Alternative Aircraft and Pavement Deicers and Anti-Icing Formulations with Improved Environmental Characteristics

DETAILS

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ALTERNATIVE AIRCRAFT AND PAVEMENT DEICERS AND ANTI-ICING FORMULATIONS WITH IMPROVED ENVIRONMENTAL CHARACTERISTICS

This digest summarizes the results of ACRP Project 02-01, "Alternative Aircraft and Airfield Deicing and Anti-Icing Formulations with Reduced Aquatic Toxicity and Biochemical Oxygen Demand." The research was conducted by a project team consisting of the University of South Carolina, U.S. Geological Survey, Wisconsin State Laboratory of Hygiene, Molecular Knowledge Systems Inc., Infoscitex Corporation, CH2M HILL, and Western Washington University. The digest was prepared from the project final reports authored by George Bowman, Steven R. Corsi, Lee Ferguson, Steven W. Geis, Harris Gold, Kevin Joback, and Dean Mericas.

INTRODUCTION

Discharge of spent aircraft and airfield deicing and anti-icing fluids to receiving waters is an environmental concern at airports across the United States. The presence of these fluids in storm water runoff can increase both aquatic toxicity and biochemical oxygen demand (BOD) in the receiving waters, making expensive collection and treatment of the fluids necessary at many U.S. airports.

Airport Cooperative Research Program (ACRP) Project 02-01, "Alternative Aircraft and Airfield Deicing and Anti-Icing Formulations with Reduced Aquatic Toxicity and Biochemical Oxygen Demand," was conducted to examine the potential to develop aircraft and airfield deicing and anti-icing formulations with lower aquatic toxicity and reduced BOD. Such products could reduce infrastructure costs to airports, provide aircraft operators and airports with greater operational latitude in deicing and anti-icing operations, and improve the overall reliability of the air transportation system.

To accomplish this objective, the Project 02-01 team was tasked with:

1. Defining the present state of the art of deicing and anti-icing products with respect to minimizing their aquatic toxicity and biological oxygen demand.
2. Identifying components of deicing and anti-icing products causing aquatic toxicity and biological oxygen demand.
3. Identifying promising alternative formulations and components for deicing and anti-icing products with reduced aquatic toxicity and biological oxygen demand.
4. Evaluating the performance, efficiency, material compatibility, and environmental, operational, and safety impacts of these alternative formulations and components compared with current commercial products.
5. Describing the fate and transport of deicing and anti-icing formulation components and their degradation products.

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This Research Results Digest summarizes the key results, findings, and conclusions of ACRP Project 02-01. The complete two-volume project final report is available as ACRP Web-Only Document 3,[1] *Formulations for Aircraft and Airfield Deicing and Anti-Icing: Aquatic Toxicity and Biochemical Oxygen Demand*, and ACRP Web-Only Document 8,[2] *Final Report: Alternative Aircraft Anti-Icing Formulations with Reduced Aquatic Toxicity and Biochemical Oxygen Demand*. In this digest and the project final report, the term "deicer" is used to refer generally to aircraft deicing fluids (ADFs), aircraft anti-icing fluids (AAFs), and airfield pavement-deicing materials (PDMs), which may be in liquid or solid form.

LITERATURE AND DATA REVIEW

An extensive library of policy documents, patent literature, professional literature, project reports, and other data was compiled and reviewed as well as a collection of deicer manufacturer literature. This extensive review helped to define the current state of public (non-proprietary) knowledge regarding deicers.

Federal Aviation Administration and SAE International Policies Regarding Toxicity and Biochemical Oxygen Demand in Deicers

SAE International (formerly the Society of Automotive Engineers) develops and issues standards for aircraft and airfield pavement deicers. The Federal Aviation Administration (FAA) recommends these standards in Advisory Circulars. SAE International provides the only numerical limits related to environmental characteristics through its Aerospace Material Specification (AMS) 1424, which requires Type I fluids to have 50% lethal concentrations (LC_{50}) greater than or equal to 4,000 mg/l for several organisms.[3] No guidance is provided for the BOD content of deicers.

Characterization of Components in Commercial Deicer Products

A wide range of chemicals potentially used in deicers was identified in the literature, including 25 freezing-point depressants (FPDs), 21 surfactants, 11 corrosion inhibitors, 13 thickening agents, 6 defoamers, 9 pH modifiers, 5 dyes, 4 oils, and 4 antioxidants and antimicrobial agents. Not all of these component categories are present in all deicers; thickeners, for example, are found only in aircraft anti-icing products.

Toxicity data were available for less than one third of these chemicals, and the available data were not always comparable among different chemicals or relevant to deicing situations. Therefore, the conclusion was reached that further testing would be needed to define the toxicity of individual candidate deicer components.

Deicer manufacturers are constantly considering modifications to their products to improve performance, environmental characteristics, and cost. Nearly all Type I ADFs now meet SAE specifications for toxicity; BOD characteristics of PDMs have been improved; four manufacturers introduced new Type IV formulations in the 2007–2008 winter season; and one manufacturer introduced a new Type I formulation for the 2008–2009 winter season, with the assertion that these new formulations would be more environmentally friendly than previously available products.

Characteristics of Deicers in the Environment

The primary environmental concerns with deicers are high organic content, resulting in high BOD, and aquatic toxicity. Some fate and transport characteristics of deicers are understood, but many others have not been extensively studied. Most research on the fate and transport of deicers has focused on FPDs and, to a lesser extent, on benzotriazole-derived corrosion inhibitors and alkylphenol ethoxylate (APE) surfactants. The components with environmental characteristics that are not well understood include dyes, thickeners, pH modifiers, defoamers, other corrosion inhibitors and surfactants, and even the FPD used in pavement deicers.

FPD degradation rates are dependent on environmental factors such as medium, temperature, travel time, and established bacterial communities in soils and receiving waters. Benzotriazoles and APE

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[1] Available at http://144.171.11.107/Main/Public/Blurbs/155765.aspx or at the TRB website (www.trb.org) by searching "ACRP Web-Only Document 3"

[2] Available at http://www.trb.org/Publications/Blurbs/163310.aspx or at the TRB website (www.trb.org) by searching "ACRP Web-Only Document 8"

[3] LC_{50} is the highest concentration at which 50% of the tested organisms do not survive the test period.

have been studied at a small number of airports, but the bulk of research on APE has been in wastewater treatment and not in situations where these surfactants are released directly to receiving waters without being treated. Benzotriazoles stay mostly in solution but have been detected in soils near deicing activities. Benzotriazoles have proven to degrade slowly or not at all in the environment. Of several different pathways, some APE degradation products are more toxic than their parent compounds, express endocrine disruption potential, and have potential for sorption to sediment particles and persistence in benthic sediments.

Assessing the aquatic toxicity of deicers is a complicated issue owing to several different factors. First, toxicity in ADFs and AAFs is due primarily to proprietary additives, and the chemical identities of most of these additives are treated by the manufacturers as confidential business information. Second, different formulations have different degrees of toxicity, so different effluents with similar glycol concentrations may have very different levels of toxicity. Third, different ADF and AAF formulations have different concentrations of glycol, again posing complications to interpreting chemical analysis from effluent samples. Last, the fate and transport characteristics of additives are not necessarily the same as those of glycol, so glycol concentration and glycol surrogates such as chemical oxygen demand (COD) and BOD cannot be used as reliable indicators of additive content in effluents.

Conclusions from the literature indicate that research is necessary to better understand toxicity in ADF and AAF formulations and deicer runoff; however, available data indicate that the most likely sources of toxicity in PDMs are the FPDs.

Characteristics of Deicers in Wastewater Treatment Systems

The most commonly used FPDs (propylene glycol, ethylene glycol, acetates, and formates) are readily biodegradable under both aerobic and anaerobic methanogenic conditions. Because of the ease by which FPDs can be biodegraded, their primary impact on biological treatment systems is increased organic load.

Available literature indicates that nonylphenol ethoxylates (NPEs) may be degraded through biological treatment, but reported details on degradation and byproduct generation vary depending on the specific literature. Triazoles are unlikely to completely biodegrade in typical biological treatment systems. In sufficient concentration, they have been shown to inhibit degradation of other organic compounds, thereby decreasing treatment effectiveness of spent deicers. Recent research indicates that the effectiveness of different treatment strategies varies, with conventional activated sludge the least effective, membrane bioreactors more effective, and ozonation resulting in complete mineralization of benzotriazole and 4- and 5-methyl-1H-benzotriazole.

Operational and Infrastructure Considerations

Potential impacts on aircraft operations and infrastructure were identified in the literature. PDMs based on potassium formate and potassium acetate have been identified as potential contributors to corrosion of cadmium-plated electrical connectors in the Boeing 737 New Generation aircraft and to accelerated catalytic oxidation of carbon composite brake components. In both cases, potassium-based PDMs were in widespread use prior to material changes in the newer aircraft involved. Changes to components and maintenance procedures, including Boeing's recommended practice to eliminate cadmium corrosion through the use of corrosion-inhibiting compound (CIC) on electrical connectors, have eliminated or minimized the corrosion reactions. SAE G-12 and aircraft manufacturers have specific task groups working on these important issues.

Increased failure rates of airfield electrical components were also thought to be linked to potassium acetate PDMs. It was subsequently found that poorly maintained systems allowed PDM entry. Corrective actions and improved products and components have greatly reduced or eliminated the problems.

Reports of pavement deterioration, including degradation and disintegration, softening and stripping effects, and scaling and surface cracking were determined to be a result of alkali-silica reactivity linked to pavement deicers based on potassium acetate. Subsequent investigation determined that other factors, especially construction methods and materials, can be used to mitigate these issues.

Residues from Type II and Type IV fluids may form on aerodynamically quiet areas on aircraft, and if not removed by deicing or anti-icing, the residue may absorb rainwater (rehydrate) and subsequently freeze, restricting the movement of unpowered flight control surfaces.

Deicer Products under Development

During the past two decades there have been a number of efforts to develop more environmentally friendly deicers. Some of these new products are entering the market, while others are not yet available commercially. Octagon Process, Inc., introduced a Type I ADF based on propylene glycol and glycerol that is described as having lower 5-day BOD (BOD5) and aquatic toxicity compared to many previous Type I formulations. Battelle recently released an ADF–AAF and a PDM, both based on glycerol as the primary FPD. Battelle is also working on alternative PDM formulations that are less damaging to aircraft components and less expensive than current products. Foster-Miller has previously developed two Type I fluids and one Type II fluid, with the objective of producing environmentally advantaged formulations that consider BOD and toxicity. METSS Corporation has developed two Type I fluids using agriculturally based products intended to further reduce toxicity and BOD. While some of these formulations have been certified according to SAE standards, problems involving residue formation, foaming, and unfavorable thickening after application have been encountered during field testing. The prospects for near-term commercial availability of these products are unclear.

Methodological Issues

The literature review identified a number of methodological issues.

Biochemical Oxygen Demand. BOD5 testing and extended-length BOD testing pose unique challenges in samples containing deicers. Issues include determining proper dilutions to characterize BOD accurately, properly acclimating microorganisms, and the possibility of seeds with insufficient microorganism densities.

Analysis of Additives. There are no standard techniques for determining concentration of deicer additives such as benzotriazoles and APE. Techniques are currently in flux, necessitating regular review of literature to evaluate the most current methods.

Aquatic Toxicity. The results of acute deicer toxicity testing at low temperature were not dramatically different from those at standard temperatures, with the freshwater crustacean *C. dubia* slightly less sensitive to deicers at lower temperatures and fathead minnows (*P. promelas*) slightly more sensitive to deicers at lower temperatures. One complication when conducting toxicity tests with samples containing deicer is low dissolved oxygen resulting from high BOD. A successful method for improving dissolved oxygen levels during fathead minnow tests is to reduce the number of fish per replicate and reduce the sample volume.

Representativeness of Laboratory Analyses. Results of BOD and toxicity tests performed in a laboratory under controlled light and temperature conditions provide valuable ecological information, but such conditions do not mimic environmental conditions, especially during deicer application events.

TOXICITY CHARACTERIZATION

Baseline toxicity tests were conducted on seven Type I formulations, four Type IV formulations, and three PDMs. One group of five Type I products resulted in LC_{50} averaging about 10,000 mg/l, whereas two products showed LC_{50} near 30,000 mg/l. Type IV deicer products consistently demonstrated much greater toxicity than the Type I products, with LC_{50} near 2,500 mg/l and lower. Toxicity results were similar for marine and freshwater species.

Toxicity in fractionated Type I and Type IV deicers was associated with the presence of polyethoxylated nonionic surfactants, including both APE surfactants and aliphatic alcohol ethoxylate surfactants. Relatively high concentrations of triazole-based corrosion inhibitors in one Type IV deicer triggered toxicity in toxicity identification and evaluation (TIE) assays. Toxicity in pavement deicers is associated primarily with the FPD.

BIOCHEMICAL OXYGEN DEMAND AND CHEMICAL OXYGEN DEMAND

BOD and COD were characterized in seven deicer formulations, including ethylene glycol and propylene glycol formulations of Type I ADF, ethylene glycol and propylene glycol formulations of Type IV AAF, a liquid PDM based on potassium acetate, and solid PDMs based on sodium acetate and sodium formate. Expanded testing was conducted on one formulation of propylene glycol Type I ADF, one propylene glycol Type IV AAF, and one potassium acetate PDM to determine decay rates over a 40-day period

Table 1 Summary of BOD5 and COD results for tested deicers.

Formulation	% FPD	Values as Neat Formulation: COD (mg/kg)	Values as Neat Formulation: BOD_5 (mg/kg)	Values as Primary Source of Oxygen Demand: Primary Source	Values as Primary Source of Oxygen Demand: COD (mg/kg)	Values as Primary Source of Oxygen Demand: BOD_5 (mg/kg)
Ethylene glycol Type I	92	1,180,000	492,000	EG	1,280,000	535,000
Ethylene glycol Type IV	64	826,000	331,000	EG	1,290,000	517,000
Propylene glycol Type I	88	1,420,000	990,000	PG	1,610,000	1,130,000
Propylene glycol Type IV	50	842,000	539,000	PG	1,680,000	1,080,000
Potassium acetate (liquid)	50	315,000	247,000	Acetate	1,050,000	821,000
Sodium acetate (solid)	96	700,000	571,000	Acetate	1,010,000	826,000
Sodium formate (solid)	98	242,000	—[a]	Formate	373,000	—[a]

[a] BOD test results for sodium formate deicer were not considered reliable estimates of potential BOD exertion in environmental situations due to apparent toxicity of the formulation to BOD seed organisms.

at 20°C and 5°C in marine water and freshwater. BOD5 and COD results are presented in Table 1.

Biodegradability was examined by comparing BOD and COD results. The degradation percentage was between 40% and 82% for six of the formulations. Decay rates in the 40-day test indicate that degradation occurred more rapidly in the first 15 days than during the rest of the test period. At least 78% degradation occurred for the six formulations over the 40-day test period. Results from sodium formate PDM testing are not included owing to apparent toxicity of this formulation to organisms in the BOD seed.

Freshwater and marine water test results were comparable in the 40-day tests conducted at 20°C. Results of the 40-day freshwater tests at 5°C indicate lower degradation than those at 20°C with 23–55% degradation for ethylene glycol products, 61–77% degradation for propylene glycol products, and 86–94% for acetate-based products. Results of the 5°C marine tests indicated that degradation was significantly less in low temperatures with less than 10% degradation for the propylene glycol ADF and AAF and 69% degradation for the potassium acetate PDM.

EVALUATION OF ALTERNATIVE ADF COMPONENTS AND FORMULATIONS

The primary objective of this phase of the research was to identify and characterize alternative deicer formulations with reduced aquatic toxicity and BOD that would be operationally and commercially viable. ACRP also stressed the need to present the research findings in a format useful to chemical manufacturers in producing more environmentally friendly deicing formulations and to airport operators in evaluating alternatives to meet environmental compliance requirements.

Research Approach

A tiered approach was taken to achieve this objective. Pure candidates and simple mixtures with water were tested in tier 1. Candidates that survived tier 1 testing were subjected to tier 2 tests involving more complex mixtures.

In tier 1,

1. Candidate FPDs, thickeners, surfactants, and corrosion inhibitors were identified with improved environmental qualities compared to components of commercial aircraft deicers and anti-icers.
2. Laboratory analysis of the candidate components were conducted for BOD and aquatic toxicity.
3. Candidate components were down-selected to identify a subset for use in building candidate formulations.

In tier 2,

1. A series of testing and down-selecting of progressively more complex mixtures was conducted to arrive at a final formulation that is equivalent to, or better than, commercial formulations in current use in terms of deicing performance and environmental characteristics.

Table 2 Number of components and deicer formulations tested in tiers 1 and 2.

	Deicer Component				
Tier No.	FPD	Surfactant/Antifoam	Corrosion Inhibitor	Thickener	Deicer Formulations
1	26	19	14	6	—
2	2	3	2	3	Type IV AAF
	1[a]				Runway PDM

[a] Evaluated with two anti-caking materials.

2. Candidate anti-caking agents were identified and tested in solid FPD formulations to evaluate performance.
3. The environmental characteristics of the final formulations were determined.

Tables 2 through 4 summarize the tiered testing. The results of the tier 2 tests yielded a final selection of components for complete Type IV formulation development. Tests needed to certify the down-selected formulations, including deicing and anti-icing performance and aircraft materials compatibility, were not undertaken as part of this research.

Tier 1 Results

A combination of molecular modeling, database searches, and literature searches were used to identify candidates for each of four major functional categories of deicer components. The following numbers of candidates were identified for further experimental evaluation based on their performance characteristics related to their function in deicer formulations and their contributions to BOD and toxicity:

- FPD: 27 candidates (5 aircraft, 12 runway, and 10 for both aircraft and airfield pavement).
- Thickeners: 6 candidates.
- Surfactants: 19 candidates.
- Corrosion Inhibitors: 14 candidates.

Two candidate anti-caking additives were also identified for use in sodium formate runway deicers, and one candidate defoamer was identified for use in deicing formulations.

Upon review of the tier 1 results, there did not appear to be substantial potential to improve BOD and aquatic toxicity in Type I fluids, nor did there appear to be potential to improve upon BOD in PDMs as compared to the products in current use with the most favorable environmental characteristics. For this reason, ACRP directed the research team to focus the tier 2 testing on Type IV aircraft anti-icing formulations and anti-caking additives for sodium formate runway deicers.

Table 3 Tier 1 deicing and anti-icing formulation tests.

Key Area	Test/Evaluation
Deicing performance	Freezing point depression, viscosity, contact angle
Environmental impact	Biological oxygen demand, aquatic toxicity
Safety properties	Flash point
Cost	Supplier cost estimates

Tier 2 Results

Type IV Aircraft Anti-Icing Formulations

Table 5 lists the FPDs, surfactants, thickeners, and corrosion inhibitors that were evaluated during tier 2 testing of Type IV aircraft anti-icing formulations. Based on the results of tier 1 testing, the FPDs that were selected showed improvements in COD, BOD, aquatic toxicity, or all three over propylene gly-

Table 4 Tier 2 tests for Type IV and runway PDM.

Key Area	Test/Evaluation
Type IV AAF	
Deicing performance	Surface tension (contact angle), viscosity, foaming
Environmental impact	Biological oxygen demand, aquatic toxicity
Materials compatibility	Total immersion and sandwich corrosion testing (aluminum clad and anodized aluminum)
Runway Deicer	
Deicing performance	Water absorption, anti-caking

Table 5 Candidate components of Type IV aircraft anti-icing fluids evaluated in tier 2.

FPD	Surfactants	Thickeners	Corrosion Inhibitors
Glycerol	Tergitol L-64	Kalzan HP	TEA
Diethylene glycol (DEG)	Tergitol TMN-10	K1A96	Mazon RI 325
	Triton CG-110 with 10% Ridafoam NS 221	Carbopol EZ-4 with triethanolamine (TEA)	

col. Many surfactants tested in tier 1 had improvements in toxicity over currently used surfactants. Surfactants were selected to take advantage of these toxicity improvements as much as possible while reducing the contact angle and surface tension to ensure that the formulations completely coat the aircraft surfaces. Thickeners were selected based on their aquatic toxicity and their ability to shear in a manner similar to commercial Type IV anti-icing agents. Corrosion inhibitors were down-selected based on aquatic toxicity.

Tier 2 experiments involved the testing of progressively more complex mixtures as compared to tier 1:

- FPD + water + thickeners; FPD:water = 1:1 by weight.
- FPD + water + surfactants; FPD:water = 1:1 by weight.
- FPD + water + thickeners + surfactants; FPD: water = 1:1 by weight.
- FPD + water + thickeners + surfactants + corrosion inhibitors; FPD:water = 1:1 by weight.

FPD Selection

Diethylene glycol (DEG) and glycerol were considered to be equally promising FPD candidates through the first three stages of the tier 2 down-selection process. The properties of the two are very similar: glycerol's theoretical oxygen demand and aquatic toxicity, as measured by Microtox® testing, are lower than that of DEG, but the aquatic toxicity of DEG toward *C. dubia* and *P. promelas* is lower than glycerol's. Mammalian toxicity is nearly identical for both candidates. What proved to be a differentiator was the freezing point characteristics for mixtures of each candidate with water that suggested the higher freezing point of glycerol solutions could cause operational problems. Specifically, asymmetric evaporation of water from applied Type IV formulations may result in concentrated FPD solutions on aircraft surfaces. In the case of glycerol, this could result in formation of residues. For example, at –20°C a 90 wt% glycerol solution would partially freeze into a slurry or highly viscous solution whereas a 90 wt% DEG solution would still be completely liquid. Concentration of FPD in this manner could potentially result in the accumulation of highly viscous glycerol residues on the aircraft surface. For this reason, DEG was selected as the preferred FPD for the final formulation.

Additive Selection

Additives in the final formulation include Tergitol L-64 as the surfactant, triethanolamine (TEA) as the corrosion inhibitor, and Carbopol EZ-4 as the thickener. These additives were chosen by consideration of performance, aquatic toxicity, and cost.

Toxicity Results

Results from the stepwise toxicity testing show how toxicity changed as each additional component was included in the formulation (Table 6). These results were compared to theoretical results calculated from the toxicity of the individual components and their concentrations in the mixtures, and assuming no synergistic or antagonistic toxicity interactions. In most cases, it was valid to assume that individual component toxicity could be used to determine formulation toxicity. In the instances where this was not true, toxicity evaluation was more complicated, requiring empirical observations to understand which components were responsible for final formulation toxicity. Addition of the anti-foaming agent to the first formulation indicated a synergistic interaction for all three organisms (the formulation was more toxic than the theoretical value). Similarly, synergistic interactions in the Microtox and fathead minnow tests were observed from addition of TEA in the final formulation. In addition, different interactions were observed depending on the FPD. Of particular interest was the difference between addition of the thickener to DEG as opposed

Table 6 Comparison of theoretical values with measured test results for stepwise Type IV anti-icing formulation construction.

		Theoretical Values			Test Results		
Added Component	**Percent of Component Added to Mixture**	**Microtox EC$_{50}$[a] (mg/l)**	***C. dubia* LC[b]$_{50}$ (mg/l)**	***Fathead minnow* LC$_{50}$ (mg/l)**	**Microtox EC$_{50}$ (mg/l)**	***C. dubia* LC$_{50}$ (mg/l)**	***Fathead minnow* LC$_{50}$ (mg/l)**
DEG formulation							
Water	50	—	—	—	—	—	—
DEG	50	130,000	110,000	110,000	130,000	110,000	110,000
Carbopol EZ4 with TEA[c] (thickener)	0.0763	130,000	66,000	110,000	140,000	71,000	120,000
Tergitol L-64 (surfactant)	0.25	130,000	66,000	110,000	110,000	57,000	140,000
Ridafoam (anti-foaming agent)	0.025	12,000	66,000	110,000	25,000	25,000	59,000
TEA (corrosion inhibitor, does not include Ridafoam)—*final formulation*	0.2	110,000	66,000	110,000	43,000	53,000	89,000
Glycerol formulation							
Water	50	—	—	—	—	—	—
Glycerol	50	260,000	70,000	92,000	260,000	70,000	92,000
Carbopol EZ4 with TEA (thickener)	0.0552	260,000	70,000	92,000	43,000	66,000	71,000
Tergitol L-64 (surfactant)		260,000	70,000	92,000	18,000	75,000	63,000
Ridafoam (anti-foaming agent)		12,000	91,000	480,000	18,000	53,000	63,000

Screening toxicity results are only approximations. Screening toxicity procedures include fewer replicates, non-renewal of test solutions, shorter exposure duration for *Pimephales promelas*, and other procedural variances from definitive toxicity tests. Compounds are organized by least toxic to most toxic endpoint, determined by the most sensitive species.

[a] The Microtox EC$_{50}$ is the statistically determined concentration that would result in a 50% reduction in light emission compared to a laboratory control.

[b] The LC$_{50}$ is the statistically determined concentration that would cause death in 50% of the population exposed.

[c] TEA is triethanolamine.

to for glycerol. In the DEG formulation, results were similar to theoretical values, but a synergistic interaction for toxicity was present in this step for the glycerol formulation. This indicated that synergistic interactions for the same component were different depending on the composition of the rest of the formulation. In this case, it was only a difference in FPD that caused a difference in the synergistic interaction.

Results of definitive aquatic toxicity tests on the final formulation indicate that acute and chronic toxicity endpoints were one to three orders of magnitude greater (i.e., the toxicity was lower) than results previously published for formulations in current use (Table 7). Acute toxicity endpoints ranged from 219 to 13,800 mg/l in tests with currently used formulations, with each of the four tested products having one or more of the three endpoints at least as low as 528 mg/l. The lowest of the acute toxicity endpoints in the final DEG formulation in this research was 32,700 mg/l.

Chronic toxicity endpoints ranged from 79.4 to 1,350 mg/l in tests with currently used formulations, with each of the four tested products having one or more of the three endpoints at least as low as 130 mg/l. The lowest of the chronic toxicity endpoints in the final DEG formulation from this research was 8,970 mg/l (Table 7).

Table 7 Results from definitive aquatic toxicity testing of final Type IV DEG formulation (95% confidence interval).

	Acute Toxicity		Chronic Toxicity		
Microtox EC_{50}[a] (mg/l)	***C. dubia*** **LC_{50}[b] (mg/l)**	***P. promelas*** **LC_{50} (mg/l)**	***C. dubia*** **IC_{25}[c] (mg/l)**	***P. promelas*** **IC_{25} (mg/l)**	***S. capricorutum*** **IC_{25} (mg/l)**
54,900 (53,700–56,100)	*32,700* *(28,600–37,400)*	*126,000* *(116,000–136,000)*	8,970 (4,730–13,800)	60,200 (56,600–62,500)	42,100 (40,100-44,000)

[a] The Microtox EC_{50} is the statistically determined concentration that would result in a 50% reduction in light emission compared to a laboratory control.

[b] The LC_{50} is the statistically determined concentration that would cause death in 50% of the population exposed.

[c] The IC_{25} is the statistically determined concentration that would cause a 25% inhibition in growth (Fathead minnow) or reproduction (*C. dubia*).

In currently used formulations, surfactants were identified as the component with the greatest influence on toxicity. In the final formulation developed from this research, toxicity results indicated that the chosen surfactant had little or no influence on toxicity.

Biochemical Oxygen Demand Results

The concentration of COD in the final formulation was 752 g/kg with a relative standard deviation of 0.96%. These results are consistent with tier 1 testing results on neat DEG (COD = 1,500 g/kg), considering that the final formulation contains 50% DEG. The concentration of BOD5 could not be determined. Difficulties with seed acclimation to DEG encountered in tier 1 testing remained in tests with the final formulation.

Runway Deicers

The effectiveness of potassium carbonate and tripotassium citrate to prevent the caking of sodium formate granules was experimentally tested. The procedure involved drying the components and mixtures of the components in a desiccator, weighing the individual components and mixtures, and placing sets of sample dishes in an environmental chamber at constant temperature (30°C) and humidity (50%) for different periods of time. The percentage of powder passing through a sieve was the metric used to evaluate additive effectiveness.

No satisfactory anti-caking solution was found for sodium formate. The experimental results indicated that mixtures containing the anti-caking additives and sodium formate absorbed more moisture than the samples of sodium formate alone. Tests of the individual components found that aluminum sample dishes containing the potassium carbonate were corroded and partially dissolved after two days in the environmental chamber, which eliminated this candidate additive from further testing. Further experiments with sodium formate and mixtures of sodium formate and tripotassium citrate were continued. The results showed that although tripotassium citrate picked up a negligible amount of water, the mixtures of tripotassium citrate and sodium formate picked up more water than the sodium formate by itself, indicating that the tripotassium citrate produced a synergistic water absorption effect. No ready explanation for these observations is available, and further testing was discontinued.

Degradation Pathways for Down-Selected Deicer Components

Possible degradation pathways and degradation products for the down-selected components of the final Type IV formulation were examined to evaluate the potential for significant environmental effects.

Diethylene Glycol

Diethylene glycol is the proposed FPD. Its mixture with water constitutes more than 90% of the weight of the final deicing or anti-icing product. An evaluation of potential biodegradation pathways indicated that intermediate biodegradation products are fairly reactive and are thus are not expected to persist in the environment.

Tergitol L-64

Tergitol L-64 is a nonionic ethylene oxide/propylene oxide copolymeric surfactant marketed as readily biodegradable. The degradation pathways and products for the ethylene oxide portion of the

Table 8 Toxicity of TEA and its degradation products.

	Compound	96hr LD_{50} *P. promelas*
1	Triethanolamine	11,800 mg/l
2	Diethanolamine	1,370 mg/l
3	Ethanolamine	2,070 mg/l
4	Acetaldehyde	36.8 mg/l

surfactant should be the same as those for DEG. The degradation mechanism for the propylene oxide portion of the surfactant's molecular structure is less certain. An examination of the aquatic toxicities for possible degradation products indicates that they are fairly toxic to rainbow trout. It is also possible that these products are toxic to bacteria, which could partly account for reports of poor biodegradation.

Triethanolamine

Triethanolamine is the proposed corrosion inhibitor. It would typically be used in formulations at less than 2% by weight. Degradation byproducts are readily biodegraded and are not expected to persist in the environment. However, data on the aquatic toxicity of TEA and its degradation products to *P. promelas* indicate that the aquatic toxicity of the degradation products is significantly higher than that of TEA (Table 8).

Carbopol EZ-4

Carbopol is the proposed thickener. It is a lightly cross-linked poly(acrylic acid) polymer. Studies in the literature reported that Carbopol does not biodegrade, but also showed it does not pass through municipal wastewater treatment facilities into receiving waters because it adsorbs onto biomass and is removed with the biosolids during treatment.

CONCLUSIONS

General Conclusions

1. An alternative Type IV formulation was identified with significantly reduced toxicity compared to products in current use. The final candidate formulation has aquatic toxicity values that are greater by an order of magnitude or more (less toxic) than the least toxic commercial Type IV products tested.
2. The final formulation consists of DEG as the FPD, with a basic additive package consisting of Tergitol L-64 surfactant, TEA corrosion inhibitor, and Carbopol EZ-4 thickener.
3. Toxicity identification techniques used on currently used formulations were successful in helping to improve the toxicity profile of alternative fluids.
4. The physical properties of the alternative Type IV formulations were affected by interactions between the surfactants and thickeners.
5. Numerous potential alternative components were identified.
6. The techniques used in identifying a less-toxic Type IV formulation have potential applicability to developing Type I formulations with reduced toxicity.
7. There is no current evidence to suggest that the alternative FPD or thickener present significant concerns relative to degradation pathways and degradation products. Byproducts of the alternative surfactant and corrosion inhibitor may have greater aquatic toxicity than the parent products, but further investigation is needed for their full evaluation. DEG is preferred because of its lower freezing point and the resulting reduced risk of residue formation.

Oxygen Demand

1. Theoretical oxygen demand is a good screening criterion for oxygen demand of FPDs. The COD results for FPDs compared well with theoretical oxygen demand.
2. Conventional BOD tests produced unreliable results for some FPDs. The success of BOD testing was highly variable and dependent on how well microorganisms acclimated to FPDs.
3. COD was the most useful metric in down-selecting FPDs for oxygen demand. The reliance on COD was necessary because of the uncertainties encountered with BOD tests.
4. FPDs are the predominant source of oxygen demand in all deicer formulations. The relative concentrations of all other components are so small that any contribution to oxygen demand is insignificant.
5. No candidate FPD was found with potential for improvement of environmental characteristics compared to the least toxic Type I fluids

and pavement deicer formulations in current use.

6. DEG and glycerol were identified as promising alternative FPDs for Type IV fluid formulations.
7. Parameters such as molecular weight, freezing point depression, application rates, and transport phenomena must be considered to gain a comprehensive understanding of the potential impact of PDMs on dissolved oxygen in receiving waters.

Aquatic Toxicity

1. Screening-level toxicity testing identified potentially viable alternative components in each of the categories of FPD, surfactants, corrosion inhibitors, and thickeners. Identified candidates included 7 FPDs, 11 surfactants, 9 corrosion inhibitors, and 6 thickeners.
2. Empirical observations are necessary to understand which components are responsible for the toxicity of final formulations.

Pavement Deicers

1. There was significant synergistic interaction between sodium formate and tripotassium citrate that cannot be readily explained. Resolution of these counterintuitive results was beyond the scope of this investigation.

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