

**Report No. CDOT-DTD-R-2000-12
Phase I - Final Report**

Preliminary Environmental Evaluation of Caliber M1000 Deicer for Use in Colorado

Prof. William M. Lewis



December 2000

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**COLORADO DEPARTMENT OF TRANSPORTATION
RESEARCH BRANCH**

**Preliminary Environmental Evaluation of Caliber M1000
Deicer for Use in Colorado**

by

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Prepared by
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16. Abstract The Caliber M1000 deicer investigated in this study can be described as a magnesium chloride deicer containing substantially more phosphorus, ammonia, and organic matter than were typical of magnesium chloride previously used by CDOT. Application in regions which exercise strong control over site-specific phosphorus mobilization can be problematic. Use of this deicer on montane roadways that do not constitute conflicts with existing regulations could still experience measurable impairment of surface waters through eutrophication. While dilution beyond the roadway would limit the spatial extent of such exceedences, the presence of unionized ammonia concentrations above the standard on a frequent basis during the winter could be harmful to aquatic life some distance from the roadway. The large amount of organic matter raises questions of oxygen demand in standing water remote from the point of application. Implementation If CDOT proceeds with the use of Caliber M1000, some additional studies might be relevant.			
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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 for causing impairment of the environment, and particularly of aquatic environments through which deicers flow after leaving the roadway.
2. During 1997-99, CDOT conducted an extensive evaluation of two brands of magnesium chloride deicer (Lewis 1999). During 1999, CDOT also developed an interest in a new brand of deicer (Caliber M1000), which it has not yet used extensively. CDOT supported a preliminary environmental study during summer and fall of 2000. The results of this study are summarized here.
3. The environmental assessment of Caliber M1000 deicer 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 of Caliber M1000 included: (1) analysis and environmental evaluation of constituents in the deicer, (2) experimental tests of oxygen demand caused by the deicer, (3) modelling of the effects of phosphorus in the deicer, and (4) modelling of the effects of ammonia in the deicer. All of the studies were conducted on a sample of Caliber M1000 obtained from CDOT's storage tanks during April of 2000.
4. Studies of chemical composition showed that the main inorganic components of Caliber M1000 deicer are very similar to the two magnesium chloride deicers that were tested during 1997-99. Dissolved inorganic solids total about 31% of the total mass of the deicer, and more than 95% of the mass of inorganic solids is accounted for by magnesium and chloride. Calcium, sodium,

potassium, and sulfate also are easily detectable, but are 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 were lower than those found previously in analysis of magnesium chloride deicers.
6. Caliber M1000 contains substantial amounts of phosphorus in soluble form. Total phosphorus in the sample exceeds background concentrations by a factor of approximately 20,000, and exceeds the concentrations that were previously observed in magnesium chloride deicers by a factor of 10-20. The sample of Caliber M1000 also contained concentrations of ammonia (60 mg/L) exceeding that of previously analyzed magnesium chloride deicers by a factor of 10-15, although the ratio to background concentrations of inorganic nitrogen was not so extreme as for phosphorus.
7. Caliber M1000 contains a large amount of organic matter (about 33,000 mg/L, or 16,000 times background).
8. The overall compositional analysis of the deicer indicates that Caliber M1000 is a magnesium chloride deicer containing high amounts of phosphorus, ammonia, and organic matter.
9. Oxygen demand for Caliber M1000 was studied by use of water taken from three montane sites. Varying concentrations of Caliber M1000 were incubated at low temperatures for 24 hours with fresh stream water, and decline in oxygen was measured. Decline in oxygen following the addition of Caliber M1000 in amounts up to 5%, which exceeds the concentration that would be expected for water leaving a roadway that had been treated with Caliber M1000, showed no respiratory response to the presence of the deicer, even though the deicer contains abundant

organic matter. Thus the experiments indicate that the potential of the deicer to cause suppression of oxygen concentrations in receiving waters is low near the road. Oxygen demand may, however, be evident in standing water or may be expressed at points remote from the road.

10. Potential environmental effects of the phosphorus from Caliber M1000 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 size, and for specific watersheds that would be good candidates for treatment with Caliber M1000. For hypothetical watersheds, the influence of Caliber M1000 application on mean annual background phosphorus concentrations would be 20% or higher for watersheds as large as 50 square miles; use of Caliber M1000 within small watersheds (one square mile) would approximately double the annual mean total phosphorus concentration of stream water. For specific watersheds where application would be likely, percent increase over background would be lowest for Tenmile Creek (27%) and highest for Straight Creek (105%). Use of Caliber M1000 in Summit County could increase total phosphorus load to Lake Dillon, which is regulated for phosphorus control, by as much as 250 pounds per year.
11. Potential environmental effects of unionized ammonia from Caliber M1000 were studied through modelling. Assumptions about application rates were the same as those used for the studies of phosphorus, and the amount of total ammonia was estimated from the analysis of the Caliber M1000 that was taken in April 2000. The ratio of unionized ammonia derived from Caliber M1000 to the stream standard for aquatic life was estimated for a range of pH values. At a pH ranging from 8.5 to 9.0 (as shown by laboratory dilution), the ammonia content of the deicer would cause roadway runoff to exceed the cold water standard for protection of aquatic life at points beyond the roadway. A 100-fold dilution beyond the roadway would be necessary to eliminate the likelihood of an exceedence of the stream standard. Ammonia in the deicer

raises the possibility of toxicity to aquatic life beyond the edge of the roadway, but probably not at great distances from the roadway.

The study of Caliber M1000 shows that it is similar in some respects to magnesium chloride deicers previously used by CDOT, but contains 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 demand.

Introduction

Chemical deicers can decrease traffic congestion and hazards associated with winter precipitation, especially in montane environments. Chemical deicers also may be environmentally beneficial 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 the potential for support of aquatic life is reduced.

The advantages of using chemical deicers must be weighed against any potential for environmental impairment that might be associated with these mixtures. Because chemical deicers pass into the drainage network, the issue of greatest concern environmentally is the welfare of aquatic life. Points of interest environmentally for any chemical deicer include potential for direct toxicity at 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 has been conducted through support from CDOT (Lewis 1999). The study of magnesium chloride showed that it is important for CDOT to make specific restrictions on contaminants and anticorrosion additives that are present in magnesium chloride deicer. 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 interests in deicers other than the magnesium chloride compounds that were the subject of the analysis reported in 1999. One deicer of interest to CDOT is Caliber M1000, which is marketed as an alternative to the magnesium chloride deicers that were tested earlier; Caliber M1000 is considered more effective at low temperatures. For this reason, CDOT has supported a preliminary study of the environmental effects of Caliber M1000. This study, the results of which are reported here,

is less comprehensive than the study of magnesium chloride, but benefits from the possibility of direct comparisons with data obtained previously for magnesium chloride deicers.

The study of Caliber M1000 has four components: (1) evaluation of chemical composition and potential for toxicity or other environmental effects, (2) studies of oxygen demand, (3) modelling of effects of phosphorus addition through the use of deicer, and (4) modelling of effects of ammonia addition through 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 then gives an overview of the environmental implications for use of Caliber M1000.

Analysis and Interpretation of Constituents

Chemical deicers are expected to contain a broad range of constituents. Generally, these fall under three headings: main ingredients, corrosion inhibitors, and contaminants (Lewis 1997). Main ingredients account for 95% or more of substances dissolved in the deicer. Corrosion inhibitors are typically added in concentrations of a few percent, and often are proprietary in nature. They commonly include small organic molecules, phosphates, or other compounds that mask metal parts from contact with the salts that typically compose the bulk of 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 therefore they may reflect the presence of virtually any substance present in the raw materials from which they are derived. For example, magnesium chloride deicers contain metals and nutrients in varying amounts (Lewis 1999), even though these substances (with the exception of zinc in some cases) are not added intentionally to the deicer, and perform no specific function related to use of the deicer.

There are two general 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 that are known to be associated with specific substances at known concentrations. A second approach is bioassay, which is a way of evaluating the toxicity of a substance or a mixture of substances through its exposure to selected kinds of organisms under controlled conditions. Both types of tests have been performed on magnesium chloride deicer (Lewis 1999). For present purposes, the analysis of constituents is limited to the first of these approaches, i.e., analysis and interpretation of chemical constituents based on thresholds of response known from water quality regulations.

Samples of Caliber M1000 were obtained from CDOT storage tanks during April, 2000. The sample was part of the bulk material that was stored for use by CDOT during winter, 1999-2000. The sample is treated here as representative, although there is variation from one purchase of deicer to another in some cases (Lewis 1999).

The bulk deicer was analyzed by standard laboratory procedures for constituents. Methods are given in Appendix A of this report.

Major Inorganic Constituents

The major inorganic constituents of the Caliber M1000 deicer are essentially identical to those of magnesium chloride deicers that were evaluated during 1997-99. The main cation in the mixture is magnesium. Substantial amounts of calcium, sodium, and potassium are also present, but magnesium makes up about 95% of cations by mass. Chloride is the main anion. The total ionic content is about 31% by mass of the liquid deicer.

Nutrients

Table 1 summarizes the concentrations of phosphorus and nitrogen in Caliber M1000. These two elements are the main nutrients controlling 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. Therefore, the addition of phosphorus or nitrogen to aquatic habitats may cause the development of excessive growth of aquatic photosynthetic organisms, which include both algae and aquatic vascular plants.

Caliber M1000 contains substantial amounts of phosphorus. The total amount of phosphorus is close to 200 mg/L. For comparative purposes, one might consider the background phosphorus concentrations for streams in Summit County, which would be in the vicinity of 0.005-0.010 mg/L (Lewis et al. 1984). Thus the phosphorus content of the deicer at the time it is applied to the roadway exceeds the background concentrations in an unpolluted montane environment by a factor of approximately 20,000. At lower elevations, where concentrations of phosphorus are higher under almost all circumstances than in the mountains, the ratio of phosphorus in the deicer to that in the environment would be much lower, but still would reach 1,000 or more.

For purposes of environmental analysis, phosphorus typically is analyzed as three fractions: soluble reactive phosphorus (SRP, sometime called orthophosphate), total soluble phosphorus, and particulate phosphorus. Soluble reactive phosphorus consists for the most part of inorganic phosphorus in the form of ionized phosphoric acid (H_2PO_4^-). Because the test that is used in making the measurement of this fraction is sensitive to certain phosphorus-containing organic molecules, however, it cannot be assumed that all of the SRP is entirely inorganic. The SRP fraction has the highest bioavailability, i.e., it is readily taken up from the water, even at low concentrations, by algae or aquatic vascular plants.

Total dissolved phosphorus (TDP) is analyzed by use of a digestion procedure that converts organic phosphorus to inorganic phosphorus so that it can be measured readily by the inorganic

phosphorus measurement technique. Prior to the analysis, the sample is filtered for the removal of particulate phosphorus. Total dissolved phosphorus contains the SRP fraction. If the SRP measurement is subtracted from the total soluble phosphorus measurement, the difference is an estimate of dissolved organic phosphorus (DOP). Phosphorus-containing organic molecules include nucleic acids, phospholipids, certain types of detergents, and many other naturally-occurring and synthesized compounds.

Particulate phosphorus (PP) typically is analyzed separately from the soluble fractions. The water is passed through a filter and the material in the filter, which is designated particulate matter, is analyzed by a digestion procedure that liberates the phosphorus, allowing it to be analyzed as inorganic phosphorus.

For Caliber M1000, most of the phosphorus is soluble (Table 1). Of the total soluble phosphorus, approximately half is SRP and the other half is organic. The predominance of the SRP fraction indicates that the phosphorus in Caliber M1000 would have a high degree of bioavailability, i.e., it has high potential to stimulate the growth of aquatic plants, including both vascular plants and algae.

The environmental significance of the phosphorus content of Caliber M1000 cannot be judged without context. The chemical deicer is applied to the roadway, and shows substantial dilution on and very near the roadway. Therefore, an environmental evaluation must include some consideration of the expected dilution. In addition, the relative significance of phosphorus added through the chemical deicer is dependent on the amounts of phosphorus in the receiving water. These multiple factors can be considered together most conveniently by use of a simple model, which is described in another section of this report.

Caliber M1000 also contains substantial amounts of inorganic nitrogen in the form of ammonia (Table 1). Nitrate is not present in quantity. Concentrations of ammonium in Caliber M1000 exceed

Constituent	Milligrams per Liter			
	Caliber M1000	Magnesium Chloride	Environmental Ratio, Caliber M1000 ⁴	
<i>Major Ions</i>				
Ca ⁺⁺	900	1,800	45	
Mg ⁺⁺	79,000	80,000	23,000	
Na ⁺	2,000	2,700	570	
K ⁺	1,300	680	2,600	
SO ₄ ⁼	2,300	-	1,000	
Cl ⁻	224,000	230,000	58,000	
<i>Nutrients</i>				
Soluble Reactive P	57	4	30,000	
Total Soluble P	130	12	25,000	
Particulate P	- ¹	1	-	
Total P	187	14	20,000	
Total Ammonia N ²	52	4	1,000	
Nitrate N	-	-	-	
<i>Other Inorganics</i>				
Cu	Sol	0.1	0.2	20
	Tot	0.2	0.6	-
As	Sol	1.5	2.4	10
	Tot	1.4	-	-
Cd	Sol	0.01	0.01	7
	Tot	0.02	0.11	-
Cr	Sol	<2.0	<2.0	<50
	Tot	<2.0	<2.0	-
Hg	Sol	<0.01	<0.02	<13
	Tot	<0.01	<0.02	-
Ni	Sol	<1.0	<2.0	<35
	Tot	1.0	<2.0	-
Pb	Sol	<2.0	<1.0	<1700
	Tot	<2.0	<1.0	-
Se ³	Sol	-	-	-
	Tot	-	<0.2	-
Zn	Sol	0.3	<2.0	220
	Tot	0.8	<2.0	-
<i>Organic Matter</i>				
Total Organic Carbon	33,000	2,000	16,000	

¹ Insignificant due to low particulate content of the deicer.

² Ammonium N is both a plant nutrient and, at high concentrations, a toxin for aquatic life; ratio shown here is for ammonia in deicer to total background inorganic N.

³ Poor analytical results consistent with low concentrations.

⁴ Ratio of constituent in Caliber M1000 to expected background (major ions, nutrients) or stream standard for support of aquatic life (other substances); ratios above 500 for nutrients or other inorganics indicate potential for environmental effects; estimates assume hardness=50 mg/L.

Table 1. Concentration of various constituents of Caliber M1000 Deicer, and comparative data for magnesium chloride deicers used by CDOT in 1997-1998 (median of values reported by Lewis 1999; ammonia data from 1996-97 deicer). Sol=soluble, Tot=total (regulations apply to soluble fraction).

those of typical secondary effluent by a factor of 2-5. Inorganic nitrogen as ammonia (mostly present at ammonium, NH_4^+) is a potent plant nutrient because ammonia is the most highly available form of inorganic nitrogen for plants (including algae). The ammonia in undiluted deicer exceeds by a factor of about 1,000 the concentration of inorganic nitrogen in mountain streams, and exceeds the concentrations in waters of lower elevation by a smaller amount (ca. 100).

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 the multiplier effect of nitrogen. Because phosphorus is more abundant than nitrogen in the deicer, the main focus on eutrophication potential for the deicer should be on phosphorus rather than nitrogen. Even so, the presence of substantial amounts of ammonium 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 ammonium (NH_4^+), can be associated with toxicity to aquatic life in water because ammonium is in equilibrium with ammonium hydroxide and free unionized ammonia (NH_3). Free unionized ammonia (NH_3) is toxic and is regulated for the protection of aquatic life (Colorado Water Quality Control Commission 2000). Thus while the ammonium ion (NH_4^+) stimulates plant growth, its equilibrium partner (NH_3) 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 as water quality standards in Colorado. The best basis for evaluating this aspect of the significance of ammonium in deicer is through simple modelling, parallel to that described above for phosphorus but focusing on toxicity rather than eutrophication. Modelling of this type will be described in another section of this report.

Other Inorganic Substances

Table 1 includes the results of analyses for 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 are typically analyzed and evaluated along with metals (arsenic, selenium). For comparative purposes, the table includes concentrations that were typical of magnesium chloride deicer used by CDOT during winter, 1997-1998 (Lewis 1999).

Concentrations of metals and related substances in the Caliber M1000 deicer were all equal to or lower than concentrations observed in magnesium chloride deicer in 1997-1998. One way of evaluating the potential for toxicity of these contaminants 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 within the boundaries of the relevant stream standard for protection of aquatic life in mountain streams. These ratios are shown in the final column of Table 1. A 500-fold dilution is an important 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 its point of merger with receiving waters would occur very rapidly.

None of the "other inorganic" substances that are shown in Table 1 exceed concentrations that would be inconsistent with the stream standards for protection of aquatic life. Therefore, there are no obvious candidates for environmental concern on the list of substances in Table 1 under the heading "Other Inorganics."

Organic Matter

Analysis of organic content in the deicer by use of a carbon analyzer showed total organic carbon content of 33 mg/L. Because organic matter is approximately 50% carbon by mass, this

corresponds to a total organic load of about 60,000 mg/L. This is a very large amount of organic matter by comparison with the magnesium chloride deicers that were analyzed previously (see Table 1), or by comparison with background concentration (approximately 4 mg/L in winter). The Caliber M1000 deicer contains organic matter as a major constituent, i.e., the amount of organic matter is too large to be an inadvertent inclusion in the mixture.

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. Presumably the manufacturer would select a type of organic matter known to be non-toxic, but this could only be verified by bioassay experiments, which were not conducted for this particular study. Bulk addition of organic matter would raise the possibility that organic contaminants, as well as the main ingredients are present, and this issue has not been studied.

An issue of direct relevance to receiving waters is potential oxygen demand that might be associated with the organic matter. Oxygen demand was studied directly in experiments described below:

Oxygen Demand of Caliber M1000

Deicing compounds that contain substantial amounts of organic carbon may produce depression of oxygen concentrations in streams. As organic matter from the deicer is carried from a roadway into a stream with runoff, the organic matter will be subject to breakdown by microbes. The breakdown process for organic matter requires oxygen, which is drawn by the microbes from the water. If the resultant depression of oxygen in the stream is large, 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 stream, and the conditions in the stream. One way to test the degree to which a given deicer might affect oxygen concentration in a stream is through the

measurement of oxygen depletion in stream water under controlled conditions involving addition of deicer to stream water. This was the concept behind tests of oxygen demand by Caliber M1000 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 the evaluation of chemical deicer because the incubation period is too long (effects near the source, which would occur within a day or less, are of greatest 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 equal to or somewhat greater than the maximum amount anticipated from 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 deicer.

The protocol that was used for Caliber M1000 is essentially identical to that used previously for magnesium chloride deicer (Lewis 1999). Water from three streams was used in the test (Laskey Gulch near the mouth; South Clear Creek at Georgetown; St. Vrain Creek in Lyons). Four treatments were used for each of these water sources: no deicer (control), 0.33% deicer, 1% deicer, and 5% deicer. The expected dilution of Caliber M1000, which is applied in the same manner as magnesium chloride deicer, is about 1 to 500 (0.2%) at points near a roadway where Caliber M1000 deicer is being used (Lewis 1999). Therefore, the test concentrations, except for the control, all exceeded the expected amount of deicer in stream water.

The stream water samples were collected on June 6, 2000 and were used the following day for 24-hour incubations. Each treatment for each site was tested in duplicate. In addition, six incubations

Water Source	Amount Caliber M1000, %	Oxygen Consumption, mg/L/d	(range)
Deionized (Blank 1)	0	-0.05	(0.10)
Deionized (Blank 2)	0	0.06	(0.06)
Deionized (Blank 3)	1.00	0.00	(0.06)
Laskey Gulch	0	0.38	(0.04)
Laskey Gulch	0.33	0.39	(0.09)
Laskey Gulch	1.00	0.32	(0.06)
Laskey Gulch	5.00	0.38	(0.07)
South Clear Creek	0	0.40	(0.08)
South Clear Creek	0.33	0.35	(0.06)
South Clear Creek	1.00	0.40	(0.05)
South Clear Creek	5.00	0.41	(0.02)
St. Vrain Creek	0	0.20	(0.03)
St. Vrain Creek	0.33	0.20	(0.03)
St. Vrain Creek	1.00	0.18	(0.04)
St. Vrain Creek	5.00	0.16	(0.01)

Table 2. Summary of oxygen consumption data (respiration estimates) for Caliber M1000. Each line gives results for two replicates

of deionized water (lacking biological activity) were incubated, and deicer at 1% was added to two of these.

Temperatures of incubation ranged between four and six degrees centigrade, which was close to the ambient temperature of the water at the time of collection. The incubations were conducted in 333-ml BOD bottles that were kept closed to prevent contact of the water with the atmosphere. An initial oxygen reading was taken from each BOD bottle, and the bottle was incubated in the dark for 24 hours, after which a final oxygen reading was taken. The difference between the two readings provides the basis for estimation of milligrams of oxygen per liter per day consumed in each bottle.

Results

The results of the oxygen demand tests are given in Table 2. As expected, the oxygen demand for each of the three sources of stream water, in the absence of any addition of Caliber M1000, was very low, reflecting the unpolluted condition of these montane waters. Also, there was some range in the oxygen demand from one site to the next: St. Vrain Creek showed lower oxygen demand than Laskey Gulch and South Clear Creek, although all three values were low.

Addition of Caliber M1000 deicer up to final concentrations as high as 5% did not cause any measurable change in oxygen consumption in any of the three sources of stream water. In other words, the organic matter present in Caliber M1000 did not cause a significant stimulation of microbial metabolism, even at a concentration of deicer considerably above that which would be expected in relation to roadway runoff. There is some scatter among the data points, as expected due to experimental error and natural variation, but the data for a given site produced results within a narrow range regardless of the amount of deicer added, up to and including 5%.

Use of the Results in Modelling

The effect of an oxygen-demanding substance on ambient stream concentrations of oxygen can be modeled if the rate of oxygen consumption is known and certain physical properties of the receiving water are known (reaeration rate, i.e., rate of exchange between the atmospheric oxygen source and oxygen in the water). The study of Caliber M1000 was to have included a projection of effects through modelling of this type, but the modelling has no basis because the rate of oxygen consumption induced by Caliber M1000 is not detectable. The modelling effort was directed to ammonia instead (see below).

Significance of the Organic Matter in the Deicer

Given that the Caliber M1000 contains a very large amount of organic matter (approximately 16 times background), it is surprising that the tests showed no detectable oxygen demand. The organic matter used in the deicer may be relatively refractory (i.e., not readily used by most microbes), or the microbes that are present in mountain stream water may be poorly equipped physiologically to use this particular type of organic matter, which may not be present in their environment. The results indicate that the deicer would not cause great oxygen demand close to the roadway, even though it contains a large amount of organic matter. Oxygen demand might develop in ways that are not well represented in the experiments, however. For example, a microbial community might become acclimated to the use of this particular source of organic matter as a result of repeated exposure, thus causing the streams to develop oxygen demand in response to the deicer over a period of time. Alternatively, the deicer might generate oxygen demand if it were allowed to stand in ponds, wetlands, or lakes over a considerable period of time, even though it does not demonstrate oxygen demand in stream water over short intervals under laboratory conditions.

Phosphorus: Evaluation of Potential Effects by Modelling

Concentrations of phosphorus in Caliber M1000 are very high by comparison with concentrations expected in montane receiving waters, which have very low background concentrations of phosphorus. Because substantial dilution of the deicer is expected, however, it is difficult to evaluate potential environmental effects of the phosphorus contained in the deicer without taking into account the application rates and the expected dilution of the phosphorus after it leaves the roadway. A simple model was constructed for the purpose of exploring this combination of factors as needed to support an evaluation of the environmental significance of phosphorus in the Caliber M1000 deicer.

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

Concentration of phosphorus in the deicer is also a necessary assumption for modelling. For present purposes, a concentration of 190 mg/L total P (Table 1) is used for modelling. It is anticipated that there is some variation in this number from one sales lot to the next, but such a variation is not documented as yet.

Given the assumed concentration and the assumed application rate, it is possible to calculate the annual yield of phosphorus per unit length of roadway. For 12,000 liters per one mile and 190 mg/L of P, the total annual yield per lane mile would be 4.8 pounds, or 2.2 kg. For a two-lane road, the yield would be 9.6 pounds per mile, and for a four-lane road the yield would be 19.2 pounds per mile.

Background concentration of P is also need 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 extensive studies of background conditions in Summit County (Lewis 1984, as later revised with more extensive data). These equations are used in modelling to predict the expected background concentrations under any given conditions of runoff. For purposes of modelling, runoff is assumed to be 300 millimeters per year, but the model can accommodate other assumptions about runoff 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 various anthropogenic phosphorus sources are present in montane environments, many montane environments approach background conditions for phosphorus, and thus the most appropriate basis for evaluating phosphorus 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 allow a direct comparison with mass transport from roadways. Figure 1 shows the comparison. On the y axis of Figure 1 is the mean annual phosphorus concentration (discharge-weighted), and on the x axis is the ratio of road miles to watershed area. At a ratio of zero, the roadway is not contributing any phosphorus from Caliber M1000; expected concentrations are equal to the background concentration. As the ratio increases, the proportionate contribution of Caliber M1000 to the annual discharge-weighted mean concentration increases progressively.

It is possible to estimate the ratio of roadway miles to watershed area for selected watersheds where the application of Caliber M1000 would be expected. These estimates are shown in Figure 1 and in Table 3.

Another approach to the comparison of road miles to watershed area is hypothetical, by reference to stream order (or watershed size). With the simplifying assumption that montane watersheds are approximately three times as long as broad, and that the roadway passes through the long

access of the watershed, some generalized estimates are possible for the effect of Caliber M1000 on mean annual concentrations. These estimates are shown in Table 4 for watersheds ranging in size from 1 to almost 400 miles².

As shown by Figure 1 and Tables 3 and 4, Caliber M1000 would in 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 anti-degradation standard equal to 15%: a change in the concentration of any regulated substance by more than 15% with respect to background is prohibited. While not all the waters that might receive Caliber M1000 in runoff would be covered by the anti-degradation rule, the rule does provide some basis for judging environmental effects on a percentage basis. As shown in Table 3, three of the watersheds within which Caliber M1000 would likely be applied could show, in response to the application, increases in mean annual phosphorus concentration ranging between 27 and 105%, i.e., substantially in excess of 15%. As shown in Table 4, sufficient dilution would be available only for watersheds approaching 50 square miles in the case of two-lane roads or 100 square miles in the case of four-lane roads. Even in these cases, substantial boosts in the phosphorus concentration could occur in areas where a road transects headwaters of large watersheds.

The general conclusion from the phosphorus modelling is that the concentrations of phosphorus in the sample of Caliber M1000 analyzed for this study are too high to be consistent with maintenance of characteristically low phosphorus concentrations in montane streams. Increase in phosphorus concentration could lead to increased growth of attached algae in streams and could affect algal abundance and transparency in lakes or ponds where waters are impounded. Addition of phosphorus through Caliber M1000 to the Lake Dillon watershed is especially problematic, as it would be expected to reach as much 250 pounds per year, an amount equal to about half of the total point-source discharge of phosphorus from wastewater treatment plants in the Lake Dillon watershed.

Watershed	Road Mi	Lanes	Watershed Area mi ²	Ratio*	P ug/L	Increase** %
Clear Cr abv Georgetown	12	4	80	0.30	7.4	31.4
Tenmile Cr	12	4	93	0.26	7.1	27.0
Straight Cr abv Silverthorne	9	4	18	1.00	11.5	104.8

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

** Increase above background.

Table 3. Model output showing the expected effect of Caliber M1000 on mean annual phosphorus concentrations of select montane watersheds.

Stream Order	Area mi ²	Length miles	Ratio* for 2 Lanes	P ug/L	Increase, %	Ratio* for 4 Lanes	P ug/L	Increase, %
1	1.2	0.6	0.54	8.8	56.2	1.07	11.9	112.5
2	3.9	1.1	0.29	7.3	30.8	0.59	9.1	61.6
3	11.6	2.0	0.17	6.6	17.8	0.34	7.6	35.6
4	38.6	3.6	0.09	6.1	9.7	0.19	6.7	19.5
5	115.0	6.2	0.05	5.9	5.6	0.11	6.2	11.3
6	386.0	11.3	0.03	5.8	3.1	0.06	5.9	6.2

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

Table 4. Effect of Caliber M1000 on phosphorus concentrations in watersheds of various size.

Use of Modelling to Evaluate Potential Ammonia Toxicity

Because the Caliber M1000 deicer contains a substantial amount of ammonia, 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 a large number of factors, however, and therefore must be evaluated by modelling.

A simple model was created for the evaluation of toxicity caused by ammonia in the Caliber M1000 deicer. Assumptions concerning rate of application of the deicer were the same as those used in the phosphorus modelling, and the amount of total ammonia was set to 60 mg/L (Table 1). 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. 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 a concentration of unionized ammonia for a range of pH values that might be typical of runoff. The concentration of unionized ammonia is then expressed as a ratio to the stream standard for unionized ammonia as it relates to the protection of aquatic life (0.02 mg/L for chronic exposure of cold water aquatic life). Ratios in excess of one would indicate that water leaving the roadway would be likely to exceed stream standards for protection of aquatic life.

The results of ammonia modelling are shown in Table 5. As indicated by the table, the pH of the 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 by Table 5, the Caliber M1000 deicer, at 60 mg/L of total ammonia, would be expected to cross the threshold between compliance and non-compliance with the stream standard at the

point of departure from the roadway at a pH of about 7.1. At a pH of 8.0, the deicer would exceed the standard by eightfold at the edge of the runway.

Table 5 raises two questions: (1) what pH can be expected for roadway runoff, and (2) how far from the roadway would exceedance of stream standards be expected to extend? 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. The laboratory dilution of the Caliber M1000 produced the following results for pH: dilution 1 to 100, pH 9.0; dilution 1 to 500, pH 9.0; dilution 1 to 1000, pH 8.9. Because the expected dilution is close to 500 at the edge of the roadway, the pH would be close to 9.0 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 during 1997-98 across the boundary between the roadway and the receiving waters, dilution of several thousand-fold occurs typically within short distances from the runway, e.g., 20 yards, but this would be insufficient at pH 9.0 (Table 5).

Conclusions and Recommendations

The Caliber M1000 deicer can be described as a magnesium chloride deicer that contains substantially more phosphorus, ammonia, and organic matter than were typical of magnesium chloride deicers previously used by CDOT. Application of Caliber M1000 is especially problematic in Summit County, which exercises strong control over phosphorus mobilization as a result of the site-specific standard on phosphorus on Lake Dillon. Applications to montane roadways outside Summit County would not be in direct conflict with existing regulations, but could cause measurable impairment of

pH	Unionized Ammonia mg/L	Ratio to Standard
6.5	0.00	0.24
7.0	0.01	0.75
7.5	0.05	2.36
8.0	0.15	7.48
8.5	0.47	23.6
9.0	1.50	74.8

Table 5. Results of modelling leading to estimates of the concentration of unionized ammonia in runoff leaving a roadway treated with Caliber M1000, and the ratio of unionized ammonia concentrations in the runoff to the stream standard for unionized ammonia. Conditions for modelling and the results shown in this table include the following: temperature 5°C, total ammonia in the deicer 60 mg/L, dilution on the roadway 500 to 1.

surface waters through eutrophication. Total ammonia in the deicer 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 exceedences, the presence of unionized ammonia concentrations above the standard on a frequent basis during the winter could be harmful to aquatic life some distance from the roadway. The large amount of organic matter raises questions of oxygen demand in standing water or remote from the point of application.

The Caliber M1000 deicer, as represented by the sample that was taken from CDOT storage in spring of 2000, presents the possibility of environmental problems that need to be weighted against the advantages of using this deicer. While problems that might be caused by this deicer are not profound or irreversible, they may be sufficient justification for restrictions on the use of the deicer, a search for other deicers that do not present these problems, or a call for reformulation, if that is possible without compromise of performance.

If CDOT proceeds with the use of Caliber M1000, some additional types of studies might be relevant. First, for purposes of evaluating questions related to ammonia, it is necessary to know more about the pH of runoff as it passes away from the roadway. A second matter that requires further study is the amount of variability in chemical composition for the Caliber M1000 deicer. The question of variability is especially important for phosphorus and ammonia. A third question is whether phosphorus in the deicer is partially immobilized by contact with soil en route to streams. The final questions are whether the organic matter in the deicer is to any degree toxic, and under what circumstances it will decompose, thus producing oxygen demand.

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.

USGS. 2000. Water resources data Colorado water year 1999. U.S. Department of the Interior, U.S. Geological Survey Water Data Report CO-99-1, 2.

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. Draft Final Action Documents. 26 July 2000.

Lewis, W.M. Jr. Magnesium chloride deicer: a literature review with emphasis on the State of Colorado. 7 July 1997.

Appendix A

Methods for the Analysis of Samples

		Method	Reference
<i>Major Ions</i>			
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
<i>Nutrients</i>			
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
<i>Other Inorganics</i>			
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

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

Table A1. Summary of analytical methods.