Report No. CDOT-DTD-R-2001-17
Phase II - Final Report

Evaluation and Comparison of Three Chemical Deicers for Use in Colorado

Prof. William M. Lewis

DOT
DEPARTMENT OF TRANSPORTATION
RESEARCH

August 2001

COLORADO DEPARTMENT OF TRANSPORTATION
RESEARCH BRANCH

Evaluation and Comparison of Three Chemical Deicers for Use in Colorado

by

Principal Investigator
Prof. William M. Lewis
Western Environmental Analysts

Report No. CDOT-DTD-R-2001-17
Phase II - Final Report

Prepared by
Colorado Department of Transportation
Research Branch

August 2001

Colorado Department of Transportation
Research Branch
4201 E. Arkansas Ave.
Denver, CO 80222
(303) 757-9506

Table of Contents

Executive Summary

1. The Colorado Department of Transportation has an interest in chemical deicers because of the potential for these compounds to improve traffic volume and safety and reduce the application of sand and salt mixtures. Because chemical deicers are applied in large quantities, CDOT assesses, through its research branch, potential of specific deicers to cause impairment of aquatic environments through which deicers flow after leaving the roadway.
2. During 1997-99, CDOT supported an extensive evaluation of two brands of magnesium chloride deicer (Lewis 1999). Since 1999, CDOT has developed an interest in other types of deicers that may give better performance in the coldest weather. During 2001, CDOT supported a preliminary environmental study of two of these deicers (Caliber M1000, Caliber M2000). The results of this study are summarized here, along with comparisons of the two deicers with magnesium chloride deicer in use by CDOT during 2000-2001.
3. The environmental assessment of Caliber M1000 and Caliber M2000 deicers was less extensive than that of the earlier studies of magnesium chloride deicers during 1997-99 in that it did not include field sampling or bioassay experiments. The study benefited, however, from direct comparisons with some of the results from the earlier studies of magnesium chloride deicer. The scope of work for the study included: (1) analysis and environmental evaluation of constituents in the deicers, (2) experimental tests of oxygen demand caused by the deicers, (3) modelling of the effects of phosphorus in the deicers, and (4) modelling of the

effects of ammonia in the deicers. The studies were conducted on samples of magnesium chloride deicer and Caliber M1000 obtained from CDOT's storage tanks during March 2001, and a sample of Caliber M2000 obtained from the vendor during March 2001.

4. Studies of chemical composition showed that the main inorganic components of Caliber M1000 and Caliber M2000 deicer were very similar to those of the magnesium chloride deicer. Dissolved inorganic solids comprised 30% to 45% of all three deicers, and more than 95% of the mass of inorganic solids for all three deicers was accounted for by magnesium and chloride. Calcium, sodium, potassium, and sulfate also were easily detectable, but were present in small amounts relative to magnesium and chloride.

5. Contaminants, including heavy metals and other related substances with the potential to be toxic to aquatic life, were analyzed, and in a number of cases were detected, but in no case showed evidence of being present in amounts that would, following dilution of the deicer on the roadway, be inconsistent with regulatory limits on concentrations for the protection of aquatic life. In general, the concentrations of contaminants in all three deicers were lower than those found previously in analysis of magnesium chloride deicers.

6. The magnesium chloride deicer contained amounts of phosphorus that would pose negligible risk of raising environmental concentrations of P. In contrast, Caliber M1000 and Caliber M2000 contained substantial amounts of phosphorus, most of which was in soluble form. Total phosphorus in the samples exceeded background concentrations by a factor of approximately 7000 (Caliber M1000) to

14,000 (Caliber M2000). Caliber M1000 and Caliber M2000 also contained high concentrations of ammonia (31-43 mg/L), unlike the magnesium chloride deicer.

7. Caliber M1000 contained a large amount of organic matter (about 24,000 mg/L, or 6000 times background); Caliber M2000 contained even more (65,000 mg/L; 16,000 times background.

8. The overall compositional analysis of the deicer indicates that Caliber M1000 and Caliber M2000 are based on magnesium chloride deicer, but contain much higher amounts of phosphorus, ammonia, and organic matter than magnesium chloride deicer.

9. Oxygen demand for Caliber M1000 and Caliber M2000 was studied by use of water taken from a montane source (the St. Vrain). Decline in oxygen was measured following the addition of 0.2% deicer to the stream water; 0.2% is the concentration that would be expected for water leaving a roadway that had been treated with deicer. All three deicers showed low rates of oxygen consumption over short time intervals (24 to 48 hours). Over 6 days, however, Caliber M1000 and Caliber M2000 deicers showed a large amount of oxygen consumption (complete depletion of oxygen in the experimental chambers), whereas oxygen consumption by magnesium chloride was much lower. The large amounts of organic matter in the Caliber M1000 and Caliber M2000 deicers appear to have stimulated rapid microbial growth following a lag of a few days during which microbial populations grew or acclimated metabolically to the organic matter in these deicers.

10. Potential environmental effects of the phosphorus from the deicers were explored through modelling. For modelling purposes, the application rates expected by CDOT were used and phosphorus content of the sample that was analyzed was also used. A model was constructed that computes the percent increment over background phosphorus concentrations for watersheds of various sizes, and for specific watersheds that would be good candidates for treatment with deicers. For hypothetical watersheds, the influence of magnesium chloride deicer on mean winter and spring background phosphorus concentrations would be negligible. For Caliber M1000, watersheds smaller than 10 square miles would show increases in phosphorus concentration between 15% and 40% in response to use of the deicer. For Caliber M2000, watersheds smaller than 10 square miles would show increases ranging from 25% to 80%. For specific watersheds where application would be likely, percent increase over background would be lowest for Tenmile Creek (10% for Caliber M1000; 19% for Caliber M2000) and highest for Straight Creek (39% for Caliber M1000; 74% for Caliber M2000). Use of Caliber M1000 or Caliber M2000 in Summit County could measurably increase total phosphorus load to Lake Dillon, which has a site-specific phosphorus standard.

11. Potential environmental effects of unionized ammonia from deicers were studied through modelling. Assumptions about application rates were the same as those used for the studies of phosphorus. The ratios of unionized ammonia derived from deicers to the stream standard for aquatic life were estimated for a range of pH values. At a pH near 9.0 (as shown by laboratory dilution of deicers), the

ammonia content of all three deicers would cause roadway runoff to exceed the standard for protection of cold water aquatic life at points beyond the roadway. A 5-fold dilution, which would probably occur very near the road, would be necessary to eliminate the likelihood of an exceedance of the stream standard for magnesium chloride deicer; Caliber M1000 would require as much as 38-fold dilution, and Caliber M2000 would require as much as 54-fold dilution. Ammonia in the Caliber M1000 and Caliber M2000 deicers raises the possibility of toxicity to aquatic life beyond the edge of the roadway, but probably not at great distances from the roadway.

12. Caliber M1000 and Caliber M2000 are similar in some respects to magnesium chloride deicer used by CDOT, but contain substantially more phosphorus, ammonia, and organic matter. Phosphorus raises concerns about elevated concentrations and loads of phosphorus in montane environments, where phosphorus is typically scarce, ammonia raises some concerns about toxicity to aquatic life at points beyond the roadway, and organic matter is a potential source of oxygen depletion.

Introduction

Use of chemical deicers may increase traffic flow and reduce road hazards associated with winter precipitation, especially in montane environments. Chemical deicers also many offer certain environmental benefits in that they may allow reduction in the use of salt and sand mixtures, which create air pollution and fill stream channels with sand to such an extent that their potential for support of aquatic life is reduced. The advantages of using chemical deicers, however, must be weighted against potential for environmental impairment that might be associated with these chemical mixtures. Because chemical deicers pass into the drainage network, the issue of greatest concern environmentally is the welfare of aquatic life. Subjects of interest environmentally related to any chemical deicer include the potential for direct toxicity in concentrations expected in runoff from roadways, potential for nutrient enrichment (eutrophication), and potential for rapid use of oxygen leading to stress on aquatic life.

A comprehensive study of magnesium chloride deicers was conducted by CDOT during 1997-1999 (Lewis 1999). The study showed that it is important for CDOT to make specific restrictions on contaminants and anticorrosion additives that are present in magnesium chloride deicers. If the restrictions are maintained, the chance for environmental impairment through the use of these deicers is very low and is limited to points very close to roadways where large amounts of deicer are used.

CDOT has interest in deicers other than magnesium chloride deicers. Two deicers of current interest to CDOT include Caliber M1000 and Caliber M2000. These deicers are marketed as an alternative to the magnesium chloride deicers that were tested earlier. Caliber M1000 and Caliber M2000 are considered more effective at low temperatures than magnesium chloride deicers. For this reason, CDOT has supported a study of the environmental effects of Caliber M1000 and Caliber M2000; the study includes direct comparisons with the magnesium chloride deicer currently in use by CDOT. This study, the results of which are reported here, is less comprehensive than the study of magnesium chloride deicers that was completed in 1999, but does benefit from the possibility of comparisons with data that were obtained previously.

The present study of Caliber M1000 and Caliber M2000, which included comparisons to magnesium chloride deicer in use during 2000-2001, has four components: 1) evaluation of chemical composition and potential toxicity or other environmental effects, 2) studies of oxygen demand, 3) modelling of the effects of phosphorus addition to streams through the use of deicer, and 4) modelling of the effects of ammonia addition to streams through the use of deicer. These four components of the study are reported in separate sections below. Each of the sections contains its own information on methods and results. The final section of the report gives an overview and comparison of the deicers.

Analysis and Interpretation of Constituents

The constituents of deicers fall under three broad headings: main ingredients, corrosion inhibitors, and contaminants (Lewis 1997). Main ingredients are those that account for 95% or more of the substances dissolved in the deicer. Corrosion inhibitors, if present, are typically added in concentrations of a few percent, and often are proprietary in nature. For magnesium chloride deicers, they include small organic molecules, phosphates, or other compounds that mask metal parts from contact with the salts that typically compose the bulk of the main ingredients in a chemical deicer. Contaminants may include any inorganic or organic substance that may be carried into the deicer along with the main ingredients. Although deicers typically are subject to a certain amount of processing, they are not highly refined materials and thus may contain small amounts of virtually any substance that is present in the raw materials from which they were derived. For example, magnesium chloride deicers contain metals and nutrients in varying amounts (Lewis 1999), even though these substances, except as included in corrosion inhibitors, are not added intentionally to the deicer and perform no specific function related to the deicer.

There are two ways of evaluating chemical constituents of deicer from the viewpoint of water quality and welfare of aquatic life. The first is chemical analysis of the deicer followed by interpretation based on toxicity or other kinds of responses known to be associated with specific substances at specific concentrations. The second approach is bioassay, which is a way of evaluating the toxicity of a substance or a mixture of substances through the exposure of selected kinds of organisms to varied concentrations under controlled conditions. Both of these types of tests have been performed on magnesium chloride deicer (Lewis 1999). For the present study, the analysis of constituents is limited to the first of the two approaches, i.e., analysis and interpretation of chemical constituents based on thresholds of response known from thresholds that have been established for water quality regulations.

Samples of magnesium chloride and Caliber M1000 deicer were collected on 7 March 2001 at the CDOT Region 1 site. Samples were placed in chemically-clean polyethylene containers following appropriate flushing of the discharge hose from the storage tanks. Caliber M2000 was obtained directly from the vendor, GMCO, at 2611 South Yarrow Street in Lakewood, Colorado.

The deicers were analyzed for constituents by standard laboratory procedures. Methods are given in Appendix A of this report.

Major Inorganic Constituents

The major inorganic constituents are listed in Table 1 for all three deicers. Magnesium chloride deicer serves as a convenient baseline because it has been analyzed previously (Lewis 1999). As expected, the dominant major constituents were magnesium and chloride in the magnesium chloride deicer. Concentrations of both of these ions are somewhat higher than in previous analyses, but some variation in specific formulations is expected. Easily measurable amounts of sodium, potassium, sulfate, and calcium were also present, but these contributed far less than magnesium and chloride to the total mass of dissolved salts.

Magnesium and chloride also were the two main ionic constituents of Caliber M1000 and Caliber M2000. In other words, both the Caliber M1000 and Caliber M2000 were formulated from a magnesium chloride base. Caliber M1000 contained somewhat more of both magnesium and chloride than the magnesium chloride deicer, and Caliber M2000 contained somewhat less, but the variations were not great. Other major ions were present in easily measurable but modest amounts. Caliber M2000, however, showed substantially higher sulfate concentrations than either magnesium chloride or Caliber M1000.

Nutrients

Table 1 also summarizes the concentrations of phosphorus and nitrogen in the three deicers. These two elements often regulate the abundance of algae and other photosynthetic forms of aquatic life. Although aquatic organisms require more than 20 substances for continuous growth, phosphorus and nitrogen are the most likely of these to be in short supply. Addition of phosphorus or nitrogen to aquatic habitats may, therefore, cause the development of excessive growth of aquatic photosynthetic organisms, which include both algae and aquatic vascular plants.

For purposes of environmental evaluation, phosphorus was analyzed as three fractions: soluble reactive phosphorus (SRP, sometimes called orthophosphate), total dissolved phosphorus (TDP), and particulate phosphorus (PP). SRP consists for the most part of inorganic phosphorus in the form of ionized phosphorus acid ($H_2PO_4^-$). The analysis is sensitive to some phosphorus-containing organic molecules, however, and for this reason it cannot be assured that all of SRP is inorganic. The SRP fraction has the highest bioavailability, i.e., it is readily taken up from water at low concentrations by algae or aquatic vascular plants, and has the most immediate stimulating effect on growth of these organisms.

Total dissolved phosphorus was analyzed by use of a digestion procedure that converts organic phosphorus into inorganic phosphorus, which then was measured by the same inorganic phosphorus test that is used for SRP. The sample was first filtered for removal of particulate phosphorus. Total dissolved phosphorus contains the SRP fraction. If SRP is subtracted from TDP, the difference is an estimate of dissolved organic phosphorus (DOP). DOP contains molecules such as nucleic acids, phospholipids, detergents, and numerous other naturally-occurring and synthetic compounds.

Particulate phosphorus (PP) was analyzed separately from the soluble fractions. Water was passed through a filter and the particulate matter on the filter was digested by a procedure that liberated the phosphorus, which then was analyzed as inorganic phosphorus.

The magnesium chloride sample included in this study contained relatively small amounts of phosphorus (Table 1). The concentrations of phosphorus in the sample correspond to only about 20% of the concentrations that would be expected from municipal secondary effluent; previous analysis of phosphorus in magnesium chloride deicers have shown higher concentrations (Lewis 1999). The background phosphorus concentrations for streams in Summit County are in the vicinity of 0.005 to 0.010 mg/L (Lewis et al. 1984). Phosphorus on the roadways expected to be diluted by a factor of approximately 500 by melting precipitation. Assuming that precipitation has very low or negligible phosphorus content, which is commonly the case, a mixture of deicer and dilution water would contain phosphorus concentrations of only a few thousands of a milligram per liter, i.e., concentrations within the observed range for montane waters in Colorado. For magnesium chloride, most of the total phosphorus was soluble.

Caliber M1000 had total phosphorus concentrations 70 times as high as magnesium chloride deicer and Caliber M2000 had total phosphorus concentrations 130 times as high as magnesium chloride deicer. The phosphorus concentrations of Caliber M1000 exceeded environmental background concentrations by a factor of about 10,000;

for Caliber M2000, the factor was about 20,000. Even after dilution on the roadway is accounted for, these deicers could be expected to cause significant enrichment in receiving waters with low background, as is the case at high elevation. The amount of increase in concentration caused by deicers under various conditions is explored further by modelling, as reported in a separate section of this report. Most of the phosphorus for both Caliber M1000 and Caliber M2000 was soluble, i.e. it could be readily used by plants (including algae), and therefore could be expected to stimulate plant growth.

Magnesium chloride deicer contains relatively little ammonia, but Caliber M1000 and Caliber M2000 both contain amounts of ammonia exceeding the amounts that would be expected for secondary effluent, and 10,000 to 20,000 times as high as background in streams of undisturbed watersheds (Lewis et al. 1999). Inorganic nitrogen as ammonia (mostly present as the ammonium ion, NH_4^+) is a potent plant nutrient because ammonia is the most highly available form of inorganic nitrogen for plants, including algae. Thus, ammonia is of some interest from the viewpoint of nutrient enrichment.

Phosphorus is generally considered to be a more harmful agent of eutrophication than nitrogen in most inland waters. Also, phosphorus is needed in smaller amounts than nitrogen, which means that the multiplier effect of phosphorus on growth of aquatic plants is larger than for nitrogen. Because phosphorus is more abundant than nitrogen in the deicer, the main focus for analysis of eutrophication potential should be on phosphorus rather than nitrogen. Even so, the presence of substantial amounts of ammonia in the deicer is potentially of environmental interest because the inorganic nitrogen content of ammonium could magnify the potential biotic responses to phosphorus in the deicer.

Ammonia, although mostly present in water as the ammonium ion (NH_4^+), can be associated with toxicity to aquatic life in water because the ammonium ion is in equilibrium with ammonium hydroxide and free unionized ammonia (NH_3). Unionized ammonia is toxic to aquatic life and is regulated for this reason by the Colorado Water Quality Control Commission (2001). Thus while the ammonium ion stimulates plant growth, its equilibrium partner, unionized ammonia, is the cause of toxicity to invertebrates and fish above certain thresholds that are relatively low (e.g., 0.02 mg/L for trout). The thresholds of toxicity are well established and are reflected in the water quality standards for Colorado. The best basis for evaluating this aspect of the significance of ammonia in deicer is through modelling, which is reported in a subsequent section of this report.

Other Inorganic Substances

Table 1 includes the results of analyses of other inorganic substances, all of which are of interest because of their potential toxicity. The list consists of heavy metals and substances that are not true metals but typically are analyzed and evaluated along with metals (arsenic, selenium).

Concentrations of metals and related substances in the magnesium chloride deicer for year 2001 generally were lower than or similar to concentrations observed for the same type of deicer used in previous years (Lewis 1999). Concentrations of these same substances in Caliber M1000 and Caliber M2000 were similar to concentrations in the magnesium chloride deicer.

		Milligrams per Liter		
Constituent		Magnesium Chloride	Caliber M1000	Caliber M2000
Major Ions				
Ca^{++}		82	1200	1060
Mg^{++}		90,800	99,700	80,500
Na^{+}		2640	1700	1510
K^{+}		2050	1110	890
$SO_4^{=}$		850	1300	12,800
Cl^{-}		292,000	324,000	252,000
Nutrients				
Soluble Reactive P		0.4	28	40
Total Soluble P		0.7	67	116
Particulate P		0.3	3	18
Total P		1.0	70	134
Total Ammonia N[1]		4	31	43
Other Inorganics				
Cu	Sol	0.022	0.083	0.149[2]
	Tot	0.056	0.086	-
As	Sol	-	-	-
	Tot	0.523	0.778	0.911
Cd	Sol	0.007	0.007	0.005
	Tot	-	-	-
Cr	Sol	0.33	0.25	0.33
	Tot	2.46	2.37	1.84
Hg	Sol	<0.0002	<0.0002	<0.0002
	Tot	<0.0002	<0.0002	<0.0002
Ni	Sol	<0.02	0.10	0.07
	Tot	0.34	0.28	0.23
Pb	Sol	<0.05	<0.05	<0.05
	Tot	<0.05	<0.05	<0.05
Se	Sol	<0.002	<0.002	0.385
	Tot	-	-	-
Zn	Sol	2.56	0.510	0.57
	Tot	4.53	3.55	0.91
Organic Matter				
Total Organic Carbon		270	24,300	64,700

[1] Ammonia N is both a plant nutrient and, at high concentrations, a toxin for aquatic life.

[2] Total less than soluble; total omitted.

Table 1. Concentration of various constituents of three chemical deicers used by or considered for use by CDOT in 2000-2001. Sol=soluble, Tot=total.

One way of evaluating the potential for toxicity of metals and related substances in streams at high elevation, where contamination would be of greatest concern, is by a ratio showing the amount of dilution required for the deicer to fall above the relevant stream standard for protection of aquatic life in mountain streams. These ratios are shown in Table 2. A 500-fold dilution is important as a reference point because it corresponds to the expected dilution of the deicer on the roadway (including shoulders and medians: Lewis 1999). Substances requiring dilution significantly above 500 to 1 raise an implicit environmental concern because they would be likely to reach the receiving waters at concentrations inconsistent with the standards protective of aquatic life. Even so, further dilution of runoff beyond the point of merger with receiving waters generally would occur very rapidly (Lewis 1999).

None of the metals and related substances shown in Table 1 exceeded concentrations that would be inconsistent with the stream standards for protection of aquatic life. Therefore, there are no obvious environmental concerns for any of the three deicers under the heading "Other Organics" in Table 1.

Organic Matter

Analysis of the organic content of the deicers by use of a carbon analyzer showed that the magnesium chloride deicer contained the lowest amount of organic matter; the organic carbon concentration in the magnesium chloride deicer was substantially lower than measured for the same type of deicer in previous years. The organic content of the Caliber M1000 and Caliber M2000 deicers was very high. In fact, at 24,300 mg/L organic C for Caliber M1000 and 64,700 mg/L organic C for Caliber M2000, organic

		Environmental Ratio		
Constituent		Magnesium Chloride	Caliber M1000	Caliber M2000
Major Ions				
Ca^{++}		4	60	53
Mg^{++}		26,435	29,027	23,437
Na^{+}		752	485	430
K^{+}		4100	2220	1782
$SO_4^{=}$		369	565	5565
Cl^{-}		75,607	83,893	65,250
Nutrients				
Soluble Reactive P		211	14,737	21,053
Total Soluble P		135	12,885	22,308
Particulate P		60	600	3600
Total P		107	7487	14,332
Total Ammonia N		2000	15,500	21,500
Other Inorganics				
Cu	Sol	4	17	30
	Tot			
As	Sol	3	5	6
	Tot			
Cd	Sol	5	5	4
	Tot			
Cr	Sol	30	23	30
	Tot			
Hg	Sol	<2	<2	<2
	Tot			
Ni	Sol	<1	3	2
	Tot			
Pb	Sol	<42	<42	<42
	Tot			
Se	Sol	<1	<1	84
	Tot			
Zn	Sol	39	8	9
	Tot			
Organic Matter				
Total Organic Carbon		68	6075	16,175

Table 2. Ratio of concentrations for constituent in each of the three deicers to expected background concentrations (major ions, nutrients) or to chronic stream standards for support of aquatic life (other substances). Ratios above 500 for nutrients, organic matter, or other inorganics indicate potential for environmental effects. Estimates of standards for metals assume hardness=50 mg/L.

matter makes up a substantial portion of the total dissolved solids in these two deicers. In other words, it is a major constituent rather than a contaminant. Because carbon accounts for approximately half the mass of organic matter, the total organic matter content can be estimated as double the organic carbon content shown in Table 1. The amounts of organic matter in these two deicers are very high by comparison with background concentrations (approximately 4 mg/L organic C in winter).

The identity of the organic matter in the Caliber M1000 was not determined in the course of this study. In general, there are two possible concerns with organic matter: toxicity and oxygen demand in aquatic ecosystems. Manufacturers select organic matter believed to be nontoxic, but absence of toxicity has not been verified by bioassay experiments. Bulk addition of organic matter raises the possibility that organic contaminants, as well as the main organic ingredients that are added intentionally, could be present, but this issue has not been studied. Also, an issue of relevance to receiving waters is potential oxygen demand that might be associated with the organic matter. Oxygen demand was studied experimentally, as described below.

Oxygen Demand of the Deicers

Deicing compounds that contain substantial amounts of organic matter may produce depression of oxygen concentrations in surface waters. As organic matter from the deicer is carried with runoff from a roadway into a stream, for example, the organic matter will be subject to breakdown by microbes. The breakdown process requires oxygen, which is drawn by the microbes from the water. If the oxygen demand by the microbes is large, depression of oxygen concentration may result, and aquatic life may be impaired. Aquatic life in cold water environments is especially sensitive to depletion of dissolved oxygen.

The effect of a particular deicer on oxygen concentrations depends on the formulation of the deicer, the amount of the deicer that reaches the receiving water, and the conditions in the receiving water. One way to test the degree to which a given deicer might affect oxygen concentration in a receiving water is through the measurement of oxygen depletion in the water under experimental conditions involving addition of deicer to the water. This was the concept behind the tests of the three deicers for the present study.

Methods

The standard test for use of oxygen by microbes in water containing organic matter (e.g., wastewater) is the BOD test, which involves incubation of water over an extended interval (five days) at a moderately high temperature (20°C). This standard test is not very useful for evaluation of chemical deicer because effects occurring over short as well as longer duration are of interest, and because the temperature is unrealistically high for montane conditions. Furthermore, a test of oxygen demand by deicer should be based on a sample of stream water that contains an amount of deicer approximately equal to that anticipated for runoff entering a stream. Thus, while based on a protocol roughly similar to that of the standard BOD test, the oxygen demand test employed here is uniquely designed to give a more realistic view of oxygen demand by deicers.

The protocol that was used for testing the three deicers is similar to the one used previously for magnesium chloride deicer (Lewis 1999). Natural stream water was used. Previous studies showed that the source of stream water does not have much effect on the results. Therefore, a single source of stream water was used (the St. Vrain in Lyons). Six treatments were used: deionized water with no deicer (analytical control), St. Vrain water with no deicer, with and without rocks; St. Vrain water with rocks and 0.2% magnesium chloride deicer; St. Vrain water with rocks and 0.2% Caliber M1000 deicer; and St. Vrain water with rocks and 0.2% Caliber M2000 deicer. The expected dilution of the deicers when applied to the roadway is about 1 to 500 (0.2%) at points near a roadway where runoff containing deicer occurs (Lewis 1999). This was the basis for the concentration for deicer that was used in each of the treatments involving deicer. In previous tests of oxygen demand, deicer was added to stream water only. For the present study, three small rocks (~ 1 cm) were taken from the St. Vrain on the same date and at the same point where the stream water was taken. These were added to each of the bottles to which deicer was added. The purpose of adding the rocks was to make the test more realistic by allowing the presence of a natural biofilm, which would be rich in naturally occurring microbes. A treatment was run with stream water and with and without rocks in order to demonstrate the influence of the biofilm on oxygen consumption in the absence of deicer.

A stream water sample was collected from the St. Vrain River on April 19, 2001, at the Highway 36 bridge near Colorado 7 and the water was used the following day for experimental incubations. Measurements were made of the initial oxygen concentration just prior to the incubation and of the remaining oxygen following 24 h and 48 h, and 6 days of incubation. The temperature of incubation was 8°C, which was close to the ambient temperature of the water at the time of collection. The incubations were conducted in 333 milliliter BOD bottles that were kept closed to prevent contact of the water with the atmosphere, except during brief periods of oxygen measurement with an oxygen probe. The decline in oxygen between the initial oxygen reading and the reading for each of the three elapsed times following the start of the incubation was the basis for estimating the rate of oxygen consumption.

Results

The results of the oxygen demand test are given in Table 3. The analytical control with deionized water only, the purpose of which was to test for analytical problems involving the measurement of oxygen, showed no significant oxygen consumption, as expected. Addition of rocks to the analytical control caused a modest but easily measurable consumption to occur, as expected, from the presence of the biofilm. For stream water only, there were negligible rates of oxygen consumption over 24 hours but oxygen consumption became measurable after 6 days. Stream water with rocks added showed low but measurable oxygen consumption, even after 24 hours. The oxygen concentration for stream water with rocks was greater than for deionized water with rocks, presumable because the stream water offered some natural organic matter that stimulated respiration rates by the microbes.

Addition of magnesium chloride deicer at 0.2% to stream water containing rocks

Water Source	Rocks	Amount Deicer, %	Oxygen Consumption, mg/L			
			24h	48h	6d	
Deionized Analy. Control	No	0	0.03	0.04	0.05	
Deionized Analy. Control	No	0	-0.02	-0.05	0.04	
Deionized Analy. Control	No	0	-0.01	0.06	0.10	
Mean	-	-	0.00	0.00	0.06	
Deionized	Yes	0	0.28	0.60	1.66	
Deionized	Yes	0	0.15	0.24	0.79	
Deionized	Yes	0	0.15	0.34	0.96	
Mean	-	-	0.19	0.39	1.14	
St. Vrain	No	0	0.02	0.10	0.41	
St. Vrain	No	0	-0.03	0.07	0.33	
St. Vrain	No	0	0.01	0.07	0.38	
Mean	-	-	0.00	0.08	0.37	
St. Vrain	Yes	0	0.29	0.56	1.49	
St. Vrain	Yes	0	0.28	0.52	1.32	
St. Vrain	Yes	0	0.31	0.56	1.61	
Mean	-	-	0.29	0.55	1.47	
St. Vrain and MGC12	Yes	0.2	0.17	0.45	1.48	
St. Vrain and MGC12	Yes	0.2	0.21	0.50	1.69	
St. Vrain and MGC12	Yes	0.2	0.38	0.73	2.58	
Mean	-	-	0.25	0.56	1.92	
St. Vrain and M1000	Yes	0.2	0.60	1.28	9.20	*
St. Vrain and M1000	Yes	0.2	0.51	1.31	9.12	*
St. Vrain and M1000	Yes	0.2	0.34	0.82	9.15	*
Mean	-	-	0.48	1.14	9.16	*
St. Vrain and M2000	Yes	0.2	0.41	1.53	9.19	*
St. Vrain and M2000	Yes	0.2	0.69	1.74	9.18	*
St. Vrain and M2000	Yes	0.2	0.56	1.62	9.12	*
Mean	-	-	0.57	1.63	9.16	*

*All oxygen consumed.

Table 3. Summary of oxygen consumption data (respiration estimates) for three deicers in stream water (rocks were included in bottles treated with deicer and in some of the experimental controls; see text).

caused no significant increase in oxygen consumption at 24 and 48 hours. There was a suggestion of some increase in consumption over 6 days, but the increase was minor and was not statistically significant.

Stream water with rocks and Caliber M1000 showed higher oxygen consumption than stream water with magnesium chloride deicer at 24 and 48 hours as well as 6 days. Over 24 hours, the elevation of oxygen consumption was small in absolute terms, and the same was true over 48 hours. There was a strong escalation of oxygen consumption rate between 48 hours and 6 days, however, leading to complete depletion of oxygen. Two factors may account for the lag that occurred between the initial, lower rates of consumption and the higher rates of consumption that were observed toward the end of the experiment. Addition of the deicer introduced a large amount of organic matter. The microbes responded metabolically, but only to a limited extent until sufficient time had elapsed for several generations of microbes to be produced in response to the increased organic matter supply. If the population increased in this way, the rate of oxygen demand would have increased correspondingly. The rate of increase probably was not very high because the temperature was low. A second factor, which may have occurred simultaneously with the first, could have been that the organic matter added with the deicer was not well suited for use by the microbes, given their acclimation to natural organic matter in the stream, but the microbes adjusted metabolically or through proliferation of specific well suited strains over a period of several days, and thus were able to use the organic matter much more rapidly toward the end of the experiment.

The results of the experiment with Caliber M2000 were similar to those for Caliber M1000, except that the increase in oxygen demand occurred more rapidly, as might be expected given the larger amounts of organic matter in Caliber M2000. As in the case of Caliber M1000, all oxygen was exhausted by the end of the experiment.

Rates of oxygen used in stream water containing natural substrates (rocks) in the absence of the deicers were quite low. Addition of Caliber M1000 and Caliber M2000 deicers increased these rates threefold to fourfold over 24 to 48 hours. Although in a relative sense this degree of stimulation is high, the absolute rates of oxygen consumption were not high and would not be expected to cause significant oxygen depletion in a stream, which is able to take up oxygen by contact with the air. Over longer time intervals, however, with a buildup in microbial respiration rates in response to large amounts of organic matter, the rates of oxygen demand were substantially higher and could be cause for concern in aquatic habitats such as wetlands or pools that have low rates of gas exchange. The rate of oxygen consumption over long periods of incubation bears further study because of the apparently high rates of consumption following a period of adjustment by the microbes.

Phosphorus: Evaluation of Potential Effects by Use of Modelling

Concentrations of phosphorus in the magnesium chloride deicer that was tested for this study were relatively low in view of the expected dilution on the roadway (1 to 500). In contrast, concentrations of phosphorus in Caliber M1000 and Caliber M2000 were very high. As shown by Table 2, the environmental ratios for these two deicers exceeded the threshold of 500 by a wide margin. Thus the environmental ratios indicate that the expected concentrations of phosphorus in receiving waters should be studied more closely. This was accomplished by modelling.

Application rates were the first consideration in construction of a phosphorus model. It was assumed for purposes of modelling that Caliber M1000 deicer would be applied at approximately 12,000 liters per lane mile of roadway per year (Chuck Loerwald, CDOT, personal communication). This annual application rate varies in response to variation in weather between years; the model can accommodate other assumed rates as desired.

Concentration of phosphorus in the deicer also must be known for purposes of modelling. The present modelling uses the concentrations of total phosphorus shown in Table 1 for the three deicers (1 mg/L for magnesium chloride, 70 mg/L for Caliber M1000, 134 mg/L for Caliber M2000).

Given the concentrations as derived from the chemical analysis shown in Table 1 and the assumed application rates, it is possible to calculate the annual yield of phosphorus per unit length of roadway. For 12,000 liters per lane mile and 1 mg/L of phosphorus, the total annual yield per lane mile would be .025 pounds, or .012 kilograms. For a two-lane road, the yield would be twice this much per mile and for a four-lane road it would be four times as much per mile. The yield per lane mile would increase proportionately to the increase in concentration of phosphorus in the deicer.

Background concentration of P is also needed for modelling. The background concentration of P, expressed as an annual discharge-weighted mean, is a function of the amount of runoff. In years or locations with greater runoff, the mean annual concentration of P is greater. Equations for this relationship were derived from the extensive studies of background conditions in Summit County (Lewis et al. 1984, as later revised with more extensive data). These equations were used in modelling to predict the expected background concentrations at any given annual runoff. For purposes of modelling, runoff was assumed to be 300 mm per year, but the model can accommodate other assumptions about runoff as necessary to reflect variations from year to year or place to place.

Given the equations mentioned above and the amount of runoff, it is possible to calculate not only the mean annual phosphorus concentration of runoff, but also the total mass of phosphorus that would be expected to exit a watershed of given size under background conditions. Although anthropogenic phosphorus sources affect some montane environments, many such environments approach background conditions for phosphorus. Thus the most appropriate basis for evaluating phosphorus in deicers is the background condition rather than background plus point or non-point sources, which vary widely by location.

The estimates of mass transport per unit of watershed area under background conditions can be compared with mass transport of phosphorus originating from deicers. This is accomplished through estimation of the ratio of roadway miles to watershed area. Table 4 shows the results of such calculations for selected watersheds where the application of deicers is expected.

The ratio of road miles to watershed area also can be generalized by reference to stream order or watershed size. Given the simplifying assumptions that montane watersheds are approximately three times as long as broad and that the roadway passes through the long axis of the watershed, ratios can be calculated for watersheds of various sizes. These estimates are shown in Table 5 for watersheds ranging from 1 to almost 400 square miles.

As shown by Tables 4 and 5, Caliber M1000 and Caliber M2000 would under most conditions cause a substantial increase in the phosphorus concentrations of stream water relative to background. In Colorado, waters of high quality are judged by an antidegradation standard equal to 15%: a change in the concentration of any regulated substance by more than 15% of the difference between the background and the standard is prohibited. While not all the waters that might receive Caliber M1000 or Caliber M2000 in runoff would be covered by the antidegradation rule, the rule does provide

Watershed	Road Miles	Lanes	Watershed Area mi^2	Ratio*	P** µg/L	Increase*** %
Magnesium Chloride						
Clear Cr abv Georgetown	12	4	80	0.30	5.6	0.2
Tenmile Cr	12	4	93	0.26	5.6	0.1
Straight Cr abv Silverthorne	9	4	18	1.00	5.6	0.6
Caliber M1000						
Clear Cr abv Georgetown	12	4	80	0.30	6.3	11.6
Tenmile Cr	12	4	93	0.26	6.2	10.0
Straight Cr abv Silverthorne	9	4	18	1.00	7.8	38.6
Caliber M2000						
Clear Cr abv Georgetown	12	4	80	0.30	6.8	22.2
Tenmile Cr	12	4	93	0.26	6.7	19.1
Straight Cr abv Silverthorne	9	4	18	1.00	9.7	73.9

*Two-lane road miles per square mile of watershed.
**With deicer in use.
***Increase above background.

Table 4. Model output showing the expected effects of each of the three deicers on mean annual discharge-weighted mean phosphorus concentrations of selected montane watersheds.

some basis for judging the effects on a percentage basis (assuming that a standard, which does not exist for phosphorus would be double the background). As shown in Table 4, use of Caliber M2000 would be inconsistent with the 15% guideline in all cases, and use of the Caliber M1000, if formulated in a manner identical that of the sample obtained during 2001, would be inconsistent with use on I-70 above Silverthorne but would be

Stream Order	Area mi^2	Length miles	Ratio* for 2 Lanes	P µg/L	Increase, %	Ratio* for 4 Lanes	P µg/L	Increase, %
Magnesium Chloride								
1	1.2	0.6	0.54	8.8	56.2	1.07	5.6	0.6
2	3.9	1.1	0.29	7.3	30.8	0.59	5.6	0.3
3	11.6	2.0	0.17	6.6	17.8	0.34	5.6	0.2
4	38.6	3.6	0.09	6.1	9.7	0.19	5.6	0.1
5	115.0	6.2	0.05	5.9	5.6	0.11	5.6	0.1
6	386.0	11.3	0.03	5.8	3.1	0.06	5.6	0.0
Caliber M1000								
1	1.2	0.6	0.54	8.8	56.2	1.07	7.9	41.4
2	3.9	1.1	0.29	7.3	30.8	0.59	6.9	22.7
3	11.6	2.0	0.17	6.6	17.8	0.34	6.3	13.1
4	38.6	3.6	0.09	6.1	9.7	0.19	6.0	7.2
5	115.0	6.2	0.05	5.9	5.6	0.11	5.8	4.2
6	386.0	11.3	0.03	5.8	3.1	0.06	5.7	2.3
Caliber M2000								
1	1.2	0.6	0.54	8.8	56.2	1.07	10.0	79.3
2	3.9	1.1	0.29	7.3	30.8	0.59	8.0	43.4
3	11.6	2.0	0.17	6.6	17.8	0.34	7.0	25.1
4	38.6	3.6	0.09	6.1	9.7	0.19	6.4	13.7
5	115.0	6.2	0.05	5.9	5.6	0.11	6.0	8.0
6	386.0	11.3	0.03	5.8	3.1	0.06	5.8	4.3

*Two-lane road miles per square mile of watershed.

Table 5. Effect of the three deicers on phosphorus concentrations in watersheds of various size.

consistent with use in the two other locations shown in Table 4. Table 5 shows that both Caliber M1000 and Caliber M2000 would be inconsistent with the 15% guideline for watersheds of small to moderate size.

Magnesium chloride deicer, as represented by the sample analyzed in 2001, would not significantly increase phosphorus concentrations above background following dilution on the roadway, and would be consistent with a 15% antidegradation guideline for watersheds of all sizes.

The general conclusion from phosphorus modelling is that the concentrations of phosphorus in the Caliber M1000 and Caliber M2000 samples that were analyzed in this study are too high to be consistent with the maintenance of characteristically low phosphorus concentrations in montane streams under most conditions. Increase in phosphorus caused by these deicers could lead to increased growth of algae in streams and could affect algal abundance and transparency in lakes or ponds where waters are impounded. Addition of these deicers to the Lake Dillon watershed is especially problematic, given that Lake Dillon is protected by a site-specific phosphorus standard, and the phosphorus control program operated by Summit County governments relies on controlling non-point sources of all types.

Use of Modelling to Evaluate Potential Ammonia Toxicity

Both the Caliber M1000 and Caliber M2000 deicers contain substantial amounts of ammonia. Thus, there is some potential that, even after its dilution on the roadway, the deicer could cause toxicity to aquatic organisms, which are highly sensitive to the unionized form of ammonia. The probability of toxicity depends on several factors, however, and therefore must be evaluated by modelling.

A simple model was created for the evaluation of toxicity caused by ammonia in the deicers. Assumptions concerning the rate of application of the deicer were the same as those used in phosphorus modelling. The amount of total ammonia was set to the concentrations shown in Table 1 for the deicers. The amount of dilution of deicer on the roadway was set to 500 to 1. Temperature, which affects the equilibrium between ionized and unionized ammonia was set to 5°C, as appropriate for winter or spring conditions. The model can accommodate changes in any of these assumptions for the purpose of exploring alternate conditions such as lower or higher concentrations of total ammonia in the deicer, different dilution rates on the roadway, etc.

The model gives the concentration of unionized ammonia for a range of pH values that might be typical of runoff. The concentration of unionized ammonia then is expressed as a ratio to the stream standard for unionized ammonia as it relates to protection of aquatic life (0.2 mg/L for chronic exposure of coldwater aquatic life). Ratios in excess of 1 would indicate that the water leaving the roadway would be likely to exceed the stream standard for protection of aquatic life.

Results of modelling are shown in Table 6. As indicated by the table, the pH of runoff is a very important determinant of the outcome. At low pH, there is very little unionized ammonia because the equilibrium between ionized and unionized ammonia is strongly biased toward the ionized form. At higher pH, the equilibrium shifts, and more of the ammonia is in the unionized (toxic) form. As shown in Table 6, all of the deicers, including magnesium chloride, would cross the threshold of toxicity at very high pH (8.5-

9.0). Exceedances that occur at even moderate pH's (7.5) for the Caliber M1000 and Caliber M2000 deicers, but not for magnesium chloride. At high pH, the exceedances for Caliber M1000 and Caliber M2000 are very large.

Table 6 raises two questions: 1) what pH can be expected for a roadway runoff,

	pH	Unionized Ammonia mg/L	Ratio to Standard
Magnesium Chloride			
	6.5	0.00	0.02
	7.0	0.00	0.05
	7.5	0.00	0.16
	8.0	0.01	0.50
	8.5	0.03	1.58
	9.0	0.10	4.99
Caliber M1000			
	6.5	0.00	0.12
	7.0	0.01	0.39
	7.5	0.02	1.22
	8.0	0.08	3.86
	8.5	0.24	12.22
	9.0	0.77	38.63
Caliber M2000			
	6.5	0.00	0.17
	7.0	0.01	0.54
	7.5	0.03	1.69
	8.0	0.11	5.36
	8.5	0.34	16.95
	9.0	1.07	53.59

Table 6. Results of modelling leading to estimates of the concentration of unionized ammonia in runoff leaving a roadway treated with each of the three deicers included in the study, and the ratio of unionized ammonia concentrations in the runoff to the chronic stream standard for unionized ammonia. Conditions for modelling and the results shown in this table include the following: temperature 5^{o}C, dilution on the roadway 500 to 1, and total ammonia as shown in Table 1.

and 2) how far from the roadway would the exceedance of stream standards be expected to extend for a given pH? The pH of roadway runoff has not been studied, and would be expected to change with distance from the roadway as the deicer mixes with increasing amounts of dilution water. The pH of the receiving waters (streams) typically falls between 6.5 and 7.0, but the deicer is alkaline and can raise the pH. Laboratory dilution of the deicers showed pH of close to 9 at 1 to 500 dilution (magnesium chloride 9.0; Caliber M1000 9.1; Caliber M2000 8.8). Because the expected dilution is close to 1 to 500 at the edge of the roadway, the pH would be close to 9 at that point, and thus would correspond to concentrations of unionized ammonia in excess of the stream standard. Concentrations of unionized ammonia exceeding the stream standard might extend some distance from the roadway. As shown in transect studies that were conducted in 1997-1998 across the boundary between the roadway and the first receiving water, dilution of several thousand-fold typically occurs in short distances, i.e., 20 yards, but this might still be insufficient at pH 9 for deicers containing large amounts of ammonia.

Conclusions and Recommendations

Caliber M1000 and Caliber M2000 deicers can be described as having a magnesium chloride base to which large amounts of organic matter have been added. Either as a contaminant or as additive (probably as an inadvertent contaminant), these two deicers contain substantially more phosphorus and ammonia than does the magnesium chloride deicer in use by CDOT during 2000-2001. Application of Caliber M1000 and Caliber M2000 is problematic at high elevations, and especially in Summit

County, which exercises strong control over phosphorus loads as a result of the site-specific phosphorus standard on Lake Dillon. Applications of Caliber M1000 and Caliber M2000 deicers to montane roadways outside Summit County would not be in direct conflict with existing regulations, but could cause some impairment of surface waters through eutrophication. Total ammonia in Caliber M1000 and Caliber M2000 could produce concentrations of unionized ammonia exceeding the chronic standard for protection of aquatic life. Although dilution beyond the roadway would limit the spatial extent of any such exceedances, the presence of unionized ammonia concentrations above the standards on a frequent basis during the winter could be harmful to aquatic life some distance from the roadway. Also, the large amount of organic matter present in these two deicers raises questions of oxygen demand in standing water, even at points remote from the point of application.

The Caliber M1000 and Caliber M2000 deicers, if fairly represented by the samples that were taken for the present study, indicate the possibility of environmental problems that should be weighed against advantages of using these deicers as opposed to magnesium chloride deicer, which shows no indication of similar risks in its current formulation. While problems caused by the Caliber M1000 and Caliber M2000 deicer probably are not profound or irreversible, they may be sufficient justification for restrictions on the use of these deicers or for a continuing search for other formulations that reduce the magnitude of the problems documented here.

Expanded use of Caliber M1000 or Caliber M2000 deicer by CDOT might be justification for some additional studies. It is necessary, in evaluating questions related to ammonia, to know more about the pH of runoff as it leaves the roadway. In addition, the variability in chemical composition of these deicers from one lot to the next should be determined. This is especially important with respect to phosphorus and ammonia content. A final question is whether phosphorus in the deicer is partially immobilized by contact with soil en route to streams. It would also be desirable to know whether the organic matter in the deicer is to any degree toxic, although there is no indication presently that it is.

References

Lewis, W.M. Jr. 1999. Studies of environmental effects of magnesium chloride deicer in Colorado. Final Report, Colorado Department of Transportation, Denver, Colorado.

Lewis, W.M. Jr., J.F. Saunders, III, D.W. Crumpacker, Sr., and C. Brendecke. 1984. Eutrophication and land use: Lake Dillon, Colorado. Springer-Verlag, New York. 202p.

Lewis, W.M. Jr., J.M. Melack, W.H. McDowell, M. McClain, and J.E. Richey. 1999. Nitrogen yields from undisturbed watersheds in the Americas. *Biogeochemistry* 46: 149-162.

Colorado Water Quality Control Commission. Regulation Number 31. The basic standards of methodologies for surface water. 20 March 2001.

Lewis, W.M. Jr. 1997. Magnesium chloride deicer: a literature review with emphasis on the State of Colorado. Final Report, Colorado Department of Transportation, Denver Colorado.

Appendix A

Methods for the Analysis of Samples

		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
N	Ammonia	Indophenol Blue	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 A1. Summary of analytical methods.