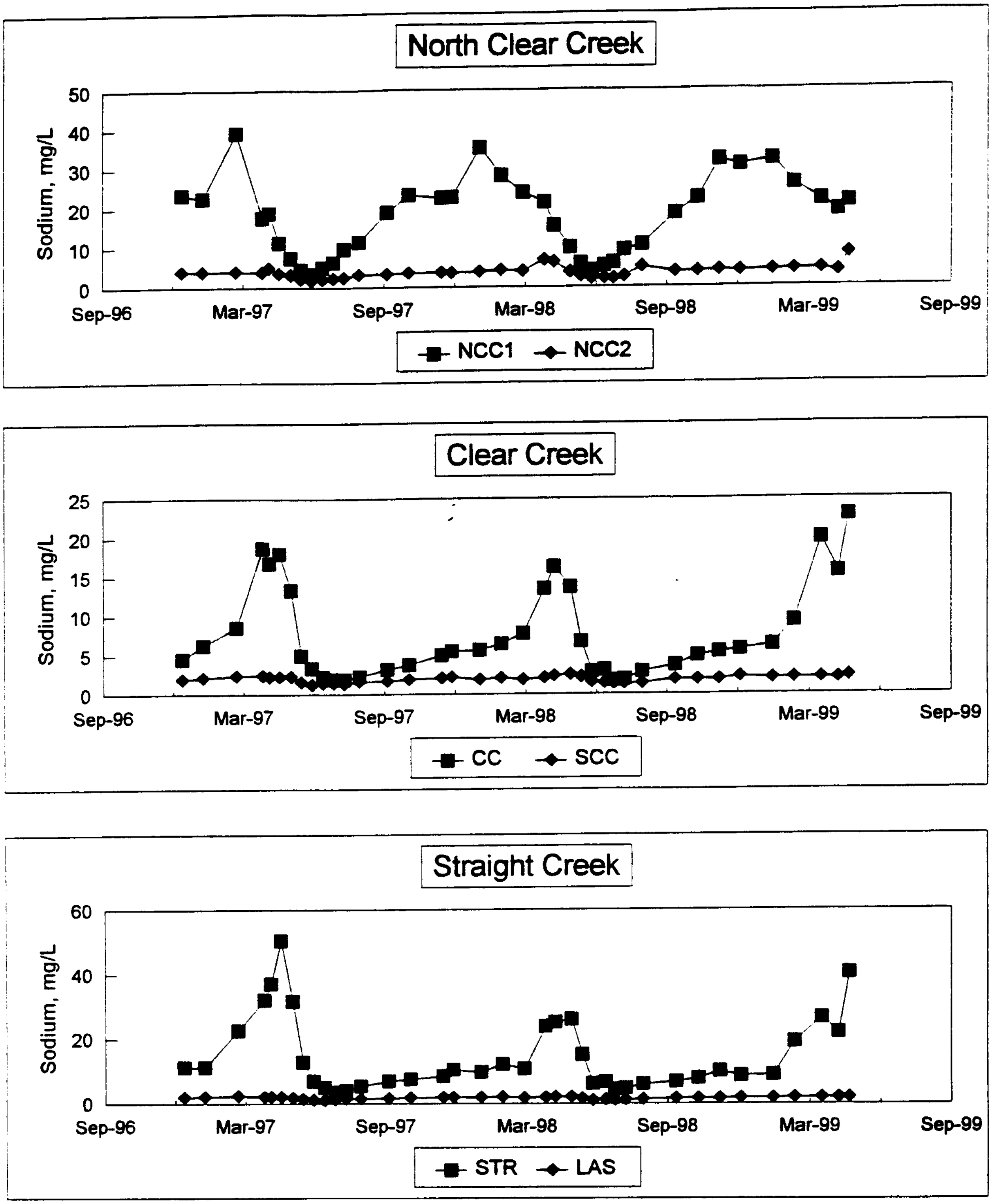

Figure 16. Sodium concentrations.

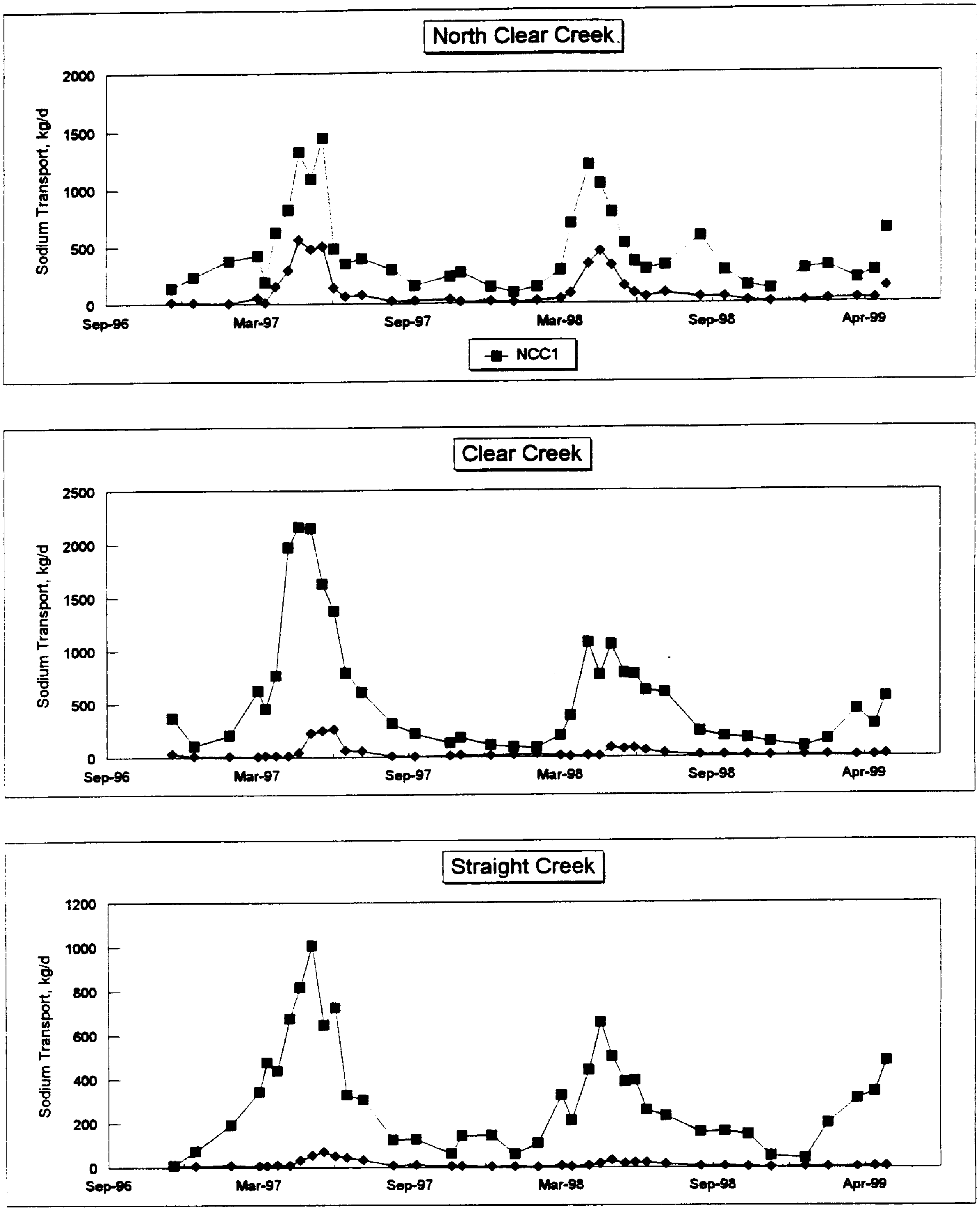

Figure 17. Sodium transport.

	Transport[1]		Weighted Concentration[2]		Peak Concentration[2]		Added as Salt/Sand[1]		Added as % Transport	
Stations	1997	1998	1997	1998	1997	1998	1997	1998	1997	1998
West Portal Area										
Laskey (Control)	6800	3900	1.5	3.0	4.9	6.8	0	0	0	0
Straight Creek (Deicer, Salt/Sand)	106,000	83,000	8.2	9.9	39.2	35.2	170,000	110,000	161	133
East Portal Area										
South Clear Creek (Control)[3]	18,000	10,900	1.5	1.6	2.4	2.5	0	0	0	0
Upper Clear Creek (Deicer, Salt/Sand)	242,000	139,000	3.7	3.7	18.7	16.3	271,000	196,000	113	143
North Clear Creek										
Upper (Control)	37,200	33,200	2.3	1.5	2.4	2.2	31,900	23,200	86	70
Lower (Deicer, Salt/Sand)	155,000	146,000	7.7	8.6	50.5	26.1	122,000	60,300	79	41

[1]kg per year; discharge is shown in Table 19.
[2]mg/L
[3]South Clear Creek receives small amounts of salt and sand (undocumented).

Table 21. Sodium: mass transport and concentrations.

between those of chloride and magnesium. Concentrations in all cases are below those that could be considered harmful to aquatic organisms.

Mass Balance for Inorganic Trace Substances

Following the discovery of measurable amounts of some heavy metals and other inorganic substances in the undiluted deicer, the scope of work for the environmental analysis was changed so as to incorporate measurement of concentration and mass transport of these substances at the field sites. Field work on these substances was initiated in November 1997 and extended through April 1999.

Table 22 lists the inorganic trace substances that were analyzed in samples from all 6 field stations (both total recoverable and soluble forms). Two-thirds of the substances never or scarcely ever exceeded the detection limits. Three metals consistently exceeded detection limits or exceeded detection limits with sufficient frequency to warrant further analysis: cadmium, copper, and zinc.

Figures 18 through 20 show the concentrations of the three metals of interest at each of the six stations. The concentrations shown in these figures are for total recoverable amounts. The concentrations for soluble amounts are not shown separately because they are close to the concentrations for total recoverable in most cases. Each figure also shows the chronic standard (applicable to soluble metals), which must be computed from hardness on a date-by-date basis.

Because all of the sampling sites are located within the mineral belt of Colorado, influences of mining must be taken into account in evaluating concentrations of metals. In addition, background concentrations of metals within the mineral belt may be higher than

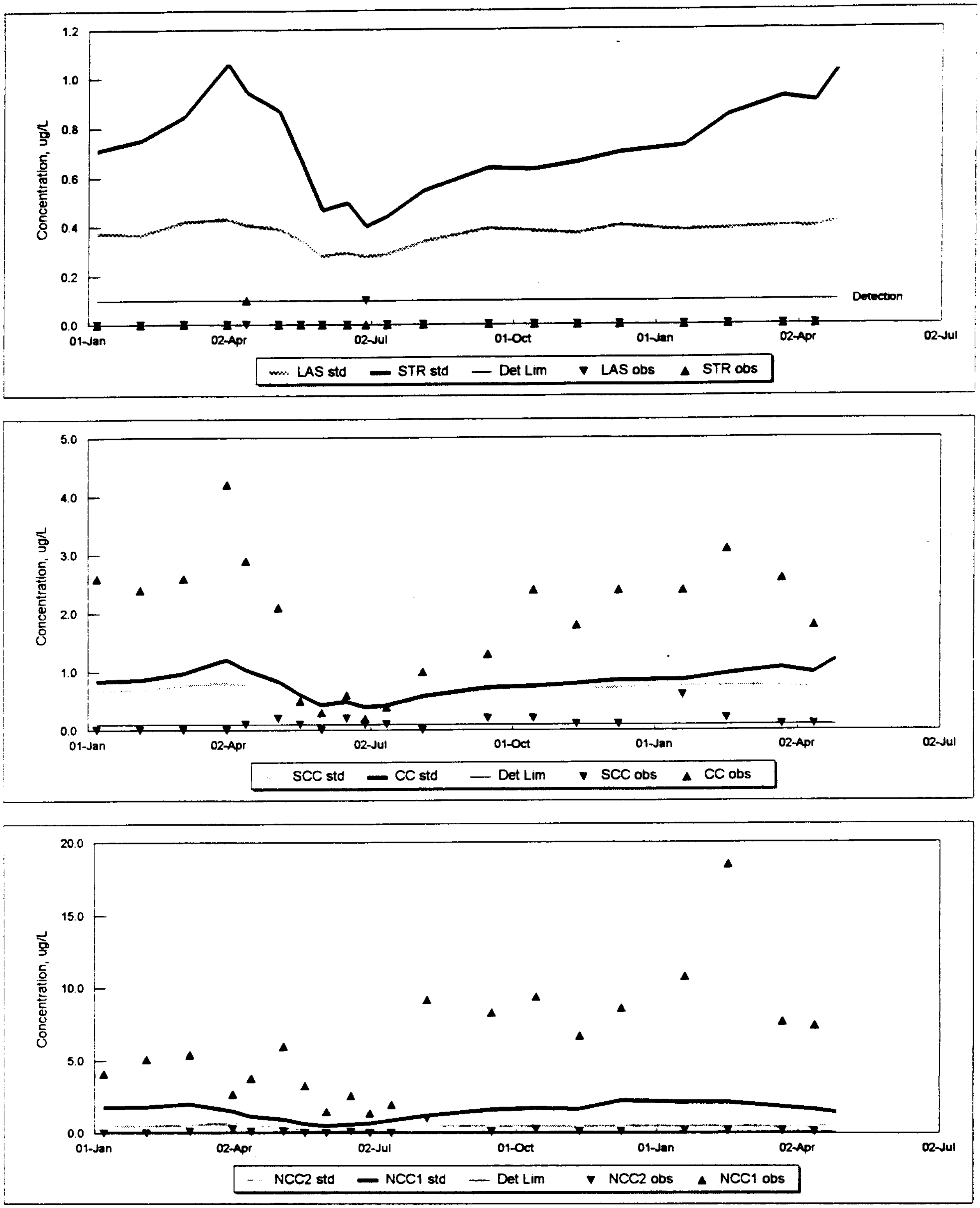

Figure 18. Total recoverable cadmium (points) and standards for cadmium (lines: soluble, chronic).

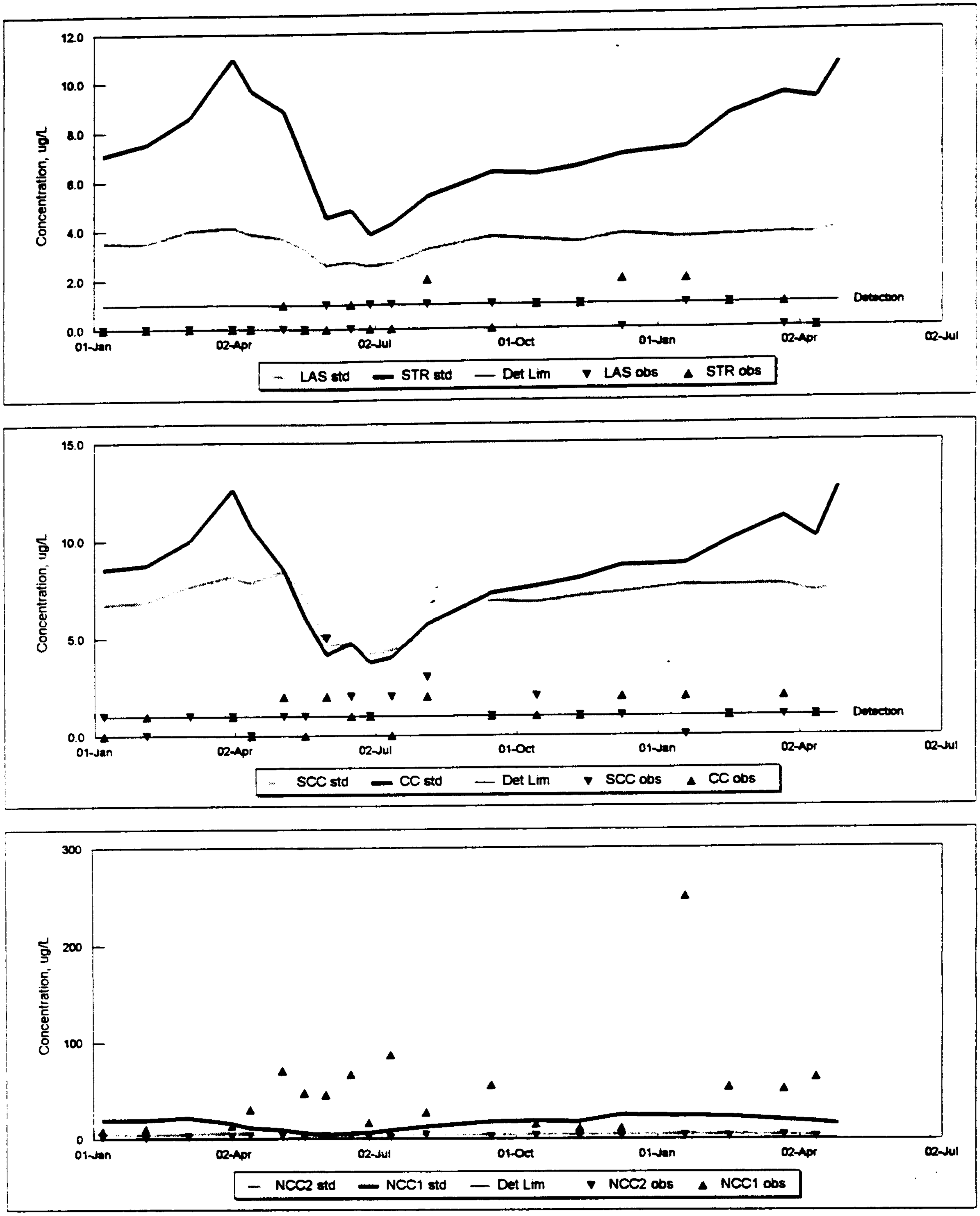

Figure 19. Total recoverable copper (points) and standards for copper (lines: soluble, chronic).

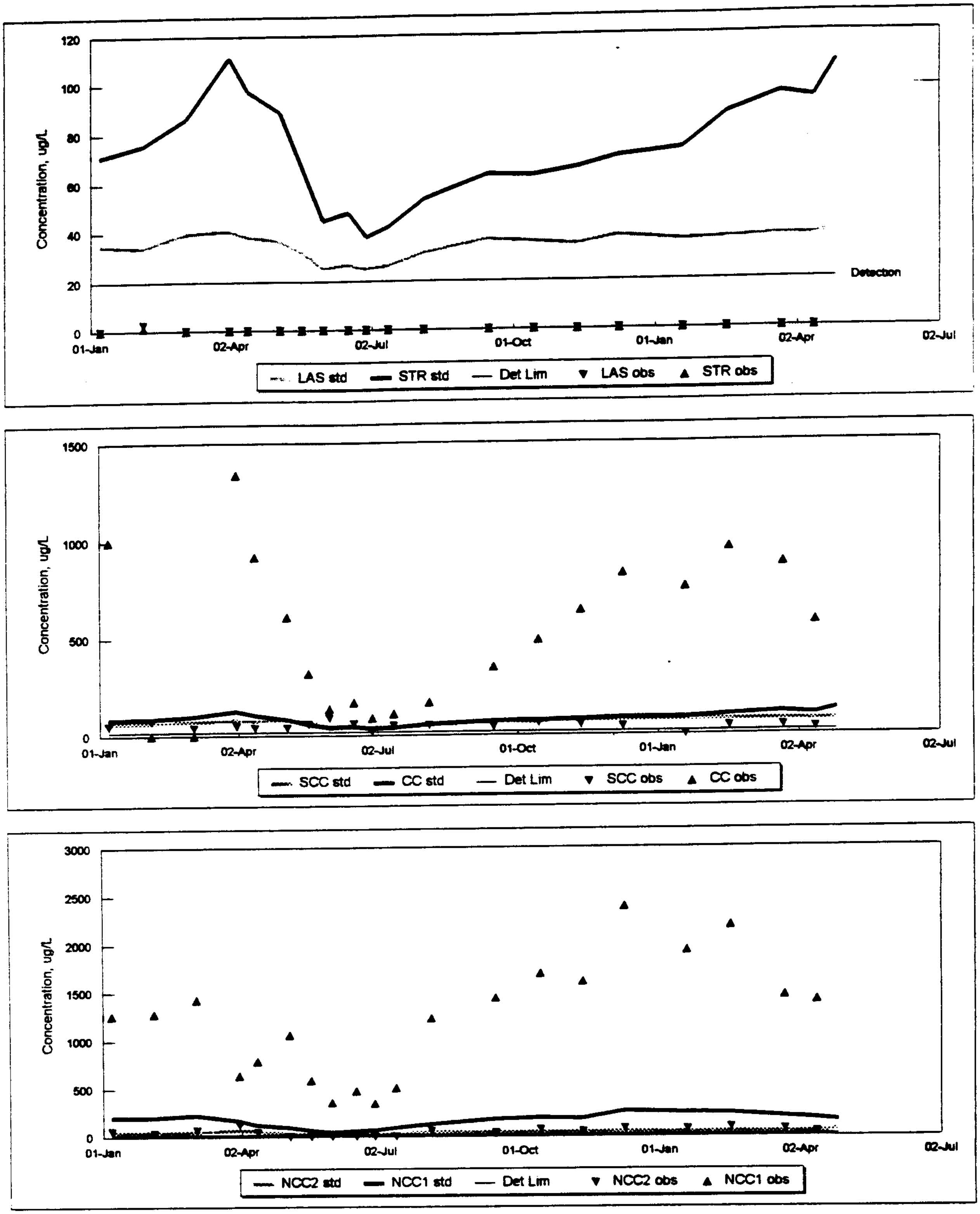

Figure 20. Total recoverable zinc (points) and standards for zinc (lines: soluble, chronic).

	Detection Limit, μg/L	Values above Detection*	Maximum Value	Regulatory Limit**
Soluble				
Cu	1	82	250	11
As	10	0	<10	150
Cd	0.1	77	18.5	1.1
Cr (III)	20	1	20	65
Hg	0.02	0	<0.02	0.1***
Ni	20	10	40	89
Pb	10	0	<10	3.5
Se	2	14	4	5
Zn	20	80	2390	111
Total Recoverable				
Cu	1	114	370	–
As	10	0	40	–
Cd	0.5	49	12.4	–
Cr (III)	20	31	60	–
Hg	0.2	1	0.2	–
Ni	20	25	60	–
Pb	10	10	36	–
Se	2	7	4	–
Zn	20	85	2070	–

*For a total of 6 stations, 22 dates = 132 samples (a few values missing for some estimates); for mercury, there were 15 dates instead of 22.
**Aquatic life standard, μg/L. Standards vary from site to site and, for some metals, from date to date. Shown here is lowest of the medians for the 3 stations receiving deicer (chronic limit). Standards are based on the soluble fraction rather than total amount.
***Limits differ where consumption of fish flesh is an issue.

Table 22. Overview of information on trace substances at the 6 field sites.

elsewhere in the Rockies. Table 23 provides some guidelines for interpretation. The least complicated interpretations from the viewpoint of deicer would be for the West Portal area (Straight Creek, Laskey Gulch), where there is no known influence of mining on water quality. Interpretations are more complex for South Clear Creek and the upper main stem of North Clear Creek, all of which show some influence of mining. The most extreme examples of influence of mining are found in the lower North Clear Creek drainage and upper Clear Creek.

Figures 18 through 20 show the concentrations of copper, cadmium, and zinc at the two sampling sites in the West Portal area, which is not significantly affected by mine drainage. Water from both Laskey Gulch (the control site) and Straight Creek (which receives runoff from deicer as well as salt with sand) remained well below the numeric standards. Furthermore, there is no indication of systematic differences in concentrations between Laskey Gulch and Straight Creek.

Figures 18 through 20 also show comparisons of South Clear Creek and the upper main stem of Clear Creek. Historic mining affects concentrations in both drainages. Concentrations exceeded standards for both sites, but the exceedances were far more extreme and consistent for the main stem of Clear Creek, where mining effects are most intense, than for South Clear Creek.

Tables 24 - 26 show the results of the mass balance analysis for cadmium, copper, and zinc at the six study sites. The weighted concentrations of cadmium and zinc are a direct reflection of the amount of mine drainage, whereas the concentrations of copper are extreme only at the lower North Clear Creek site. The information in Tables 24 - 26 allows a comparison of the annual mass transport for metals at all sites with the amount added to the roadways as a trace component of deicer. In no case do the amounts of metals added to the roadway along with

Sampling Location	Influence of Mining
West Portal Area	
Laskey (Control)	None
Straight Creek (Deicer, Salt/Sand)	None
East Portal Area	
South CC (Control)	Moderate
Upper CC (Deicer, Salt/Sand)	Moderate
North Clear Creek	
Upper (Control)	High
Lower (Deicer, Salt/Sand)	High

Table 23. Summary of information on potential effect of metals derived from mining on water quality at the 6 sampling sites used in the study of deicer.

Stations	Discharge m^3/yr	Weighted Mean Concentration $\mu g/L$	Peak Concentration $\mu g/L$	Transport, kg/yr	Added to Road with Deicer kg/yr	Percent Added with Deicer
Straight Creek						
Laskey (Control)	2580	0.5	1.0	1	0	0
Main Stem (Deicer, Salt/Sand)	9640	0.5	0.6	5	0.02	0.37
Clear Creek						
South CC (Control)	6830	0.5	1.0	4	0	0
Upper CC (Deicer, Salt/Sand)	38,100	1.0	4.8	39	0.09	0.24
North Clear Creek						
Upper (Control)	11,200	0.5	0.8	6	0.00	0.01
Lower (Deicer)	14,700	5.5	12.4	80	0.01	0.01

Table 24. Transport of cadmium (total recoverable) at study sites: 1 November 1997 - 31 October 1998.

Stations	Discharge m^3/yr	Weighted Mean Concentration $\mu g/L$	Peak Concentration $\mu g/L$	Transport, kg/yr	Added to Road with Deicer kg/yr	Percent Added with Deicer
Straight Creek						
Laskey (Control)	2580	5.1	7	13	0	0
Main Stem (Deicer, Salt/Sand)	9640	3.3	28	32	0.22	0.69
Clear Creek						
South CC (Control)	6830	5.5	17	38	0	0
Upper CC (Deicer, Salt/Sand)	38,100	4.1	12	157	0.59	0.38
North Clear Creek						
Upper (Control)	11,200	5.9	10	66	0.01	0.01
Lower (Deicer)	14,700	144	300	2121	0.04	0.00

Table 25. Transport of copper (total recoverable) at study sites: 1 November 1997 - 31 October 1998.

Stations	Discharge m^3/yr	Weighted Mean Concentration μg/L	Peak Concentration μg/L	Transport, kg/yr	Added to Road with Deicer kg/yr	Percent Added with Deicer
Straight Creek						
Laskey (Control)	2580	20	20	52	0	0
Main Stem (Deicer, Salt/Sand)	9640	20	20	190	<1.47	<0.77
Clear Creek						
South CC (Control)	6380	70	100	440	0	0
Upper CC (Deicer, Salt/Sand)	38,100	260	1280	9900	<0.17	<0.02
North Clear Creek						
Upper (Control)	10,200	50	600	530	0.0	0.00
Lower (Deicer)	14,700	930	1890	13,700	<0.01	0.00

Table 26. Transport of zinc (total recoverable) at study sites: 1 November 1997 - 31 October 1998.

deicer reach 1% of the total transport. Both the background transport and augmentation of transport by mining in watersheds where mining has occurred far exceed transport that could be attributed to deicer.

Phosphorus

Table 27 summarizes mass balance data for phosphorus. Contributions of deicer to P transport do not exceed 5%. If phosphate rust inhibitors were used, however, the augmentation of P transport would be much greater (as much as 25%).

In general, comparisons of concentrations in Straight Creek and Laskey Gulch with concentrations in the other four drainages shows that the overwhelming source of metals in the mineral belt is mining. No influence of deicer on concentration or transport of metals or transported metals is detectable where deicer is in use.

Community Analysis

A community analysis was made of attached algae at all six study reaches. Attached algae were chosen for this analysis because they are not mobile and therefore reflect the conditions where they are collected, and because they respond to both metals and nutrients.

The objective of the community analysis was to quantify the abundances of all species of attached algae in each one of the six study segments, and then to compare the community composition across sites. If the application of deicers has a strong effect on community

Stations	Discharge m^3/yr	Weighted Mean Concentration $\mu g/L$	Peak Concentration $\mu g/L$	Transport, kg/yr	Added to Road with Deicer kg/yr	Percent Added with Deicer
Straight Creek						
Laskey (Control)	2580	4.5	6.6	12	0	0
Main Stem (Deicer, Salt/Sand)	9640	6.6	13.3	64	2.8	4.3
Clear Creek						
South CC (Control)	6380	5.5	11.3	38	0	0
Upper CC (Deicer, Salt/Sand)	38,100	6.1	13.3	230	12.2	5.2
North Clear Creek						
Upper (Control)	10,200	15.7	25.7	175	0.11	0.1
Lower (Deicer)	14,700	28.2	76.4	410	0.73	0.2

Table 27. Transport of phosphorus at study sites: 1 November 1997 - 31 October 1998.

composition, sites receiving deicer should differ significantly from those not receiving the deicer. Metals pollution from mining must be taken into account, however (see previous section).

The samples of attached algae were taken on September 19, 1997. Four separate replicate samples were taken from each study reach. Attached algae were scraped from rocks collected at random for each replicate. The amount of area scraped was quantified, and the final counts were then related back to the areas that were scraped. Algae scraped from the surfaces in all cases were rinsed into clean glass bottles and preserved.

All four replicates for each site were counted quantitatively at appropriate magnification; counts were made at the species level of identification. A mean was obtained for the four replicates for each study segment, and comparisons were then made of the means across different study segments.

Across all six study sites, 79 algal species were identified. Of this total, 58 were diatoms, 9 were green algae (chlorophytes), 1 was a golden brown alga (Chrysophyta), and 11 were blue-green algae (Cyanophyta).

The total number of cells per square millimeter ranged considerably from one replicate to another within a given study segment. Patchiness of this type is expected for attached algae. The total density of cells also varied from site to site. Laskey Gulch showed the highest densities of algae at about 40,000 cells per square millimeter, and Clear Creek showed the lowest at about 1200 cells per square millimeter (Table 28).

Control sites show consistently higher algal abundance than sites receiving deicer treatment. This observation is difficult to interpret. First, because there are only three pairs of sites, the possibility of the three control sites differing consistently from the three treatment sites

	Upper North Clear Creek	Lower North Clear Creek	C-T	South Clear Creek	Georgetown Clear Creek	C-T	Laskey Gulch	Straight above Laskey	C-T
BACILLARIOPHYTA									
Achnanthes linearis f.curta	0.0	200.8	-200.8	0.0	0.0	0.0	0.0	0.0	0.0
Achnanthes microcephala	0.0	379.7	-379.7	0.0	0.0	0.0	0.0	0.0	0.0
Achnanthes minutissima	4.0	0.0	4.0	254.6	62.6	192.0	196.8	286.1	-89.4
Diatoma mesodon	27.6	0.0	27.6	28.1	1.1	27.1	0.8	1.6	-0.8
Fragiliara pinnata	21.0	0.0	21.0	38.4	0.0	38.4	2.4	1.1	1.3
Fragilaria vaucheriae	1.3	0.0	1.3	71.0	13.1	57.9	0.0	32.0	-32.0
Gomphonema angustatum	0.5	0.0	0.5	10.5	0.3	10.2	0.0	349.7	-349.7
Gomphonema olivaceum	3.0	0.0	3.0	1.1	1.9	-0.8	0.0	33.6	-33.6
Gomphonema subclavatum	0.0	0.0	0.0	6.3	0.8	5.5	3.7	72.5	-68.8
Hannaea arcus var. arcus	60.3	0.0	60.3	26.1	6.5	19.6	1.9	134.4	-132.5
Nitzschia paleacea	2.4	2.9	-0.5	43.1	0.3	42.9	0.0	2.4	-2.4
Synedra ulna var. contracta	107.7	0.0	107.7	0.0	0.0	0.0	0.2	0.0	0.2
Synedra ulna var. ulna	60.2	0.0	60.2	6.1	0.0	6.1	0.0	2.4	-2.4
CHLOROPHYTA									
Ulothrix sp.	20.8	0.0	20.8	1.6	0.7	0.9	0.0	0.0	0.0
Zygnema sp.	0.0	0.0	0.0	99.3	0.0	99.3	0.0	0.0	0.0
CHRYSOPHYTA									
Hydrurus foetidus	102.7	0.0	102.7	28.2	44.2	-16.1	141.1	190.1	-48.9
CYANOPHYTA									
Chamaesiphon sp.	270.1	221.7	48.5	2085.1	83.6	2001.5	6324.0	121.8	6202.2
Clastidium sp.	2.5	0.0	2.5	277.5	69.9	207.6	483.2	83.4	399.8
Homoeothrix sp. 1	170.0	11.3	158.8	5255.2	196.3	5058.9	33498.1	1984.5	31513.6
Homoeothrix sp. 2	135.8	29.4	106.4	1118.7	705.5	413.2	1943.5	4559.4	-2615.9
Leptolyngbya nana	170.0	375.6	-205.6	237.3	11.0	226.3	0.0	354.0	-354.0
Leptolyngbya sp.	0.0	0.0	0.0	54.6	0.0	54.6	0.0	0.0	0.0
Phormidium autumnale	11568.9	5.0	11564.0	3077.8	15.6	3062.2	15.5	27.8	-12.4
Pseudanabaena sp.	18.9	119.0	-100.1	19.8	0.0	19.8	0.0	0.0	0.0
Total Cell Counts (including minor taxa not shown)	12839.0	1356.3	11482.7	12818.9	1239.2	11579.7	42624.6	8291.3	34333.3

Table 28. Dominant species, abundances (cells/mm^2) at the six sites and differences of control sites (C) from sites receiving deicer (T).

is 25%, i.e., very little statistical significance can be attributed to the observed differences. If these differences were to hold up over more extensive comparisons, they might well be explained by the tendency of the control site in each case to be a lower order stream than the treatment site, and to be receiving less suspended particulate material. In other words, the role of suspended particulate matter, which may mask and thus reduce the development of attached algae, could be confused here with the role of deicers. Also, metals from mining probably affect algae at the Clear Creek and lower North Clear Creek site. An alternate kind comparison is based on the kinds of algae rather than the total abundances, as indicated below.

As shown by Table 28, there is a great deal of overlap in the dominant members of the attached algal community from one segment to another. There are numerous ways to compare community composition from one site to another on a quantitative basis. For this community analysis, percent similarity in species composition was used as an index for comparing communities (percent similarity includes species type and relative abundance). The total number of species in a particular segment ranged from 34 - 67 and had a median of 54. The total numberof species shared between any two segments taken at random varied between 5 and 25, and had a median of 18. Percent of species shared between sites was calculated for all possible pairings of sites. Various groupings of sites were then compared with each other, as shown in Figure 21.

Figure 21 shows all possible pairings of segments. Three of the pairings consist of an upstream control segment and a downstream segment receiving deicer. If the addition of deicer has a strong effect on species composition of algal communities, these pairings should be more dissimilar than pairings taken at random. As shown by the figure, this is not the case: control and

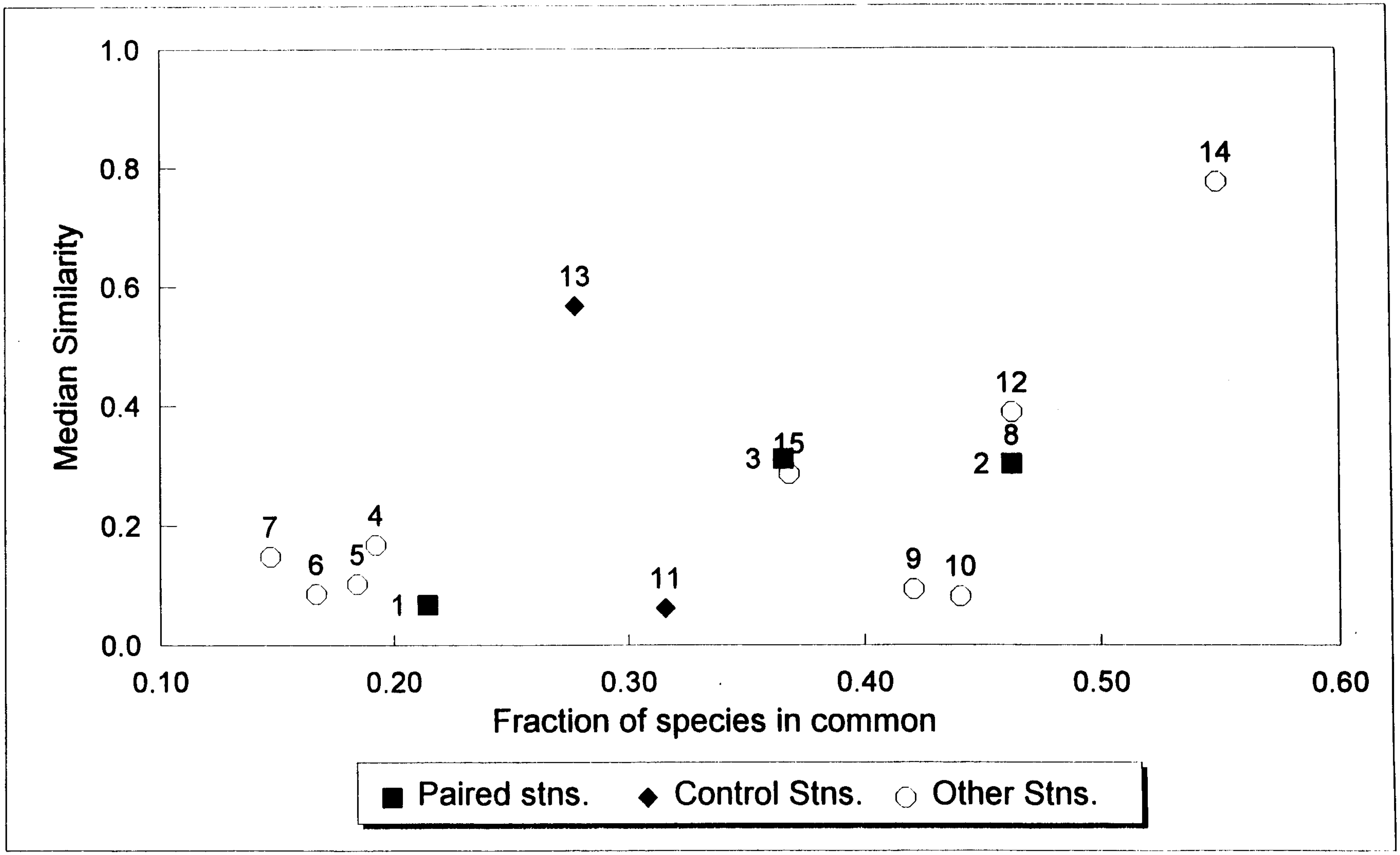

Figure 21. Similarity of algal community composition for all possible pairwise combinations of the six stations.

treatment segments show similarities that fall in the mid-range of all observable similarities (even though two of the treatment segments are affected by metals from mining).

Another way of viewing similarity data has to do with similarity of pairs of stations not receiving deicer. If the deicer has a strong effect on community composition, segments receiving no deicer should be more similar in community composition than other pairs of segments. As shown by the figure, this is not the case. The one set of paired stations (Laskey Gulch, Straight Creek) where metals pollution from mining is not a complicating factor shows an intermediate degree of similarity, i.e., does not indicate any quantifiable effect of deicer.

Overall, the community composition of attached algae shows no evidence for effects of deicer on community composition of attached algae, although the comparisons across sites are complicated by metals pollution and application of salt and sand along with deicer. Because there is a large scope of variation in community composition of attached algae, subtle differences caused by deicers materials might go undetected in a test of this type.

The study described here would be sensitive only to sustained differences in algal communities. Differences restricted to the deicing season are not ruled out by this study, but would be more difficult to quantify because of the scarcity of algae during runoff season, and difficulties of winter sampling.

Synoptic Sampling

Synoptic sampling was conducted on I-70 between the East Portal and Georgetown during April 1998. The purpose of the sampling was to establish rates of dilution for magnesium chloride deicer as a function of distance from the highway. Samples were collected along transects beginning on one side of the highway and moving away from the highway along drainage pathways leading to the nearest large stream (in this case, Clear Creek).

The synoptic sampling was conducted just following a spring storm (3 April, 1998). The storm was anticipated and magnesium chloride was applied in a typical manner just prior to and during the early phases of the storm. Salt with sand was also applied in a typical manner.

Table 29 summarizes the results of the synoptic sampling. The first line of the table gives the concentrations of a selection of substances in the undiluted deicer, for purposes of comparison. Subsequent lines in the table give the number of the transect, the distance from the highway on the transect, and the concentrations of elements in the water at the point of sampling. Included in the table are magnesium (one of the two major components of magnesium chloride deicer), sodium (the main soluble cationic component of salt and sand mixtures), calcium (a cation found only in small amounts in the deicer), and a selection of heavy metals that are strictly regulated in montane waters for the protection of aquatic life (zinc, copper, lead, and cadmium). For each transect, the first sample consisted of slush just at the edge of the highway, and the last sample consisted of the main stem flow of Clear Creek.

As shown by Table 29, slush very near the paved surface varies considerably in its chemical composition but, as shown by the magnesium concentrations, reflects a large amount of dilution of magnesium chloride deicer. In one case, the slush showed a dilution of approximately 600 to 1 (transect 2), and in other cases the slush showed dilutions exceeding 10,000 to 1.

Concentrations of magnesium did not always decline away from the paved surface. Sometimes they increased, although all of the absolute concentrations were very low. Increases

Site*	Distance	Mg	Na	Ca	Zn	Cu	Pb	Cd
Deicer		80,000	2700**	2200	<2	0.6	<1	0.12
1(S)	0	6.4	64	2	0.78	0.192	0.235	0.0022
1	0.5	3.4	3	16	<.02	0.009	<.01	<.0005
1(CC)	1.9	8.5	37	31	<.02	0.009	<.01	<.0005
2(S)	0	131	526	27	0.12	0.033	0.027	0.0008
2	10	2.7	3	7	<.02	0.005	<.01	<.0005
2	114	4.8	10	13	<.02	0.007	<.01	<.0005
2	141	4.9	11	13	<.02	0.006	<.01	<.0005
2(CC)	231	7.9	31	29	<.02	0.004	<.01	<.0005
3(S)	0	1.7	17	<1	1	0.29	0.32	0.0041
3	8	6.6	6	21	<.02	0.007	<.01	<.0005
3	21	6.9	7	22	<.02	0.005	<.01	<.0005
3	38	6.7	7	21	<.02	<.001	<.01	<.0005
3(CC)	67	8.4	19	24	<.02	0.003	<.01	<.0005
4(S)	10	2.2	10	1	3	0.56	-	0.0094
4	20	14	110	16	0.56	0.054	0.185	0.0020
4	75	14	108	17	0.44	0.067	0.245	0.0024
4	125	12.4	97	18	0.4	0.035	0.32	0.0013
4(CC)	250	9.2	15	26	0.77	0.013	<.01	0.0025

*Site 1 is 200 m west of Exit 218, south side of I70; Site 2 is near mile marker 219; Site 3 is near mile marker 224; Site 4 is in Georgetown, just west of the confluence of South Clear Creek and Clear Creek.

**Application of salt with sand strongly affects this constituent.

Table 29. Results of synoptic sampling (mg/L). The terminal sample in each series is Clear Creek (CC); the initial sample is slush just beside the paved surface (S).

in concentration may reflect the averaging of roadway runoff, and probably also some natural contributions of magnesium from soils near the road. Concentrations of magnesium rapidly converged with those of Clear Creek, which is affected not only by the highway, but also by a large amount of naturally vegetated surface and mine drainage in the Clear Creek watershed.

Sodium shows patterns similar to those of magnesium: concentrations in some cases increased away from the edge of the highway, but reflected large amounts of dilution on and near the highway.

Chloride was not measured, but would likely show patterns similar to those of major cations. Given the strength of dilution (Figure 22), chloride would be very unlikely to exceed the stream standard in any sample 1 m or more from the road surface in this sample series.

Heavy metals behaved differently than the other substances listed in Table 29. Concentrations were consistently higher in slush near the roadway than at points more distant or in Clear Creek. Concentrations of magnesium, the most sensitive indicator of deicer dilution, showed that higher concentrations of metals very near the highway reflect contamination of the highway by factors other than deicer (e.g., wear of metallic parts on vehicles, spillage, etc). Even at a small distance from the highway, however, the concentrations of these substances were very low, indicating high amounts of dilution as runoff passed away from the highway.

In overview, the data on magnesium indicate a dilution of 5000-fold or higher at distances 10 m or greater from the paved surfaces. In addition, concentrations of heavy metals, the main source of which is not deicer, are reduced by very high dilution away from the roadway.

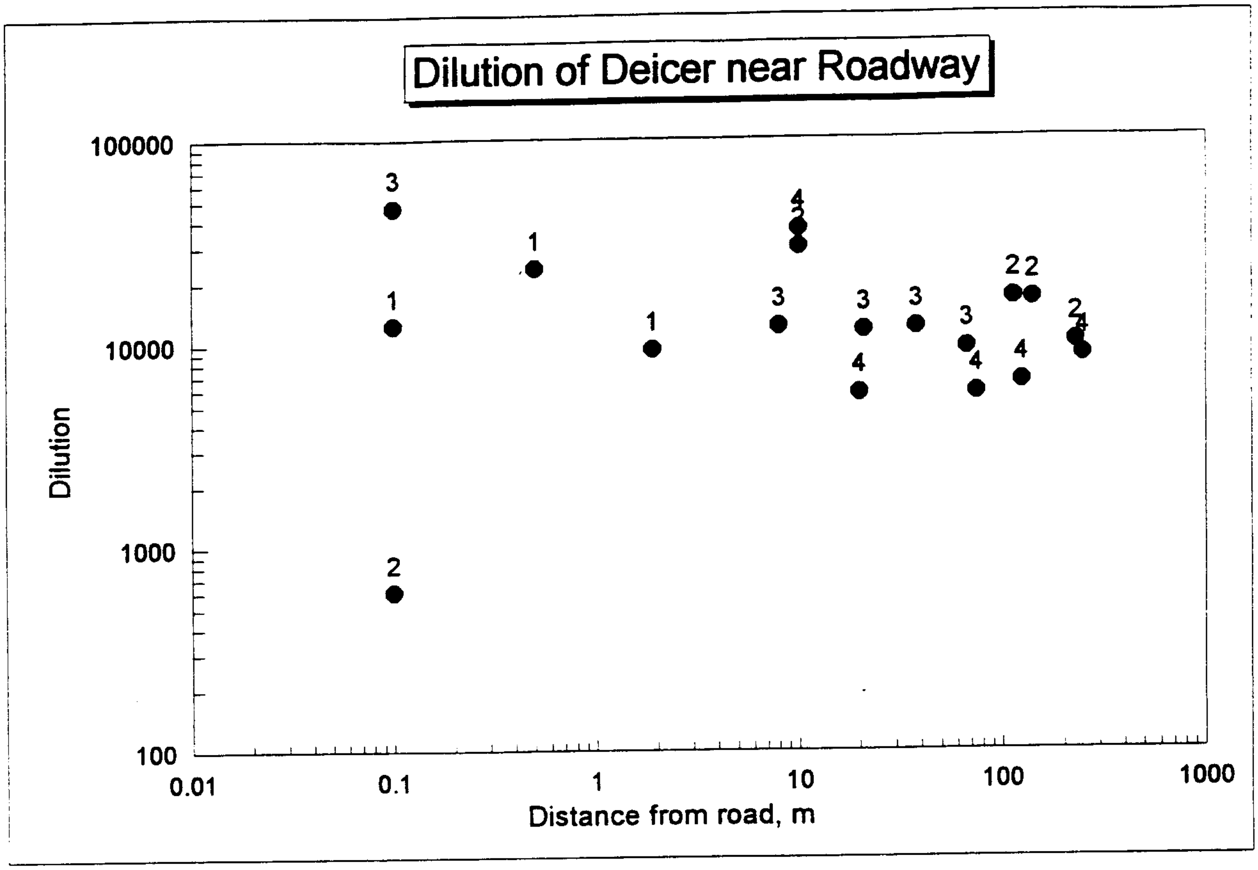

Figure 22. Dilution of deicer as related to distance from side of paved surface (I-70, east of tunnel). Dilutions above 10,000 are likely to be higher than shown on graph (see text).

Figure 22[5] summarizes the information on dilution. The points on the graph show the ratio of magnesium concentrations in undiluted deicer to the observed concentrations at various distances from the highway. The figure gives a lower bound (minimum) value for the dilution rather than the actual value, because there is no correction in the figure for magnesium that runoff picks up from soils as the water passes away from the highway.

Water Quality in Boreal Toad Habitat

Habitat suitable for the boreal toad (*Bufo borealis*) is located close to I-70 at the highest elevations. Some of these habitats receive runoff from I-70, and thus should be evaluated from the viewpoint of deicer components.

Two habitats were selected for study. Both of these habitats are located near the East Portal of the Eisenhower Tunnel near I-70. The first habitat, which will be referred to here as the north wetland, is located on the north side of the highway and is up slope from the highway. It does not receive highway runoff and therefore serves as a control for evaluation of water quality.

A second wetland is located in the same area, but downslope of the highway. This wetland will be referred to as the south wetland. Both wetlands have breeding populations of the boreal toad and are being continuously monitored by the Colorado Division of Wildlife.

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[5]The term "dilution" as used here and elsewhere in this report encompasses all factors that cause a reduction in concentration. Adsorption on a solid surface can reduce the concentration of a dissolved substance and would necessarily be lumped here with true dilution (addition of water), from which it cannot be distinguished on the basis of data from this study.

Both wetlands contain standing water that may be as deep as a foot or more in some locations during the season of toad breeding and maturation (June and early July). During this season, both wetlands show substantial throughflow of water. During early July, the amount of water in both wetlands begins to decline. Samples were taken of water flowing out of the north wetland on its south side (designated as the main sampling site for the north wetland). The south wetland receives water at two or three points (depending on month), and has a diffuse outflow. One of the inflows is fed by a highway culvert. Routine samples were restricted to this inflow (designated here as the main sampling site for the south wetland), which would represent the most direct influence of highway runoff, and would dominate a portion of the wetland prior to mixing with other flows, i.e., it was chosen as a likely worst case condition for the highway influence. During 1997, a single sample was taken from the main sampling site for each wetland on each sampling date when water was available for sampling. Samples were also taken of two to three additional channels carrying water from the highway to the south wetland. During 1998, the sampling was repeated, but only the two main sites were sampled.

Analyses of water quality included the full spectrum of major ions and trace inorganic substances that were dealt with in the water quality studies for the six stream sampling stations.

Table 30 shows the concentrations of major ions for the two wetlands as well as highway runoff passing toward the south wetland. The information on calcium serves as a gage of the background similarity in the two wetlands because calcium is not a major component of road application materials (either deicer or salt and sand). The data on calcium suggest that the north wetland may have slightly higher background concentrations of major ions. This difference is probably an artifact of the longer period of sampling for the north wetland, where the main

	Ca		Mg		Na		Cl		Sampling Dates*	
Location	1997	1998	1997	1998	1997	1998	1997	1998	1997	1998
North Wetland (Main)	8.9	7.5	2.6	2.0	1.0	1.0	0.2	0.2	7	4
South Wetland (Main)	5.0	4.6	2.3	3.3	4.5	4.5	2.5	6.8	3	3
South Wetland (Secondary)	2.0	–	6.4	–	2.8	–	2.6	–	5	–

*Sampled when flowing: North 1997, June - October; North 1998, June - July; South 1997, June - July; South 1998, June.

Table 30. Median concentrations (mg/L) for major ions in waters flowing to or from two wetlands (north = control; south = influenced by runoff) with reproducing populations of the boreal toad.

sampling site has into late summer and fall, when evapoconcentration of water tends to increase the concentrations of major ions and other dissolved substances.

As shown by Table 30, the magnesium concentrations of the north and south wetlands were very similar. Using calcium as a guide, the magnesium concentrations should actually be lower in the south wetland than in the north wetland, but were slightly higher (a comparison of paired dates is discussed below). Thus the south wetland showed a slight magnesium enrichment by comparison with calcium. This is an expected effect of the presence of deicer in runoff reaching the south wetland. Also the secondary sites for the south wetland carried more magnesium than the north wetland, suggesting that they might show more highway influence than originally thought, but natural terrestrial sources also could account for the higher concentrations.

Sodium is substantially enriched in the south wetland because of the high sodium content of the salt with sand applied to I-70. Even so, the concentrations of sodium were not high in an absolute sense. Chloride showed a similar pattern, but with an even more extreme deviation between background concentrations, as represented by the north wetland, and concentrations in the south wetland. As in the case of sodium, however, the absolute concentrations were quite low.

Table 31 shows the result of calculations leading to an estimate of percent deicer reaching via the main sampling site of the south wetland. For each date listed in the table, the concentrations of magnesium in the north and south wetlands were compared. As expected, in each case the concentration of magnesium was slightly higher in the south wetland, reflecting the contribution of magnesium in deicer to the total magnesium concentration in the south wetland.

Sampling Date	Percent Deicer (%)
1997	
4 June	0.0005
18 June	0.0008
2 July	0.0011
1998	
1 June	0.0009
17 June	0.0022
29 June	0.0015

Table 31. Proportionate contribution of deicer to water in wetlands south of I-70 supporting a boreal toad population, as estimated from magnesium concentrations (see text for explanation).

The known concentration of magnesium in undiluted deicer, and the deviation in concentrations for the two wetlands were used in calculating the percentage contribution of deicer to the water reaching the south wetland. This calculation was done for each date. The percent of deicer reaching the wetland, estimated on the basis of magnesium, was very low (maximum, 0.002%). This low percentage reflects the large amount of dilution water that is available in June, the peak month of seasonal runoff and also the main month during which the wetland serves the reproductive and development needs of the toad. The application of deicer ceases by June, so that the percentage deicer in the wetland during the breeding season reflects only the residual deicer from winter and early spring application.

Table 32 summarizes the information on metals. Although the scope of analysis for metals was the same as for the mass balance analysis, results showed concentrations consistently below detection limits except in the case of copper and zinc. Cadmium is also included in the table for purposes of consistency with the mass balance analysis at the stream sampling sites, even though the samples in the wetlands showed concentrations primarily below the detection limit.

As shown in Table 32, concentrations of copper and zinc approached or exceeded the chronic concentration limit for cold water aquatic life in the south wetland. In fact even the north wetland reaches the regulatory limit for copper for a brief interval.

With respect to deicer, the most important question is whether the higher concentrations of copper and zinc that are present in the south wetland can be attributed primarily to deicer, or if they are of some other origin. An estimate of the contribution of deicer is possible on the basis of Table 31, which gives the proportionate amount of deicer reaching the south wetland on various dates via the main sampling site, and Table 3, which shows the concentration of copper and zinc in undiluted deicer applied to the roadway. As shown by the last line of Table 32, deicer does make a contribution to the concentrations of copper and zinc in the wetland, but the contribution is extremely small, and cannot explain why the concentrations of copper and zinc are higher in the south wetland than in the north wetland. Highway runoff contains metals and organic materials from other sources (moving parts, lubricants, leakage of transported materials, etc.), which are probably the main source of copper and zinc reaching the south wetland. In addition, salt and sand mixtures contain some soluble copper and zinc (Table 4), and in fact are a larger potential source of these two metals than the deicer.

Location	Cd (Sol) Med	Cd (Sol) Max	Cd (Sol) Std**	Cu (Sol) Med	Cu (Sol) Max	Cu (Sol) Std	Zn (Sol) Med	Zn (Sol) Max	Zn (Sol) Std
North Wetland (control)	<0.1	0.1	0.3	1.5	3	3	<20	<20	30
South Wetland (Below I-70)	<0.1	<0.1	0.4	7	7	3	70	120	30
Contribution of Deicer* (μg/L)	0.01	0.02	–	0.2	0.4	–	<4.5	<2.0	–

*For 6 paired dates (3 in 1997, 3 in 1998: See Table 29).
**Chronic standard for support of cold water aquatic life; standard varies some from date to date.

Table 32. Concentrations of metals (μg/L) in two wetlands supporting populations of the boreal toad. Contribution of deicer is estimated from data in Tables 30 and Table 3 and assumes no soil adsorption of metals in transit from highway to wetland.

Future Studies

The work reported here is the first comprehensive study of the environmental effects of magnesium chloride deicer in montane environments. As would be expected, this initial study has shown how additional research might be useful in the future. Topics of special interest for future research are listed below.

1. Variability in deicer composition. Variability in composition of magnesium chloride deicer from one vendor to another and from one lot or year to another should be quantified and made available to the State and other users. It is unknown at present whether the amounts of contaminants in magnesium chloride deicer vary only a little or a great deal. Information on this topic would be relevant to the decisions regarding frequency of screening.

2. Use of deicer in other settings. The evaluation as presented in this report applies specifically to montane environments. Magnesium chloride is also used at low elevation. It would be useful to place magnesium chloride into some kind of environmental context for low or elevation.

3. Establishment of no-effect level. The toxicity studies were designed to demonstrate the chronic concentration limits for mortality, but not the no-effect level. The no-effect level corresponds to the concentration that has no detectable physiological influence on an organism over an extended period of time.

4. Monitoring over short time intervals. The stream monitoring that was conducted during the two years of the study reported here is based on biweekly sampling. The results of this type of monitoring can be complemented by sampling at shorter time intervals at selected sites in order to get a more detailed picture of the mobilization of magnesium chloride deicer following specific storms.

5. Fate of metals. As shown by this study, deicers contain heavy metals and other substances that are of environmental concern if they exceed certain threshold concentrations as determined by the State of Colorado. A related question is whether these contaminants are of any concern due to the possibility that they might be adsorbed by soils, at least near roadways, and thus accumulate over a long period of time. A quantitative study of this subject would be of great interest to those who seek more information on long-term consequences, if any, of deicers.

6. Comparisons with salt and sand. As shown by the present study, salt and sand mixtures contain trace substances, as do deicers. A more detailed comparison would be useful,

especially since use of magnesium chloride might allow reduction in the use of salt and sand, and thus reduce the presence of trace materials that are carried by salt and sand.

General Conclusions

The overall conclusion of the study is that application of magnesium chloride deicer having a chemical composition and application rate similar to those of 1997-98 is highly unlikely to cause or contribute to environmental damage at distances greater than 20 yds from the roadway. Even very close to the roadway, the potential of magnesium chloride deicer to cause environmental damage is probably much smaller than that of other factors related to road use and maintenance, including pollution of highway surfaces by vehicles and use of salt and sand mixtures to promote traction in winter. Magnesium chloride deicer may offer net environmental benefits if its use leads to a reduction in the quantity of salt and sand applied to roadways. The environmental safety of magnesium chloride deicer depends, however, on low concentrations of contaminants and avoidance of rust inhibitors containing phosphorus. Appropriate specifications for vendors and routine testing can insure the continued environmental acceptability of magnesium chloride deicers.

Acknowledgments

This study was supported by the Research Division of the Colorado Department of Transportation. The study benefitted from the advice and assistance of the Interagency Planning

Committee and CDOT staff, including especially Werner Hutter, Rich Griffin, Ed Fink, Chuck Lowerwald, and Terri Tiehen.

Appendix A

Rule of Thumb for Estimating Minimum Desired Dilution of Magnesium Chloride Deicer:

Adaptation to Specific Sites or Specific Application Rates

The following steps allow the rule of thumb for judging adequate dilution of magnesium chloride deicer to be adapted to specific locations or specific application rates.

1. Measure or estimate the total constructed area (as m^2) per mile of highway at the site of interest. The constructed area consists of the highway itself, shoulders, median (if present), constructed embankments, frontage roads, etc. At some locations, judgement must be used in estimating the width of the constructed area. There are no hard rules for making this judgement, which may vary according to the purposes for which the calculation is being made.

2. Estimate runoff passing from the roadway during the snow season. This number is difficult to obtain because the runoff on roads typically cannot be channelized or captured in a quantitative manner. The runoff from gauged watersheds or watershed segments near the site of interest are the best source of information.

3. Multiply highway area (m^2) by amount of runoff during snow season (meters). The result will be the total amount of moisture (m^3) passing from one mile of roadway per year during the snow season.

4. Estimate application rate, (m^3/mile of roadway/yr), which may vary from year to year and from one highway to another. If the analysis is retrospective, actual application records can be obtained from CDOT for use in the calculation. If not, a characteristic number for a particular highway can usually be obtained from past applications to the highway.

5. Divide the amount of runoff for one mile of highway during the snow season by the application rate. The result is an estimate of the dilution factor, i.e., the ratio of water derived from precipitation to volume of deicer that would be expected for the entire season of application.

6. Obtain the relevant chronic water quality standard for a particular constituent of interest for screening.

7. Multiply the water quality standard by the dilution number obtained in Step 5. The result is a concentration that should not be exceeded in undiluted deicer. In other words, this final number can be used in screening deicer that is to be applied to a particular roadway.

8. This method is only an approximate. It is not a substitute for measurements that should be made in the field to verify compliance with surface water standards if there is any doubt about compliance. The method is intended to be applied to chronic standards and not to acute standards. The chronic standards are more stringent than acute standards, and therefore provide some conservatism in the application of the method.

Appendix B

Methods for the Collection and Analysis of Samples

I. Collection of deicer. Magnesium chloride deicer was collected in laboratory cleaned, one-liter nalgene bottles. Samples were taken both from CDOT storage tanks and vendor delivery trucks. Both tank and truck samples were taken from hoses that were not allowed to touch the bottle during collection of the sample. Just prior to the collection of a sample, deicer was allowed to run freely through the hose to ensure that the sample would not be influenced by contamination from the hose with dust or debris. Samples of deicer were diluted by 100x to 1000x with laboratory deionized water, depending on the specific analysis, after which the samples were handled in the same manner as water samples (see below).

II. Collection of stream water and runoff. Samples of water from streams, wetlands, and roadway runoff channels were all collected in laboratory cleaned nalgene bottles (typically one 1 L or more). Samples were dipped from the free-flowing water at a point upstream of the individual who was standing in or near the water. Water samples were stored in a cooler at the time of collection. Conductance and pH were measured in the laboratory immediately after return of samples from the field. A sample split for analysis of major ions was filtered. One portion of this split was analyzed by ion chromatography for chloride and a second split was analyzed by atomic absorption for calcium, magnesium, sodium, and potassium after addition of ultra-pure nitric acid to bring the pH of the sample below 2.0. A sample split for total recoverable metals was taken in the field and was acidified by ultra-pure nitric acid to a pH below 2.0. A split for soluble metals was filtered immediately after it was returned to the lab and then treated with ultra-pure nitric acid to lower the pH below 2.0. Acidified samples were analyzed within one month of the time of collection.

Special methods were used for phosphorus because of the low concentrations that are of interest in mountain environments.

III. Salt and sand. Samples of salt and sand were taken by CDOT personnel from the active working faces of CDOT storage piles at the locations indicated in the text. The sample quantity was approximately five kilograms for each sample site. Samples were mixed prior to sub-sampling. Chemical and biological tests of salt and sand were all based on sub-sampling of this single mixed sample for each storage pile.

IV. Deicer used in toxicity testing. Toxicity testing for a given deicer type in a given year was based on the use of deicer coming from a single, large sample (approximately 50 L) of the deicer in question.

		Method	Reference
Major Ions			
Ca		Atomic Absorption	Std Methods 3120B
Mg		Atomic Absorption	Std Methods 3120B
Na		Atomic Absorption	Std Methods 3120B
Cl[1]		Ion Chromatography	Std Methods 4110
Nutrients			
P	Soluble	Acid Molybdate/Spectrophotometry	Lewis et al. 1984[1]
P	Total Soluble	Persulfate/Acid	Lewis et al. 1984
P	Particulate	Pyrolysis/Acid	Lewis et al. 1984
P	Total	Addition of Fractions	Lewis et al. 1984
Other Inorganics			
Cu		AA/Furnace	EPA 220.2
As		AA/Furnace	EPA 4.1.3, 206.2
Cd		AA/Furnace	EPA 213.2
Cr		ICP	EPA 200.7
Hg		Cold Vapor	EPA 4.1.1, 245.1
Ni		ICP	EPA 200.7
Pb		AA/Furnace	EPA 239.2
Se		AA/Furnace	EPA 4.1.3, 270.2
Zn		ICP	EPA 200.7

[1]Low-concentration methods approved by EPA for Dillon Clean Lakes Study.

Table B1. Summary of analytical methods.